

# picoSpin™ 80: Microscale Friedel-Crafts Acylation of Ferrocene: Acetylferrocene

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## 1. Introduction

The Friedel-Crafts reaction represents a very important and broad class of electrophilic aromatic substitution reactions. The acylation reaction utilizes a Lewis acid catalyst, such as  $\text{BF}_3$  or  $\text{AlCl}_3$ , to produce an acyl cation that adds to the aromatic ring. Important reagents for acylation are acyl halides, carboxylic acids, anhydrides and ketenes. The alkyl group, R, in the acylating reagent can be an aryl or alkyl group. Acylation does not suffer from R-group rearrangement to a more stable carbocation species suffered by R groups in Friedel-Crafts alkylation reactions, a major disadvantage, because electrophilic attack in acylation is via an acylium ion (an acyl cation,  $\text{RC}\equiv\text{O}^+$ ). With anhydrides, the mineral acid phosphoric acid ( $\text{H}_3\text{PO}_4$ ) can be used as the Lewis acid catalyst, and acylation with nitriles ( $\text{RCN}$ ; the *Hoesch reaction*) employs  $\text{HCl}$  and  $\text{ZnCl}_2$ .

Acylation requires an electron rich aromatic ring system and cannot contain any electron withdrawing substituents on the ring. Ferrocene (bis( $\eta^5$ -cyclopentadienyl)iron;  $\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)_2$ ) is an organometallic compound containing iron (Fe) "sandwiched" between two cyclopentadienyl rings opposite the central metal atom. The cyclopentadienyl rings are aromatic according to Hückel's rule, they are planar, cyclic, conjugated and satisfy the  $4n+2$  rule. Because of their high electron density, acylation of ferrocene is accomplished under milder conditions using phosphoric acid as acid catalyst. The acyl group (RCO) is deactivating, stopping the reaction cleanly after the addition of one group per aromatic ring. Thus, in this microscale Friedel-Crafts acylation reaction of ferrocene with acetic anhydride using phosphoric acid as the Lewis acid catalyst, the major product is acetylferrocene ( $[\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)(\text{C}_5\text{H}_5)]$ ), with minor presence of diacetylferrocene ( $\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)_2$ ). The reaction product is isolated and purified by microscale flash column chromatography.

Column chromatography is one of many basic laboratory techniques taught in organic chemistry. It has widespread application in the organic synthetic lab because of its efficiency for separating and purifying components of a mixture. It can be applied to both liquid and solid samples, and multi-component mixtures. On a small scale, column chromatography is fast and cost effective. It is particularly useful for separating reaction mixtures containing reactants, products and byproducts.

Chromatography takes advantage of differences in polarity and binding strength components of a mixture have for column adsorbents. Adsorbents are high surface area stationary phase materials that bind solute molecules. A mobile phase solvent, or eluent, is used to desorb solute molecules, carrying them along the column to a receiving flask. As the solvent polarity is

increased, polar molecules bound more strongly to the column begin to solubilize and are carried down the column in the mobile phase. Equilibrium is established between binding to the stationary phase and solubility in the mobile phase. As the solvent polarity increases, more tightly bound polar molecules, firmly held by the adsorbent, establish equilibrium with the eluting solvent and flow along the column. This process is analogous to thin layer chromatography (TLC), gas chromatography (GC) and high performance liquid-phase chromatography (HPLC).

## 2. Purpose

The purpose of this experiment is to perform a microscale synthesis of acetylferrocene from ferrocene and acetic anhydride in an acid-catalyzed (85%  $\text{H}_3\text{PO}_4$ ) Friedel-Crafts reaction. The crude reaction product is isolated by filtration and purified on a silica gel column using flash chromatography. Two fractions will be collected from the column separation of the mixture. Ferrocene (fraction 1) is eluted first using hexanes; it appears as a yellow band in the column and represents excess reagent. The product, acetylferrocene (fraction 2), is eluted next using a 50:50 mixture of hexanes and diethyl ether solution.

Solutions of pure ferrocene and acetylferrocene, crude isolated product and column purified reaction product will be prepared and analyzed using the Thermo Scientific™ picoSpin™ 80 NMR spectrometer.

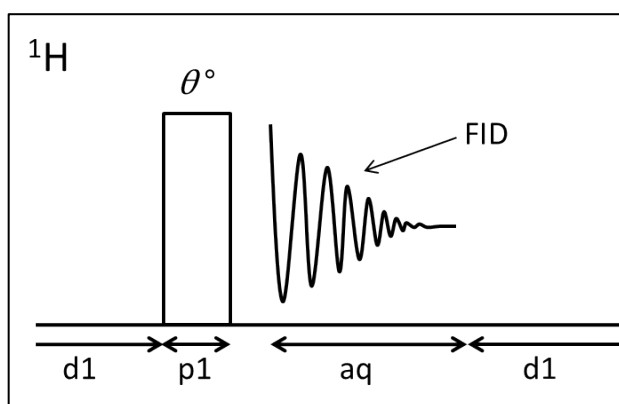
## 3. Literature

Adapted from Williamson, K. L.; Minard, R.; Masters, K. M. *Macroscale and Microscale Organic Experiments*, 5<sup>th</sup> ed., Houghton Mifflin Co., 2007.

Bozak, R. E. Acetylation of Ferrocene *J. Chem. Ed.* **1966**, *43*, 73.

## 4. Pulse Sequence

In this experiment, we use a standard 90° single pulse experiment. The recycle delay time (d1) is adjusted to maximize signal intensity prior to signal averaging the next FID.



Sequence:  $d1 - [\theta^\circ - aq - d1]_{ns}$

$\theta^\circ$ : Pulse rotation angle (flip angle)

FID: Free induction decay

d1: Recycle delay ( $\mu\text{s}$ ) for spin-lattice relaxation

p1: R.F. transmitter pulse length ( $\mu\text{s}$ )

aq: Acquisition time (ms)

ns: # of scans (individual FIDs)

## 5. Procedures and Analysis

*Time requirements:* 3-3.5 hrs

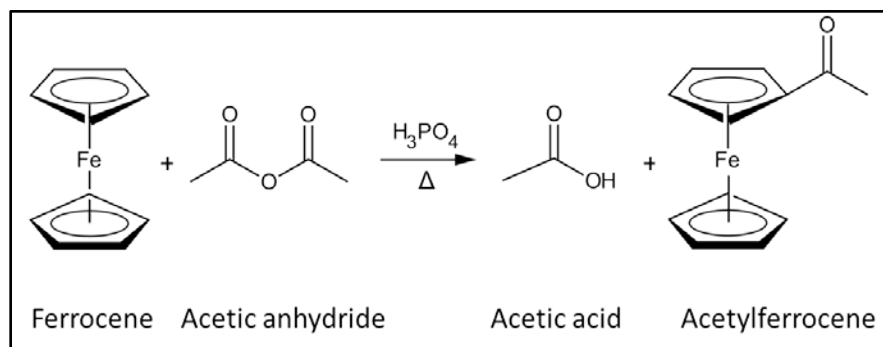
*Difficulty:* Moderate

*Sample:* Ferrocene, acetylferrocene

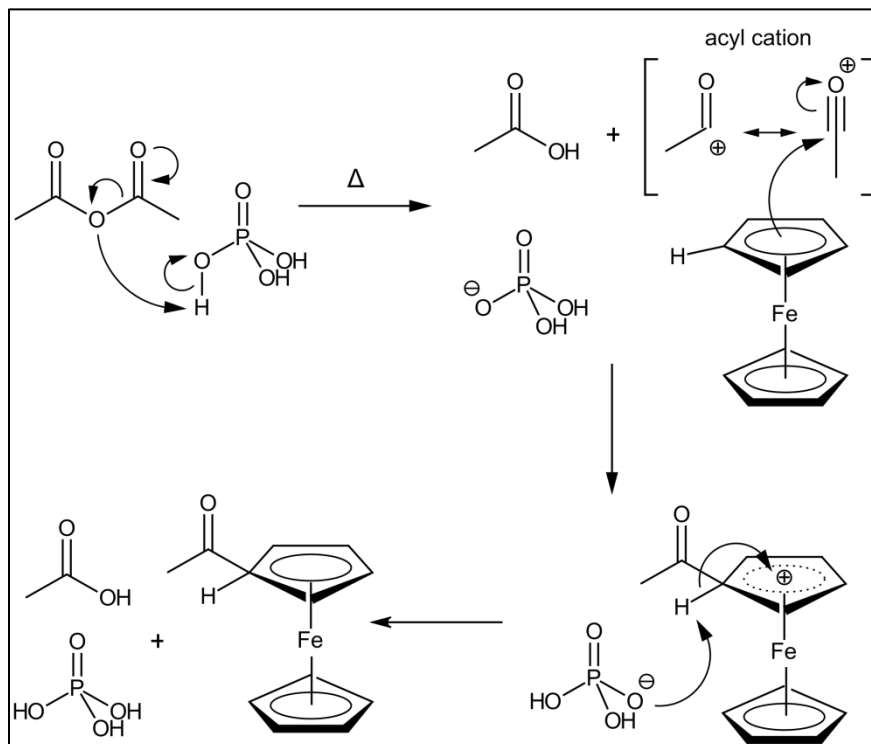
*Equipment/materials:*

- Thermo Scientific™ picoSpin™ 80
- Ferrocene (C<sub>10</sub>H<sub>10</sub>Fe)
- Acetic anhydride (C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>)
- Phosphoric acid
- Hexanes
- Diethyl ether
- Dichloromethane
- NMR solvent: CDCl<sub>3</sub> w/ 1% TMS
- NMR solvent: Acetone-d<sub>6</sub> w/ 1% TMS
- Test tube (13 x 100mm)
- Silica gel (230-425 mesh), or alumina
- Tapered Collar neoprene filter adapter
- Several 7 mL vial with PTFE cap liner
- 1 mL polypropylene syringes
- 22 gauge blunt-tip dispensing needles
- Pasteur pipet
- Pipet bulb
- Polypropylene funnel
- Weighing paper/boat
- Cotton swab/ball
- Hirsch funnel
- Filter paper
- pH paper or litmus paper
- Ring stand, ring clamp, iron ring
- 25 mL vacuum flask
- Septum stopper
- Several 10, 25 and 50 mL beakers
- Mnova NMR Processing Suite
- picoSpin accessory kit:
  - Port plugs
  - Syringe port adapter
  - Drain tube assembly

*Reaction:*



Mechanism:



Physical data:

| Substance  | FW (g/mol) | Quantity | MP (°C) | BP (°C) | Density (g/mL) |
|--|------------|----------|---------|---------|----------------|
| ferrocene  | 186.04     | 180 mg   | 172.5   | -       | 1.107          |
| acetic anhydride                                       | 102.09     | 0.7 mL   | -73.1   | 139.8   | 1.08           |
| phosphoric acid (H <sub>3</sub> PO <sub>4</sub> ), 85% | 98         | 0.2 mL   | -       | -       | 1.88           |
| acetylferrocene  | 228.07     | -        | 81-83   | -       | -              |
| hexanes  | 86.18      | 10-15 mL | -95     | 68-69   | 0.655          |
| diethyl ether  | 74.12      | 10-15 mL | -116.3  | 34.6    | 0.7134         |
| dichloromethane  | 84.93      | 2 mL     | -96.7   | 41      | 1.33           |
| chloroform-d (CDCl <sub>3</sub> ) w/1%TMS              | 120.384    | 1 mL     | -64     | 61      | 1.50           |
| chloroform*  | 119.38     | 1 mL     | -82.3   | 61.2    | 1.48           |
| acetone*   | 58.08      | 1 mL     | -95     | 56      | 0.791          |
| acetone-d <sub>6</sub> (Ac-d <sub>6</sub> ) w/ 1%TMS*  | 64.12      | 1 mL     | -94     | 56      | 0.872          |

\*Optional NMR solvents

## Safety Precautions



**CAUTION** Eye protection should be worn at all times while using this instrument. Phosphoric acid is a strong dehydrating agent; Wear protective gloves when pouring concentrated phosphoric acid. Acetic anhydride can burn the skin. Pour acetic anhydride in a fume hood. Avoid contact with skin and clothes.



**CAUTION** Avoid shock hazard. Each wall outlet used must be equipped with a 3-prong grounded outlet. The ground must be a noncurrent-carrying wire connected to earth ground at the main distribution box.

## Experimental

### *Reaction procedure*

- Add 184 mg of ferrocene to a 13 x 100 mm reaction test tube.
- Add 0.70 mL (0.76 mg) of acetic anhydride.
- Add 0.2 mL (340 mg) of 85% phosphoric acid.
- Cap the tube with a septum bearing an empty syringe needle.
- Warm the reaction tube on a steam bath or in a beaker of hot water.
- Agitate the mixture to dissolve the ferrocene.
- Once dissolve, heat the mixture an additional 10 min and then cool the tube thoroughly in an ice bath.
- Dropwise, carefully add 1 mL of ice water - mix thoroughly
- Dropwise, carefully add 3 M aqueous sodium hydroxide solution until the mixture is neutral (~3 mL) - use pH paper; avoid an excess of base.
- Collect the product on a Hirsch funnel (or by gravity filtration).
- Wash the product thoroughly with water. Press it dry between sheets of filter paper.
- Save a sample for melting point and TLC analyses (optional).
- Purify the remainder by column chromatography.

Prior to packing the column, label and tare (weigh) several 7 mL vials and 2-25 mL flasks for receiving eluting fractions.

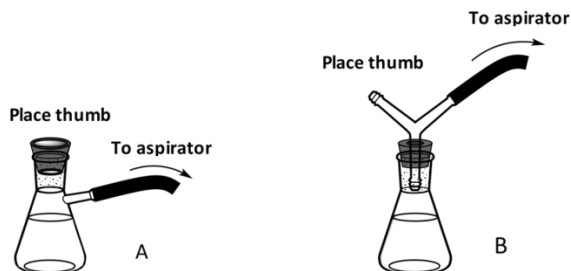
### *Preparing Samples*

Several samples will be prepared for analysis. These solutions can be prepared in chloroform ( $\text{CHCl}_3$ ), chloroform-d ( $\text{CDCl}_3$ ) or acetone- $\text{d}_6$  ( $\text{Ac-d}_6$ ). If  $\text{CHCl}_3$  is used then its proton NMR signal, at 7.24 ppm, can be used to shift reference the spectrum, otherwise the TMS signal (0 ppm) in  $\text{CDCl}_3$  or  $\text{Ac-d}_6$  is used. The sample preparation guide and spectra presented are for  $\text{CDCl}_3$  solutions.

- Prepare about 10 mL of a 50:50 mixture of hexanes and diethyl ether in a flask. Stopper the flask to prevent diethyl ether from evaporating.
- Sample 1: To a tared, labeled vial measure about 30 mg of ferrocene and dissolve in 200  $\mu\text{L}$  of  $\text{CDCl}_3$ . Record the sample weight. Cap and save for NMR analysis.
- Sample 2: To a tared, labeled vial measure about 30 mg of acetylferrocene (*Caution: toxic*) and dissolve in 200  $\mu\text{L}$  of  $\text{CDCl}_3$ . Record the sample weight. Cap and save for NMR analysis.
- Sample 3: To a tared, labeled vial measure about 20-30 mg of dried crude reaction product and dissolve in 200  $\mu\text{L}$  of  $\text{CDCl}_3$ . Record the sample weight. Cap and save for NMR analysis.
- Chromatography Sample 4: To a tared, labeled vial measure the balance of the crude reaction product. Record the sample weight. Dissolve in a minimum amount of dichloromethane. Once dissolved, add about 300 mg of silica gel (pre-weighed) and thoroughly mix the solution. Evaporate off the solvent in a hot water bath being careful not to cause bumping. (*Reminder: dichloromethane boils at 41 °C.*). This sample is used for chromatography.

### Chromatography fractions

Prior to preparing these samples, the eluting solvent must be evaporated off. A quick way to evaporate the solvent is under vacuum. Use a filter flask connected to a faucet aspirator and fitted with tapered collar neoprene (or 1-hole rubber stopper) as shown in Figure 1. Using your thumb control the vacuum pressure. Under reduced pressure, the boiling point of the eluting solvents lower to where the warmth of your hand is sufficient to cause boiling. Alternatively, in the absence of 25 mL vacuum flasks a similar apparatus can be made with a regular flask (or vial) using a 1-hole stopper and a Y-connector.



**Figure 1.** A. Evaporation flask with filter adapter. B. Flask (or vial) with Y-connector.

- Fraction 1: Collect fraction 1 in a tared, labeled 25 mL vacuum flask, 25 mL flask or 7 mL vial. Dry, weigh and record the amount of sample recovered. Add 200  $\mu\text{L}$  of  $\text{CDCl}_3$ . Cap and save for NMR analysis. (*NOTE:* There should be very little ferrocene remaining. If less than 15 mg of material is available then only prepare a solution for Fraction 2.)
- Fraction 2: Collect fraction 2 in a tared, labeled 25 mL vacuum flask, 25 mL flask or 7 mL vial. Dry, weigh and record the amount of sample recovered. Add 200  $\mu\text{L}$  of  $\text{CDCl}_3$ . Cap and save for NMR analysis.

### *Packing the Column*

Whether using a microscale or macroscale technique, it is important, and critical to the success of column chromatography, to pack the column uniformly such that it is free of air pockets and gaps. Two methods for column packing are used: dry packing and slurry packing. In dry packing, the adsorbent, silica gel or alumina, is added directly to the column and 'tapped' into place to remove cracks, gaps and air pockets, then the first eluting solvent is added to wet the column. With slurry packing, a slurry mixture of adsorbent and first eluting solvent is prepared and then poured into the column. The preferred method is slurry packing as it has a higher chance of minimizing gaps and air bubbles, but can be a difficult technique to perfect since adsorbent must stay suspended during transfer to the column.

### *Dry Packing Method*

For microscale columns using a Pasteur pipet, the dry packing method is preferred.

- Remove the cotton end of a cotton swab, or an equivalent pea-sized cotton ball, and plug a Pasteur pipet. Use a wooden stick or stir rod to tamp it into place. Do not pack it too tightly.
- Measure about 5 mL of adsorbent using a 10 mL beaker. Add dry adsorbent to a height of about 5-6 cm. Leave  $\sim 3$  cm at the top for the pre-adsorbed. (Folded weighing paper is helpful in transferring adsorbent to the column).
- Pack the column by alternately gently tapping the side of the column with a stir rod or spatula, and tamping it on the bench top. Add more column pack material as need.
- Once *chromatography sample 4* is prepared, pre-elute the column with hexanes (the first eluent). Do not let the column dry out; allow a small volume of eluent to remain above the column pack.
- Use a disposable syringe or pipet to add additional solvent.

### *Slurry Packing Method*

Slurry packing a Pasteur pipet column is difficult because the pipet opening is small and the slurry needs to be introduced rapidly. This technique is better suited to macroscale chromatographic column preparation, such as with a burette.

- Fill a 25 mL beaker to about the 5 mL line with adsorbent. Add hexanes to initially wet the adsorbent, then while swirling add additional hexanes to produce a slurry. (*Note:*

Increase the quantity of adsorbent and solvent accordingly to accommodate larger columns. With a burette, close the stopcock, and add solvent about a third of the way up the column.)

- When ready, swirl the mixture to produce a suspension, simultaneously removing air bubbles, and then quickly pour the slurry into the column.
- Fill to a height of about 5-6 cm. Leave ~3 cm at the top for the pre-adsorbed.
- Tap the side of the column to cause the adsorbent to settle.
- Do not let the column dry out; allow a small volume of eluent to remain above the column pack.
- Use a disposable syringe or pipet to add additional solvent.

#### *Adding the Sample*

- To the top of the column, add all of *chromatography sample 4*, gently tapping to settle the dry powder.

### **Chromatography of a Mixture of Ferrocene and Acetylferrocene**

#### *Eluting the Column*

Two fractions will be collected. The first fraction will be eluted using hexanes. The second fraction will be eluted with a 50:50 mix of hexanes and diethyl ether.

To make this column chromatography a 'flash' technique

- Use a pipet to add eluting solvent to fill the remaining available column space.
- Use a pipet bulb to 'push' the solvent through the column. Allowing only for gravity to percolate solvent through the column is very slow. The flash technique speeds up the process.
- Be careful not to aspirate the solvent and column pack to into the pipet bulb. Create a light seal when squeezing, and break the seal before releasing pressure on the bulb.
- Even while pushing the solvent, always maintain the solvent level just above the column pack. Add additional solvent as needed.
- Collect solvent in a small waste beaker as it passes through the column until the yellow band approaches the top of the cotton plug.
- Ferrocene (fraction 1) is eluted first with hexanes and is visible as a yellow band.
- Collect fraction 1 in the tared, labeled vial. Cap and set the vial aside.
- Replace the waste beaker under the column. Switch to the next eluting solvent.
- Acetylferrocene is eluted next (fraction 2) with a 50:50 mix of hexanes and diethyl ether, and is visible as an orange band.
- Maintain a solvent level just above the column pack.
- Continue collecting solvent in the waste beaker until the orange band approaches the top of the cotton plug, and then swap the beaker and collect this fraction in the tared vial labeled fraction 2.
- Cap and set the vial aside.



- Evaporate the solvents from the two vials (or flasks) and determine the weights of the crude residues.
- *Optional:* Recrystallize fractions from a minimum quantity of hot hexanes.
- *Optional:* Isolate and dry the crystals. Determine their weights and melting points.
- Calculate the percent recovery of the crude and recrystallized products.

### Instrumental procedure

The general procedure for sample analysis using a picoSpin NMR spectrometer is as follows:



#### *Shim*

- Ensure the NMR spectrometer is shimmed and ready to accept samples.

#### *Pre-sample preparation*

- Displace the shim fluid from the picoSpin capillary cartridge with air.
- Flush the cartridge with 0.1 mL of chloroform, and then displace the solvent with an air push. A small signal in your sample spectrum may appear at 7.24 ppm due to residual  $\text{CHCl}_3$ , it can be used to shift reference the spectrum.
- Set up the *onePulse* script according to parameters listed in the Pulse Script table.

#### *Injection*

- Using a 1 mL disposable polypropylene syringe fitted with a 1.5" long, 22 gauge blunt-tip needle, withdraw a 0.2 mL aliquot of sample.
- Inject about half the sample. Ensure all air bubbles have been displaced from the cartridge by examining the drain tube.
- Cap both the inlet and outlet ports with PEEK plugs.

#### *Acquire*

- Execute the onePulse script according to the values in the table of parameters provided
- Once the onePulse script has finished, prepare the cartridge for the next user by displacing the sample from the cartridge according to the following protocol: air, solvent, air.

Pulse Script: onePulse

| Parameter                | Value                                |
|--------------------------|--------------------------------------|
| tx frequency (tx)        | proton Larmor frequency (MHz)        |
| scans (ns)               | 16                                   |
| pulse length (p1)        | Instrument specific 90° pulse length |
| acquisition time (aq)    | 750 ms                               |
| rx recovery delay (r1)   | 500 µs                               |
| T1 recycle delay (d1)    | 8 s                                  |
| bandwidth (bw)           | 4 kHz                                |
| post-filter atten. (pfa) | 10 (11) <sup>a</sup>                 |
| phase correction (ph)    | 0 degrees (or any value)             |
| exp. filter (LB)         | 0 Hz                                 |
| max plot points          | 400                                  |
| max time to plot         | 250 ms                               |
| min freq. to plot        | -200 Hz                              |
| max freq. to plot        | +1000 Hz                             |
| zero filling (zf)        | 8192                                 |
| align-avg. data          | ✓                                    |
| live plot                | ✓                                    |
| JCAMP avg.               | ✓                                    |
| JCAMP ind.               | Unchecked                            |

<sup>a</sup> Choose the instrument's default pfa values

## 6. Processing

Download the experimental JCAMP spectra files and open them by importing into Mnova. The free induction decay (FID) will undergo automatic Fourier transformation and a spectrum will be displayed. To each spectrum, apply the following processing steps using the given settings:

| Function                                | Value                 |
|---|-----------------------|
| Zero-filling (zf) & Linear Predict (LP) | 16 k                  |
| Forward predict (FP)                    | From aq → 16 k        |
| Backward predict (BP)                   | From -2 → 0           |
| Phase Correction (PH)                   | PH0: Manually adjust  |
|   | PH1: 0                |
| Apodization                             |                       |
| Exponential (LB)                        | 0.6 Hz                |
| First Point                             | 0.5                   |
| Shift reference (CS)                    | Manually reference    |
| Peak Picking (pp)                       | Manually Select Peaks |
| Integration (I)                         | Automatic Selection   |
| Multiplet Analysis (J)                  | -                     |

- Import each data file into the same workspace in Mnova. Manually apply Ph0 phase correction to each spectrum.
- Manually shift reference each spectrum using Mnova's TMS tool. Assign the TMS signal (0 ppm) or CHCl<sub>3</sub> signal (7.24 ppm), whichever is present.
- Identify and assign each signal in the spectra.
- Save the Mnova document, print each spectrum and paste into your lab notebook.

## 7. Results

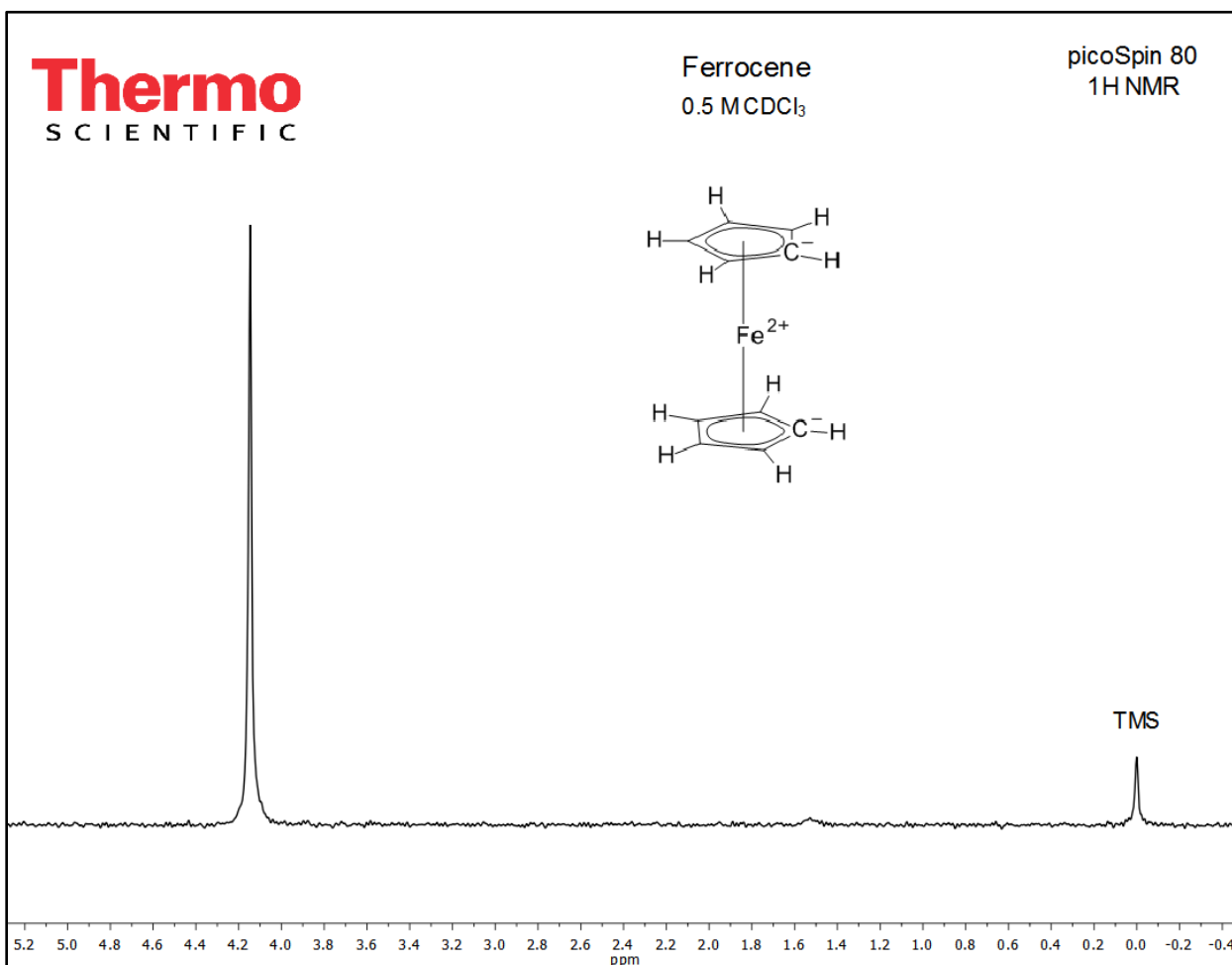
The <sup>1</sup>H NMR spectrum of a 0.5 M solution of ferrocene in CDCl<sub>3</sub> is presented in Figure 2. The spectrum dominated one signal centered at 4.14 ppm, arising from the target sample. Due to high symmetry of this metallocene, the singlet arises from excitation of 10 chemically and magnetically equivalent aromatic bis-cyclopentadienyl protons.

The <sup>1</sup>H NMR spectrum of a 0.5 M solution of acetylferrocene in CDCl<sub>3</sub> is presented in Figure 3. Acylation of one of the aromatic cyclopentadienyl rings disrupts the previous symmetry of ferrocene, resulting in three cyclopentadienyl proton signals and one acetyl proton signal. The singlet appearing at 2.38 ppm, assigned as 'c', arises from excitation of 3 acetyl (-CH<sub>3</sub>) protons. The singlet appearing at 4.19 ppm, assigned as 'b', arises from excitation of 5 protons on the unsubstituted cyclopentadienyl ring. The two multiplet signal groups appearing at 4.48 and 4.76 ppm, assigned as 'a', arise from excitation of 4 protons on the substituted cyclopentadienyl ring. The 2 ring protons closest to the acetyl group are more strongly deshielded and shift further downfield at 4.76 ppm, while the other two ring protons, being more shielded, appear at 4.46 ppm. The multiple structures derive from non-first order coupling of adjacent protons on the substituted ring.

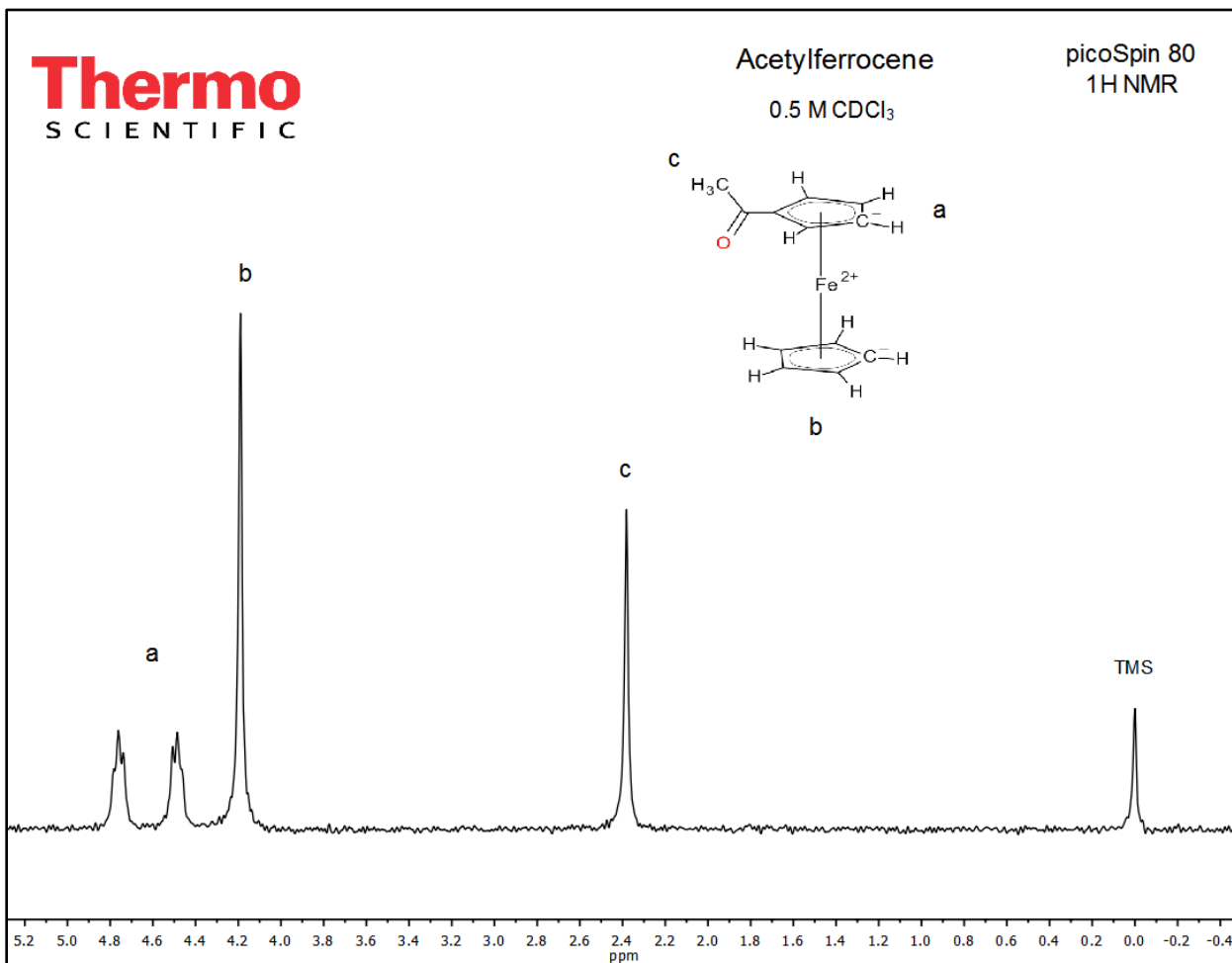
Figure 4 shows the <sup>1</sup>H NMR spectrum of crude isolated reaction product, acetylferrocene, in CDCl<sub>3</sub>. The characteristic acetyl singlet and double multiplet structures of the substituted ring of acetylferrocene is evident in this solution spectrum. The unsubstituted ring proton signal appears at 4.19 ppm. Unreacted ferrocene appears as a shoulder peak on the upfield side (4.14 ppm) of the acetylferrocene signal. These signal groups, the double multiplet structures or acetyl group protons, aid in distinguishing acetylferrocene from ferrocene in the NMR spectrum of the mixture. Diacetylferrocene, where acetyl substitution occurs on each cyclopentadienyl ring would contain only three signals, the doublet of multiplets at 4.48 and 4.76 ppm, respectively, and an acetyl signal at 2.38 ppm. It is distinguishable from acetylferrocene by the absence of the unsubstituted cyclopentadienyl signal. Integrating the spectrum can reveal the presence of diacetylferrocene. The expected signal ratio for acetylferrocene is 2:2:5:3, deviation from this ratio suggests the presence of diacetylferrocene.

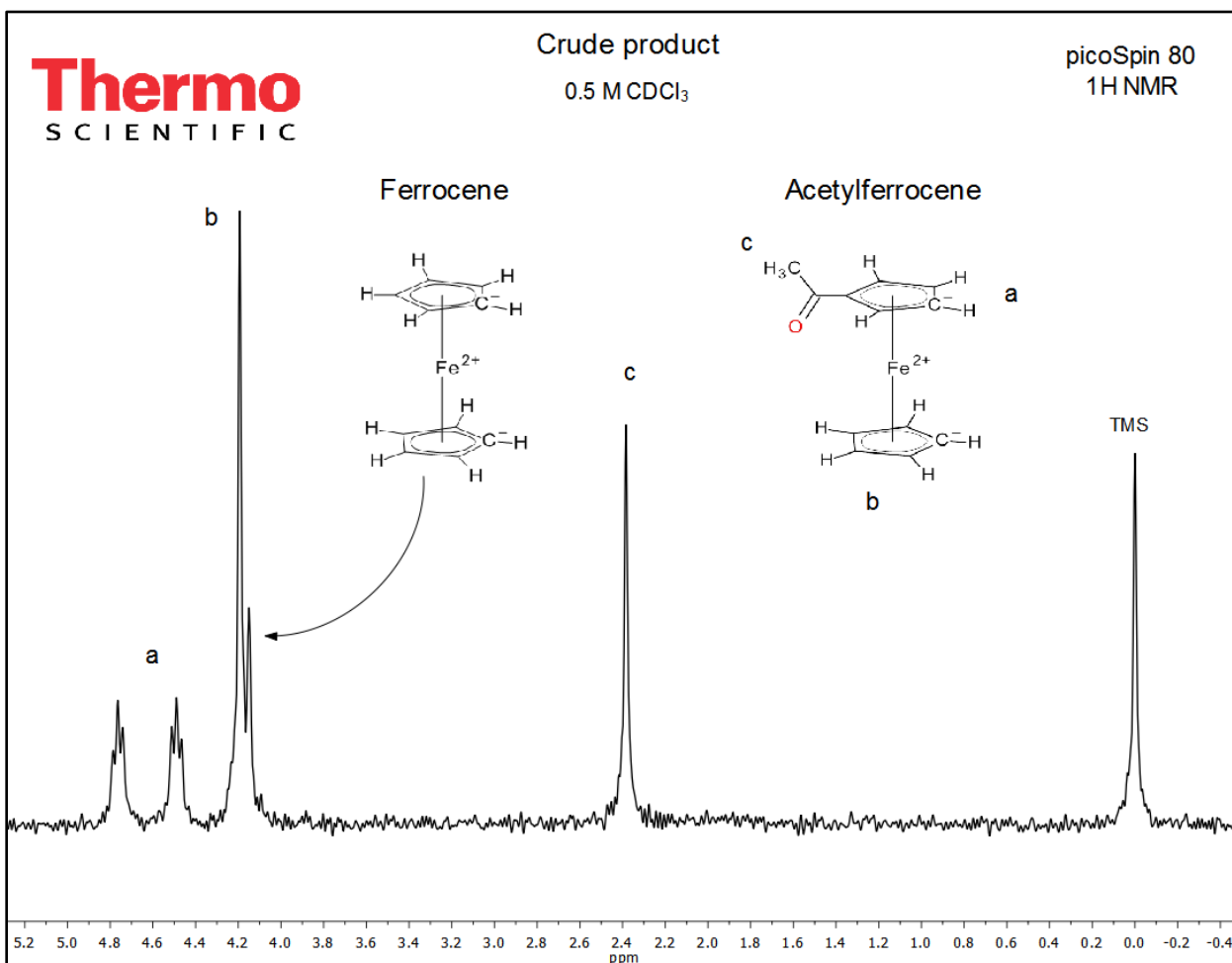
The NMR spectrum of isolated and purified product eluted from the chromatographic column, fraction 2, and recrystallized is shown in Figure 5. Similar to the crude product spectrum (Figure 4), this spectrum displays the characteristic double multiplet structures of

acetylferrocene and the acetyl singlet at 2.38 ppm. The shoulder peak due to ferrocene on the upfield side of the unsubstituted cyclopentadienyl ring of acetylferrocene signal is visibly absent as expected after the product is chromatographed on the silica gel column.

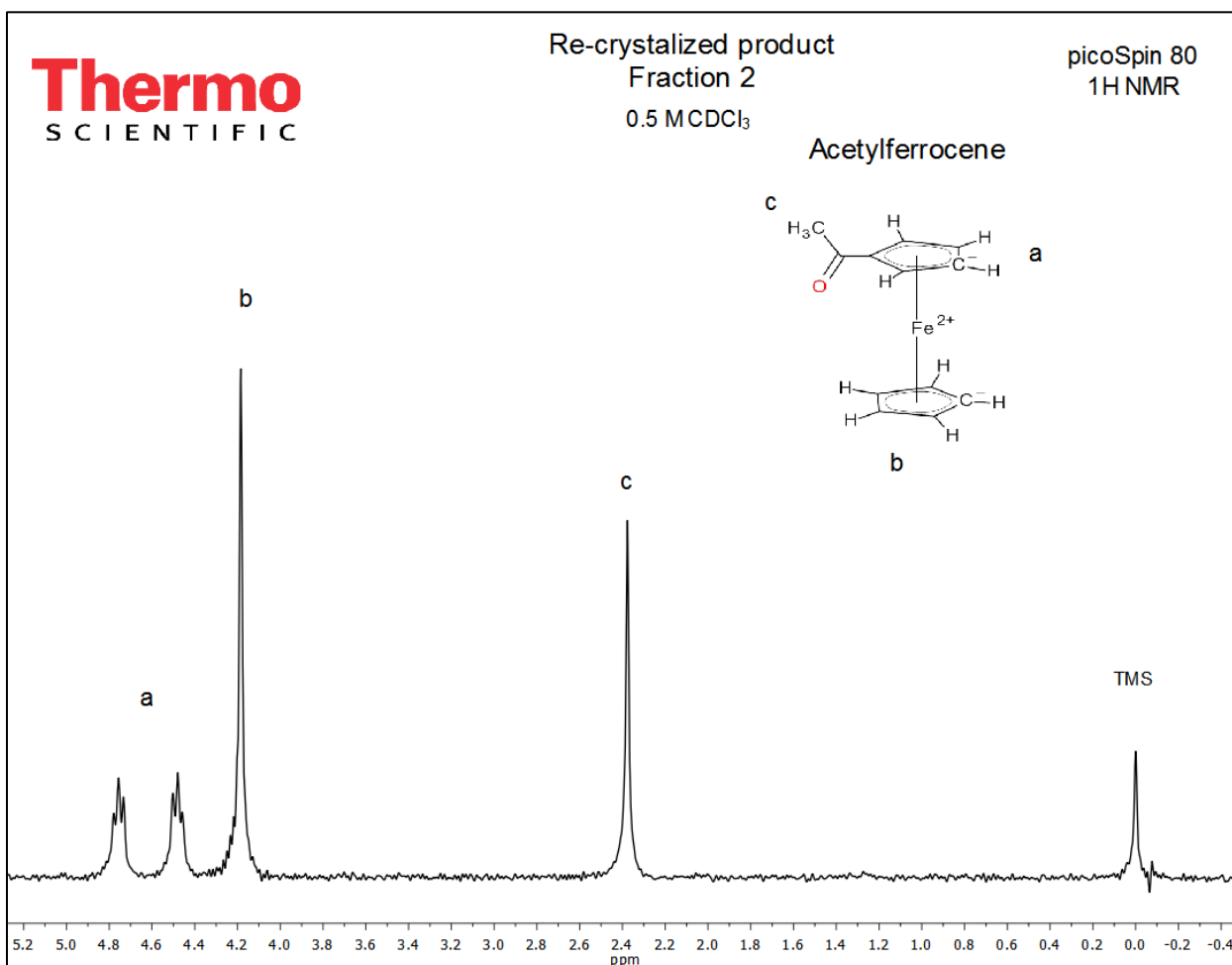


**Figure 2.** Full <sup>1</sup>H NMR (82 MHz) spectrum of a 0.5 M solution of ferrocene in CDCl<sub>3</sub>.





**Figure 4.** Full <sup>1</sup>H NMR (82 MHz) spectrum of a 0.5 M solution of crude reaction product (acetylferrocene) in CDCl<sub>3</sub> prior to column purification.



**Figure 5** Full <sup>1</sup>H NMR (820 MHz) spectrum of 0.5 M of recrystallized, chromatographic fraction 2 (acetylferrocene) in CDCl<sub>3</sub> after column separation.

Table 1. <sup>1</sup>H NMR Spectral Data

| Figure  | Compound        | Signal Group  | Chemical Shift (ppm) | Nuclides | Multiplicity |
|---------|-----------------|---|----------------------|----------|--------------|
| 2-5     | TMS             | Si(CH <sub>3</sub> ) <sub>4</sub>   | 0                    | 12 H     | Singlet      |
| 2, 4, 5 | Ferrocene       | Fe[C <sub>5</sub> H <sub>5</sub> ] <sub>2</sub>   | 4.14                 | 10 H     | Singlet      |
| 3-5     | Acetylferrocene | Fe[C <sub>5</sub> H <sub>5</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>4</sub> C(O)CH <sub>3</sub> | 2.38                 | 3 H      | Singlet      |
|         |                 | Fe[C <sub>5</sub> H <sub>5</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>4</sub> C(O)CH <sub>3</sub> | 4.19                 | 5 H      | Singlet      |
|         |                 | Fe[C <sub>5</sub> H <sub>5</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>4</sub> C(O)CH <sub>3</sub> | 4.48                 | 2 H      | Triplet      |
|         |                 | Fe[C <sub>5</sub> H <sub>5</sub> ] <sub>2</sub> C <sub>5</sub> H <sub>4</sub> C(O)CH <sub>3</sub> | 4.76                 | 2 H      | Triplet      |
|         | Water           | HOD   | 4.65                 | 1 H      | Singlet      |
|         | Chloroform      | CHCl <sub>3</sub>   | 7.24                 | 1 H      | Singlet      |
|         | Acetone         | O=C(CH <sub>3</sub> ) <sub>2</sub>  | 2.05                 | 6 H      | Singlet      |

