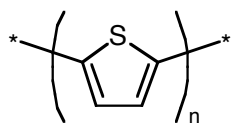


# **Synthesis of Ferrocene Derivatives:** **Altering Electron-Density of Ferrocene-Capped Thiophene**

By Bill Mitchell (2003)

## Introduction

The purpose of this project was to synthesize ferrocene end-capped monothiophene that will serve as a model to study the conductive properties of polythiophene. Polythiophene, as seen in Figure 1, is an organic polymer that is semiconducting when oxidized. It is being developed for use in photovoltaic devices because it is cheaply produced, it has high voltages compared to inorganic photovoltaic devices, and it is activated by visible light (1). The ultimate goal of this project is to develop derivatives of polythiophene to help understand the properties that would enhance the performance of transistors and photovoltaic devices (2,3).

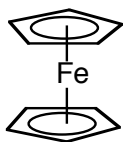


**Figure 1:** Polythiophene

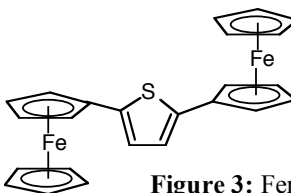
To electrochemically characterize these compounds, several factors must be taken into account. Polythiophene chains where  $n > 6$  are highly insoluble in nearly all solvents. This insolubility makes determining the fine details of the structure difficult, and classical techniques such as NMR spectroscopy are complicated, if not impossible (2). Tibodeau et al. showed that monothiophene will mirror the conductive properties of longer, insoluble polythiophenes. While longer chains of polythiophene may be more effective due to the smaller energy gap of their  $\pi$ -bonding orbitals, for this project monothiophene was used (2). This is because monothiophene is soluble in a wide range of solvents, including dichloromethane and deuteriochloroform, enabling structural determination using  $^1\text{H}$  NMR spectroscopy.

Research has shown, however, that thiophene which is unsubstituted at the 2,5<sup>x</sup> positions will polymerize during electrochemical testing, nullifying the data (2-5). To prevent polymerization, ferrocene, as seen in Figure 2, is added to create ferrocene-capped

monothiophene (2,5-biferrocenyl-thiophene), as seen in Figure 3. The ferrocene end-caps act as electroactive species to induce oxidation without polymerization (2).



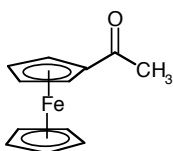
**Figure 2:** Ferrocene



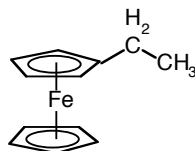
**Figure 3:** Ferrocene-capped monothiophene  
(2,5-biferrocenyl-thiophene)

Difficulty in studying conductivity is encountered when electron energies in the ferrocene caps do not match thiophene energy levels. This is because additional resistance is created that does not exist in non-capped polythiophene. As seen in Appendix A Figure A1, this resistance is caused by the energy difference in the electrons in the p-orbitals of ferrocene and monothiophene (3). The mechanism of conduction can be studied only if the resistance is minimized. This can be done by frontier orbital matching, where the energy levels are brought closer together by adding substituent groups to the ferrocene (3).

The hypothesis of the project reported here was that by adding an electron withdrawer such as an acetyl group, as seen in Figure 4, or an electron donor such as a methyl group or an ethyl group, as seen in Figure 5, the electron-energy levels of ferrocene would more closely match that of thiophene. This should improve conduction through the ferrocene-capped monothiophene.



**Figure 4:** Acetyl-ferrocene



**Figure 5:** Ethyl-ferrocene

This project has the potential to facilitate the development of smaller and more efficient photovoltaic technology. This technology could significantly reduce reliance on fossil fuels and

decrease greenhouse gas emissions. Other applications for these polymers include transistors, used for microchips, and light emitting diodes(6). Semi-conducting organic polymers, like polythiophene, have become of utmost importance because of their electrical and optical properties and could bring about a ‘next generation’ of electronic devices (2).

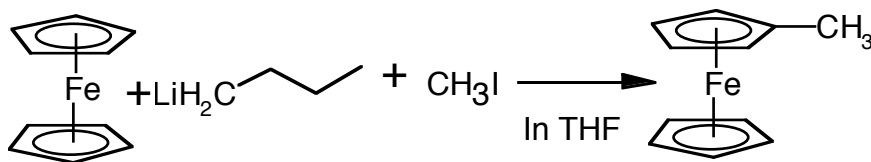
## Methods

Initially, ferrocene was substituted for ferrocene-capped monothiophene, because it was easier to synthesize. Using a method similar to the one used by F. Reibere et al., which first lithiated the ferrocene and then attached the substituent (7), the project reported here attempted to attach a methyl group to the lithiated ferrocene, however the methyl iodide failed to react. Because of this, an acetyl group was attached to the ferrocene via Freidel-Crafts synthesis and was then reduced to modify the ferrocene electron-energy levels to simulate a polythiophene chain (8). Ferrocene-capped monothiophene was then synthesized by Suzuki coupling as described by Tibodeau et al.(2).

*Synthesis of methyl-ferrocene, as seen in Figure 6:*

A 50-mL sidearm round-bottom flask was flame-dried. Then, 20 mL of tetrahydrofuran (THF) were added along with a stir bar. This was placed under a nitrogen atmosphere using a schlenk tube. Next, 0.10 g (0.54 mmol) ferrocene was added, and the nitrogen atmosphere was renewed by purging for ten minutes. This solution was cooled to 0°C, and 320 µL of 1.37 M n-butyllithium (0.54 mmol) were added and stirred for ten minutes at 0°C. The reaction was warmed to room temperature, and 67.2 µL (1.08 mmol) iodomethane were added and stirred for 15-30 minutes. The contents of the flask were evaporated using a rotary evaporator. A <sup>1</sup>H NMR analysis of the deuteriochloroform soluble portion of the product indicated that no desired

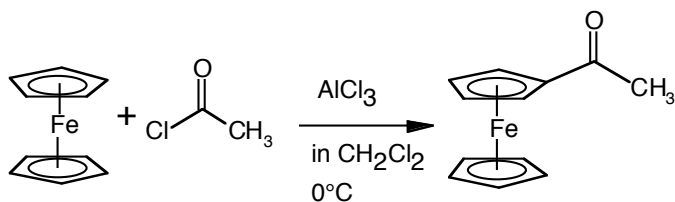
product was obtained.



**Figure 6:** Methyl-ferrocene reaction

*Synthesis of acetyl-ferrocene, as seen in Figure 7:*

Two 50-mL sidearm round-bottom flasks were flame-dried, stir bars were added, and the flasks were flushed with nitrogen. Then 20 mL dichloromethane were added to both flasks. To the first flask (*Flask 1*), 71  $\mu\text{L}$  (1.08 mmol) acetyl chloride were added. *Flask 1* was stirred and cooled to 0°C. After three minutes, 144 mg (1.08 mmol) aluminum trichloride were added to *Flask 1* at 0°C. While *Flask 1* was stirring, 200 mg (1.08 mmol) ferrocene were added to *Flask 2*, and *Flask 2* was cooled to 0°C. The contents of *Flask 1* were cannulated into *Flask 2* over the course of 30 minutes. The reaction was quenched with water, 300 mg sodium thiosulfate were added to reduce any ferrocenium ion which formed, and the mixture was washed with water in a separatory funnel. The orange dichloromethane layer was dried over magnesium sulfate, filtered, and evaporated to dryness. A  $^1\text{H}$  NMR spectroscopy analysis indicated that acetyl-ferrocene was synthesized.

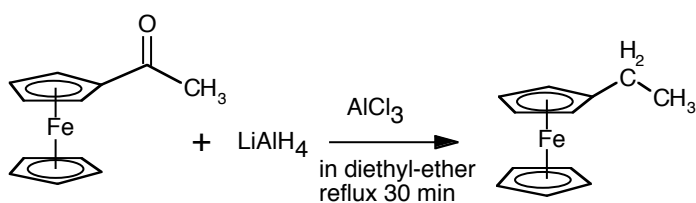


**Figure 7:** Acetyl-ferrocene reaction

*Reduction of acetyl-ferrocene, as seen in Figure 8:*

A 50-mL sidearm round-bottom flask with a stir bar and condenser was flame dried. After the flask was dried, 20 mL ether were added, and the ether was purged with nitrogen.

Then, 43 mg (0.19 mmol) acetyl-ferrocene were added and dissolved. Anhydrous aluminum chloride was added until the solution turned blue, and the flask was flushed again with nitrogen. Anhydrous lithium aluminum hydride was added in a similar manner until the solution turned yellow. The solution was refluxed for 30 minutes, then cooled to room temperature. Ice was added until hydrogen bubbles stopped evolving. The product was extracted with dichloromethane and dried over magnesium sulfate. Column chromatography (silica gel, hexane/dichloromethane 50:50) and sublimation to remove ferrocene were used to purify the product. A  $^1\text{H}$  NMR analysis of the deuteriochloroform soluble portion of the product indicated that ethyl-ferrocene was obtained.

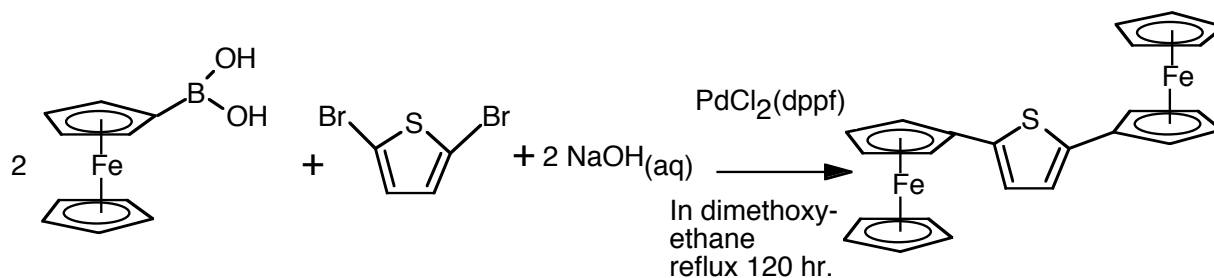


**Figure 8:** Ethyl-ferrocene reaction

*Synthesis of 2,5-biferrocenyl-thiophene, as seen in Figure 9:*

A 100-mL round-bottom sidearm two-neck flask with condenser and stir bar was charged with 1.88 g (8.2 mmol) ferrocene-boronic acid, 55 mL dimethylether, and 11 mL 3 M NaOH. The contents of the flask were stirred for ten minutes before adding 0.47 mL (4.1 mmol) 2,5-dibromo-thiophene followed by 0.12 g (0.146 mmol) 1,1' bis(diphenylphosphino)-ferrocene dichloro-palladium. The mixture was refluxed vigorously for five days, cooled to room temperature, and the solvent was evaporated using high vacuum. The mixture was extracted with ether, filtered through celite to remove any catalyst, and then evaporated to dryness. This mixture was purified by sublimation at reduced pressure and 90°C to remove any ferrocene. Further purification was done as necessary using column chromatography (silica gel, dichloromethane/

hexane 50:50), and  $^1\text{H}$  NMR spectroscopy was used to determine the fractions that contained pure 2,5-biferrocenyl-thiophene.



**Figure 9:** 2,5-Biferrocenyl-thiophene reaction (dppf = 1,1' bis-(diphenylphosphino)-ferrocene)

## Results

### *Synthesis of methyl-ferrocene:*

The synthesis of methyl-ferrocene yielded an orange crystalline solid. A thin-layer chromatography (TLC) plate (silicon dioxide) showed one spot about equal to ferrocene. A  $^1\text{H}$  NMR spectrum showed an identical spectrum to ferrocene, with a distinct ferrocene peak at  $\delta$  4.10 ppm. This reaction failed to give the desired product.

### *Synthesis of acetyl-ferrocene:*

The synthesis of acetyl-ferrocene also yielded orange crystals. A  $^1\text{H}$  NMR spectrum (see Appendix B Figure B1) showed a singlet at  $\delta$  2.40 ppm corresponding to the terminal methyl group, a singlet at  $\delta$  4.21 ppm corresponding to the cyclopentadienyl ring, a triplet at  $\delta$  4.51 ppm corresponding to two cyclopentadienyl protons, and a triplet at  $\delta$  4.78 ppm corresponding to the other two cyclopentadienyl protons.

### *Reduction of acetyl-ferrocene:*

The reduction of the acetyl group to an ethyl group yielded orange crystals. A  $^1\text{H}$  NMR spectrum (see Appendix B Figure B2) showed a triplet at  $\delta$  1.21 ppm corresponding to the

terminal methyl, a quartet at  $\delta$  3.48 ppm corresponding to the methylene protons, a peak at  $\delta$  4.21 ppm corresponding to the cyclopentadienyl ring, and triplets at  $\delta$  4.51 ppm and  $\delta$  4.78 ppm corresponding to the other cyclopentadienyl protons.

*Synthesis of 2,5-biferrocenyl-thiophene:*

The synthesis of 2,5-biferrocenyl-thiophene yielded an orange crystalline solid. Initially, TLC using silicon dioxide showed large quantities of ferrocene running slightly ahead of the 2,5-biferrocenyl-thiophene band (see Appendix C Figure C1, Figure C2). After more purification, monitored using TLC, the product was isolated. TLC using silicon dioxide showed very little ferrocene (see Appendix C Figure C2). A  $^1\text{H}$  NMR spectrum showed a singlet at  $\delta$  4.10 ppm corresponding to cyclopentadienyl rings attached only to the iron, two triplets at  $\delta$  4.28 ppm and  $\delta$  4.54 ppm corresponding to cyclopentadienyl rings that are attached to the thiophene and the iron, and a singlet at  $\delta$  6.78 ppm corresponding to the two identical thiophene protons (see Appendix B Figure B3). One problem, however, is that the coupling reaction that was used was slow, requiring reflux conditions for five days. Also, the ferrocene and ferrocene-capped thiophene bands run very close together with chromatography, as seen in Appendix C Figure C1 and Figure C2, which makes purification difficult. If the column is not perfectly packed, the bands will run together, which prevents isolation of the product.

## **Conclusion**

The synthetic techniques used in this project successfully produced acetyl and ethyl derivatives of ferrocene, but not the methyl derivative. This suggests that the Friedel-Crafts and lithium aluminum hydride processes could be applied to ferrocene-capped thiophene. The project

also showed that the current techniques to synthesize 2,5-diferrocenyl-thiophene result in only 25% yields, with ferrocene contamination that is difficult to remove.

The second goal of the project, electrochemical characterization of the derivatized compounds, was not achieved. Greater quantities of ferrocene-capped monothiophene are required for the addition of the acetyl group, due to the number of isomers that result. To produce a larger quantity in a more timely fashion would require an anhydrous synthesis in order to greatly reduce or eliminate contamination from ferrocene, the origins of which are speculated in Appendix A Figure A2.

During the summer of 2003, I will continue work on this project in the following way. To improve yields of ferrocene-capped monothiophene, a catalyst other than 1,1'-bis(diphenylphosphino)-ferrocene dichloro-palladium will be used for the Suzuki coupling, particularly a nickel or a palladium catalyst, such as  $(PPh_3)_4Pd(0)$ . In addition, a reducing agent such as butyl-lithium may be used to activate the catalyst (9). However, this might result in the synthesis of ferrocene. Reactions to test these different catalysts may be done using a deuterated solvent in an NMR tube to monitor the oxidative using  $^{31}P$  NMR spectroscopy rather than using TLC plates (10). Also, a different solvent with a higher reflux temperature, such as dioxane or toluene, will be used and might speed up the reaction.

Ultimately, the electrical properties of these derivatized ferrocene end-capped monothiophenes will be studied once a great enough quantity is synthesized. These will be compared to the non-derivatized ferrocene end-capped monothiophenes to determine if electron donation from the ethyl group or electron withdrawal from the acetyl group enhances the conduction across the ferrocene-capped monomer. These results could then be used with longer thiophene chains, up to three or four units long, to provide more detailed results (2).

Furthermore, the testing could also be done at a variety of temperatures to determine the energy barrier to charge delocalization. This additional testing would give further insight into the mechanism of thiophene conductivity, and could lead to improvements in photovoltaic devices and transistors.

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### Appendix A: 2,5-Biferrocenyl-thiophene Energy and Synthesis

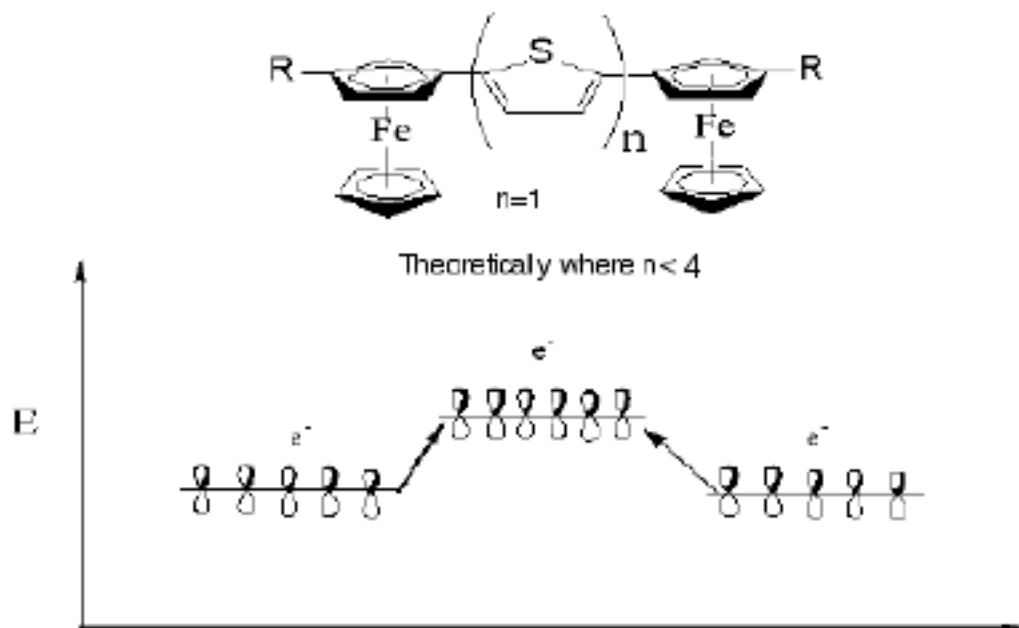


Figure A1: Frontier Orbital Matching

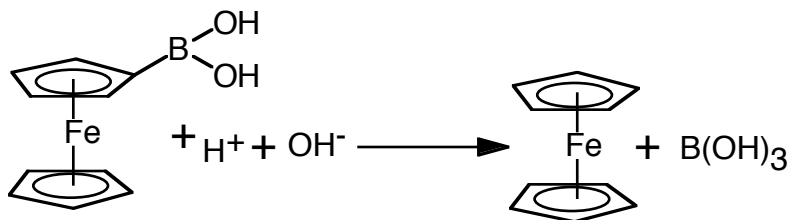


Figure A2: Speculated contamination reaction

### Appendix B: $^1H$ NMR Spectra

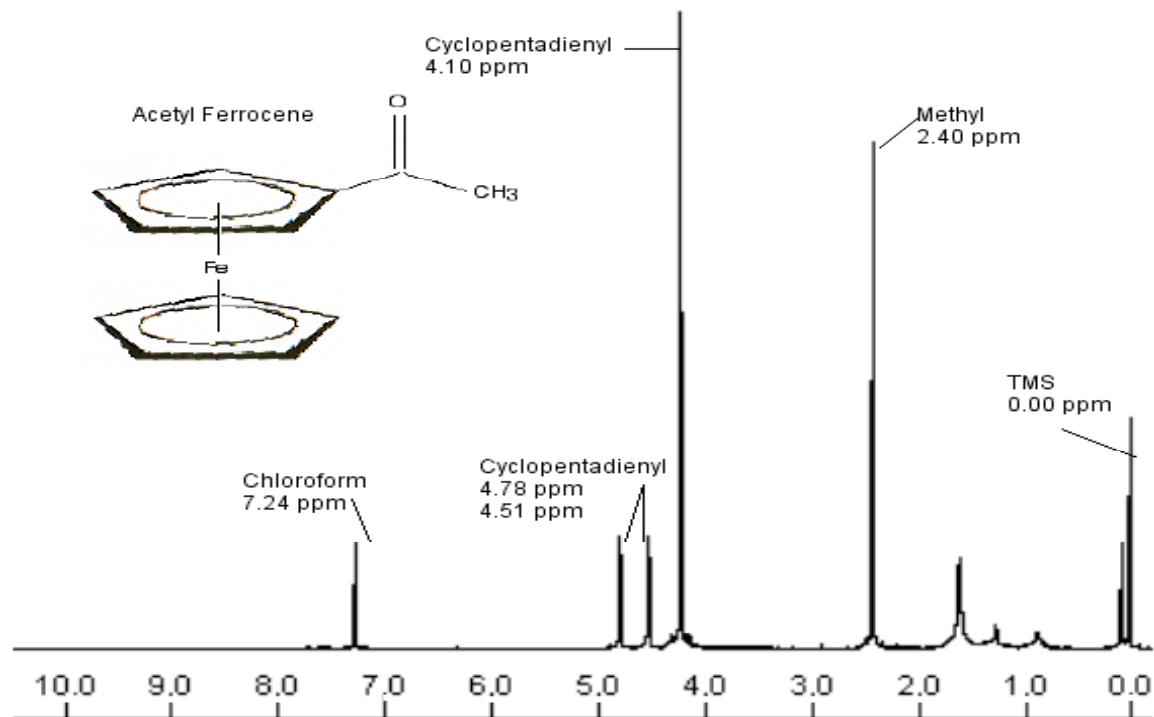


Figure B1: Acetyl-ferrocene

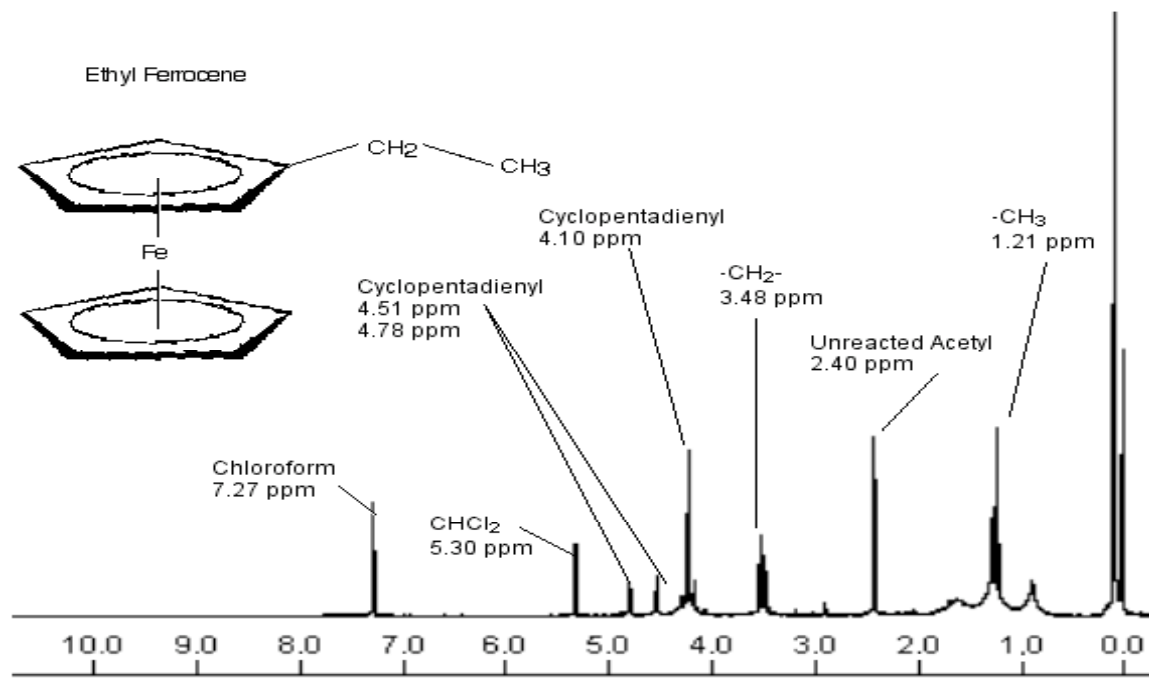
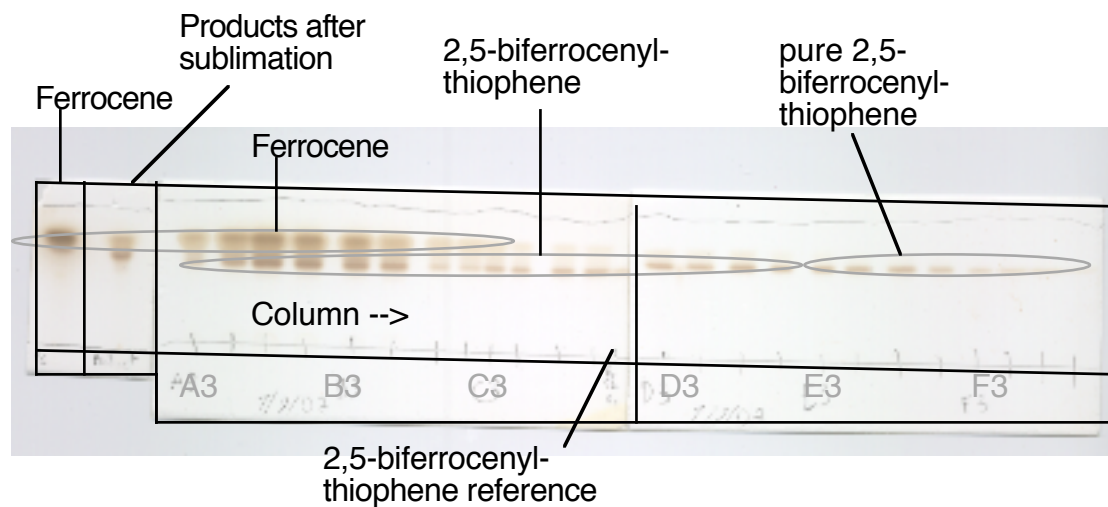


Figure B2: Ethyl-ferrocene





**Figure C2:** 2,5-biferrocenyl-thiophene after purification (50:50 hexanes : dichloromethane)