[redacted]

SYNTHESIS OF

CpFe(CO)$_2$C(O)Ph

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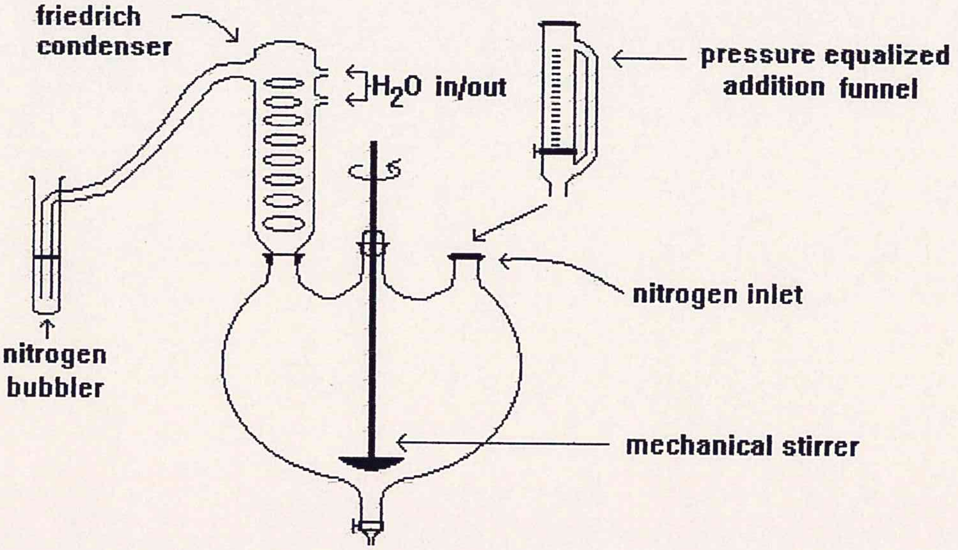
OBJECTIVE:

In this experiment I am planning to learn the technique of synthesizing the compound $CpFe(CO)_2C(O)Ph$ from $[CpFe(CO)_2]_2$. This includes some techniques for synthesizing inorganic compounds, such as under a nitrogen atmosphere and using almagum as a catalyst.

METHODOLOGY:

We will be synthesizing the compound in a 500 mL 3-necked flask. Attached to the flask will be a mechanical stirrer, a pressure equalized addition funnel, and a Friedrich condenser. The neck with the pressure equalized addition funnel will also be used as the nitrogen inlet. The Friedrich condenser will be the nitrogen outlet. The nitrogen will outlet through a bubbler so as not to allow air into the reaction flask. The setup can be seen below.



First, flush the apparatus with nitrogen for a few minutes to make sure that there is a nitrogen atmosphere in the reaction flask. Then add 30 mL of mercury to the flask, and replaced the nitrogen inlet. Sodium metal is then cut underneath a hydrocarbon solvent. About two grams of freshly cut sodium is needed. The sodium is cut into small pieces of about 0.2 gram a piece and then added to the flask. The addition of sodium is done one piece at a time because the reaction between the sodium and the mercury is very exothermic. This mixture of the sodium and the mercury is called amalgam and acts as a catalyst for the reaction.

The almagam is then allowed to cool to room temperature. 100 mL of dry THF is added to the flask and allowed to stir for a few minutes. Add 5.0 grams of $[CpFe(CO)_2]_2$ to the flask. Vigorously stir the solution under a nitrogen atmosphere for about 30 minutes. Note a color change should take place. After the stirring is complete then the amalgam is drained. With the nitrogen flowing, add 7 mL of benzoyl chloride in 50 mL of THF to the addition funnel. Add this solution dropwise to the reaction flask over a time of about 15 minutes. Then let the flask stir for an additional 15 minutes. The solution is then drained into a round bottom flask under nitrogen and the solvent removed under vacuum on a rotary evaporator. Add 25 mL of toluene to the solution. The impurities in the solution will precipitate out. The solution is the purified by suction filtered under a nitrogen flow. Three times the solution of hexane is added and the contents cooled in a dry-ice bath to give yellow crystals.

The reaction is summarized below:

$$[CpFe(CO)_2]_2 \xrightarrow{Na/Hg} Na^+[CpFe(CO)_2]^-$$

$$Na^+[CpFe(CO)_2]^- + \text{benzoyl chloride} \longrightarrow CpFe(CO)_2C(O)Ph + NaCl$$

EXPERIMENT AND RESULTS:

During the reaction of the $[CpFe(CO)_2]_2$ in the flask, the color change from a dark brown to a lighter reddish-brown color. This is a sign that the reaction from the dimer to the monomer took place. When we placed the purified solution in the dry-ice bath, we cooled the compound to cool. We believe that we froze the toluene. So when we tried to collect the crystals we could not get any. Perhaps if we did not cool the solution as much as we did we may have gotten some crystals of $CpFe(CO)_2C(O)Ph$. For the purpose of completing this experiment we will use the previously recorded spectrums of $CpFe(CO)_2C(O)Ph$ and assume a recovery of 1.9 grams of $CpFe(CO)_2C(O)Ph$ crystals from the solution.

Percent Yield:

Actual yield = 1.9 g

$$5.0g\ [CpFe(CO)_2]_2 \times \frac{1\ mol\ [CpFe(CO)_2]_2}{353.87g} \times \frac{2\ mol\ [CpFe(CO)_2]C(O)Ph}{1\ mol\ [CpFe(CO)_2]_2} \times \frac{282.63\ g}{1\ mol\ CpFe(CO)_2C(O)Ph} = 7.97g\ CpFe(CO)_2C(O)Ph$$

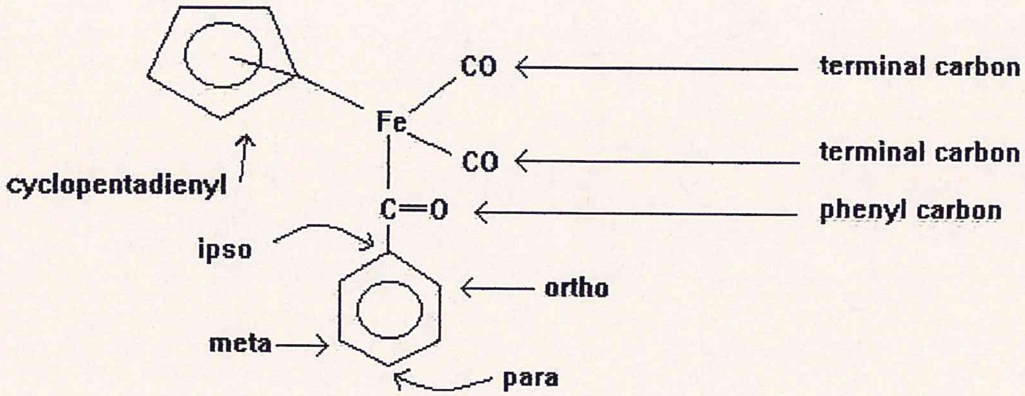
Percent yield = 1.9/7.97 x 100 = 23.8%

INTERPRETATION:

INFRARED SPECTRUM

Chemical Environment	Peak (cm^{-1})
terminal carbon	2023.46
terminal carbon	1965.59
phenyl carbon	1550.87
phenyl carbon	1575.44
phenyl carbon	1589.44
phenyl carbon	1610.56

NMR SPECTRUM



^{1}H spectrum

Chemical Environment	Peak (ppm)	Peak Type
Cyclopentadienyl	4.94	singlet
ortho	7.36	quartet
meta	7.37	quartet
para	7.48	quartet
ipso	7.49	quartet

^{13}C spectrum

Chemical Environment	Peak
C=O of phenyl	254
CO of Fe	214.02
ipso	151.04
para	130.32
meta	128.12
ortho	126.01
cyclopentadienyl	86.36

3. Experiment and Results.

The actual spectral data is found in the Appendix. The following tables contain specific peak values for the compounds: $CpFe(CO)_2C(O)Ph$, $H_4RuOs_3(CO)_{12}$, $H_2RuOs_3(CO)_{13}$, and $H_2Os_4(CO)_{13}$.

Table I. Mass Spectrometer Values for $CpFe(CO)_2C(O)Ph$.

Remaining Group	Mass Spec value in AMU
$CpFe(CO)_2C(O)Ph$	282
CpFeCO(CO)Ph	254
CpFeCOPh	226
CpFePh	198
$CpFeC_4H_4$	172
CpFeCO	149
CpPh	142
FePh	133
CpFe	121
CpC_4H_3	115
PhCO	105
FeC_3H_3	95
Ph	77
Cp	65
Fe	56
C_4H_3	51
C_3H_3	39
CO	28
H_2O	18

Jim Dupree

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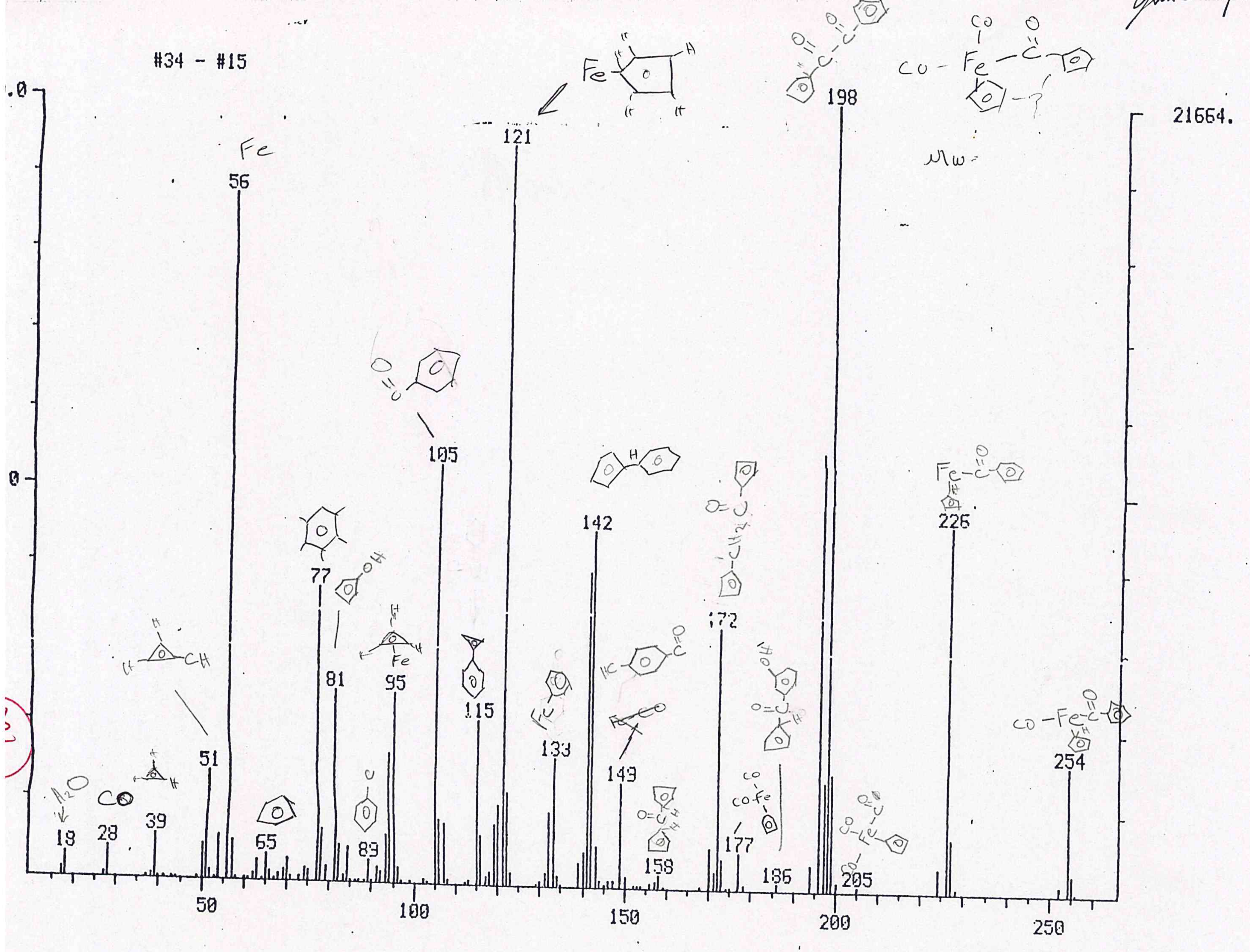


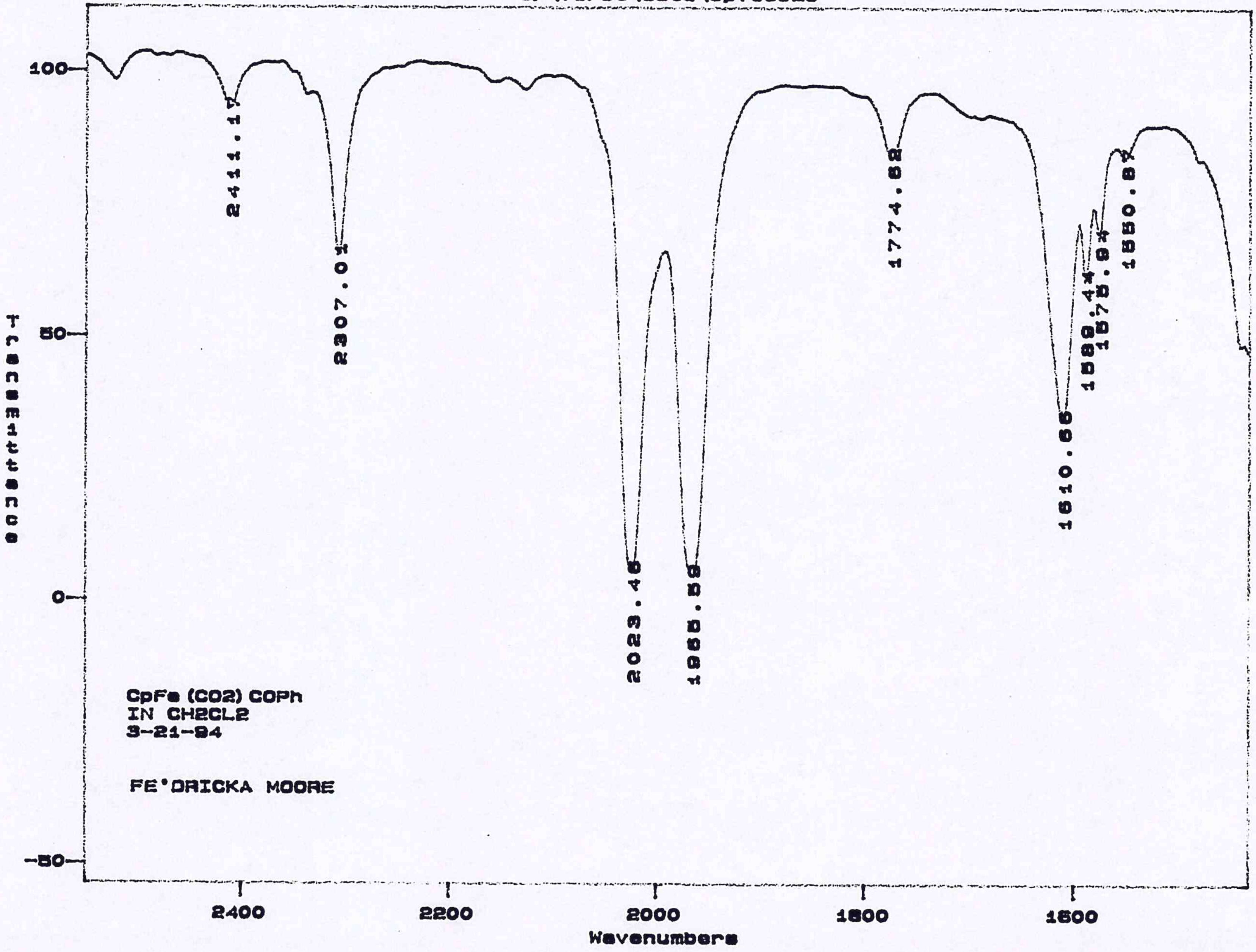
The ^1H NMR gave a single peak for the cyclopentadienyl protons. It does this because all of the protons are in the same environment and there is no coupling observed. Thus there is a very intense single peak. The protons of the phenyl roup show up where they are expected to be, in the 6.5-8.0 range. There are four chemically different protons in the phenyl ring. They are the ipso, meta, para, and ortho protons. That is why we get the four peaks for the phenyl region.

The ^{13}C spectrum gave us seven peaks. The two peaks that will be found the farthest downfield are the C double bond O groups. Oxygen pulls the electrons away from the Carbon allowing it to come into resonance in a lower field strength. The next carbons are the phenyl carbons. It is hard to tell for sure which carbon is which, but we can be fairly sure that the 151.04 peak is the ipso carbon. The para, meta, and ortho will all resonant at approximately the same location. The cyclopentadienyl carbons come into resonance last. They do this because the pi bonding effectively shields the carbons from the applied magnetic field.

CONCLUSION:

We did not actually obtain any of the monomer from the experiment. If we would have we could have run the spectrums on it and verified that it was the monomer and not some other compound. However the experiment gave us valuable experience in inorganic synthesis methods.

C: \first\data\cpfeco2c



CpFe (CO2) COPh
IN CH2CL2
3-21-94

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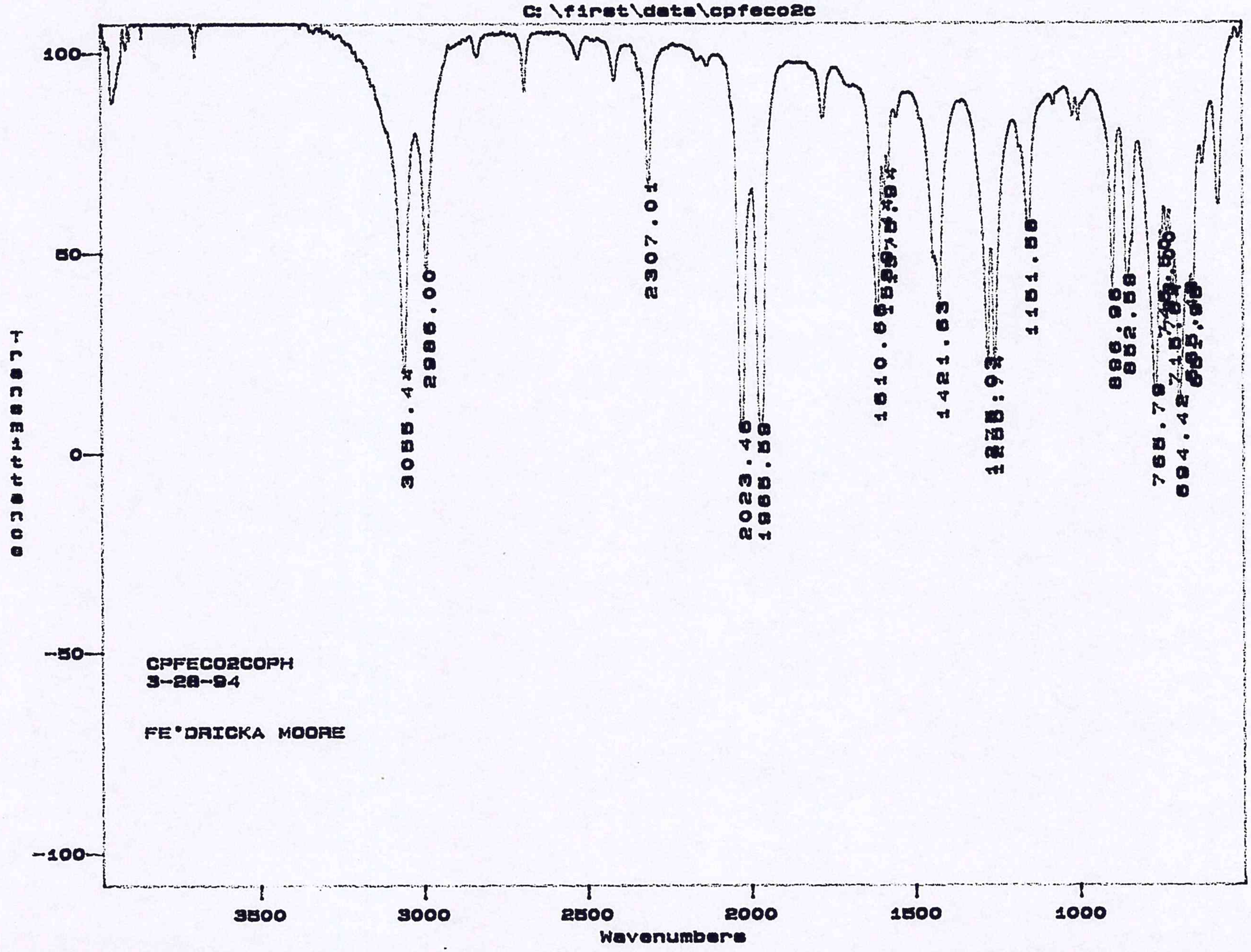
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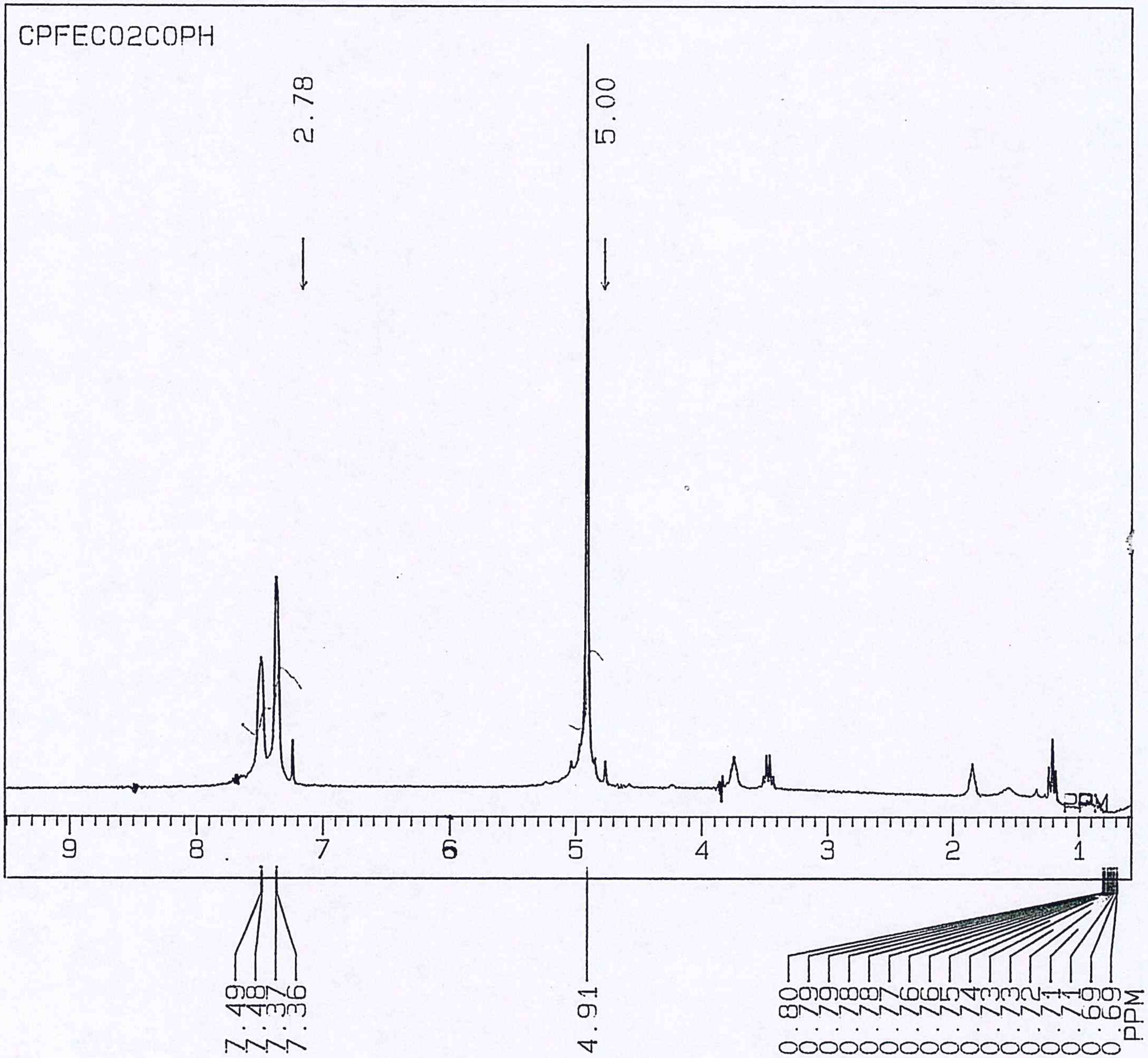
CPFECO2COPH
3-28-94
FE'DRICKA MOORE



CPF-270
LA TECH

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OBFIN        5400.0 Hz
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FREQU        5405.4 Hz
FILTR          2700 Hz
SCANS             74
ACQTM         1.516 sec
PD            3.000 sec
PW1             5.6 us
ADBIT     12
IRNUC 1H
IRSET        112.00 kHz
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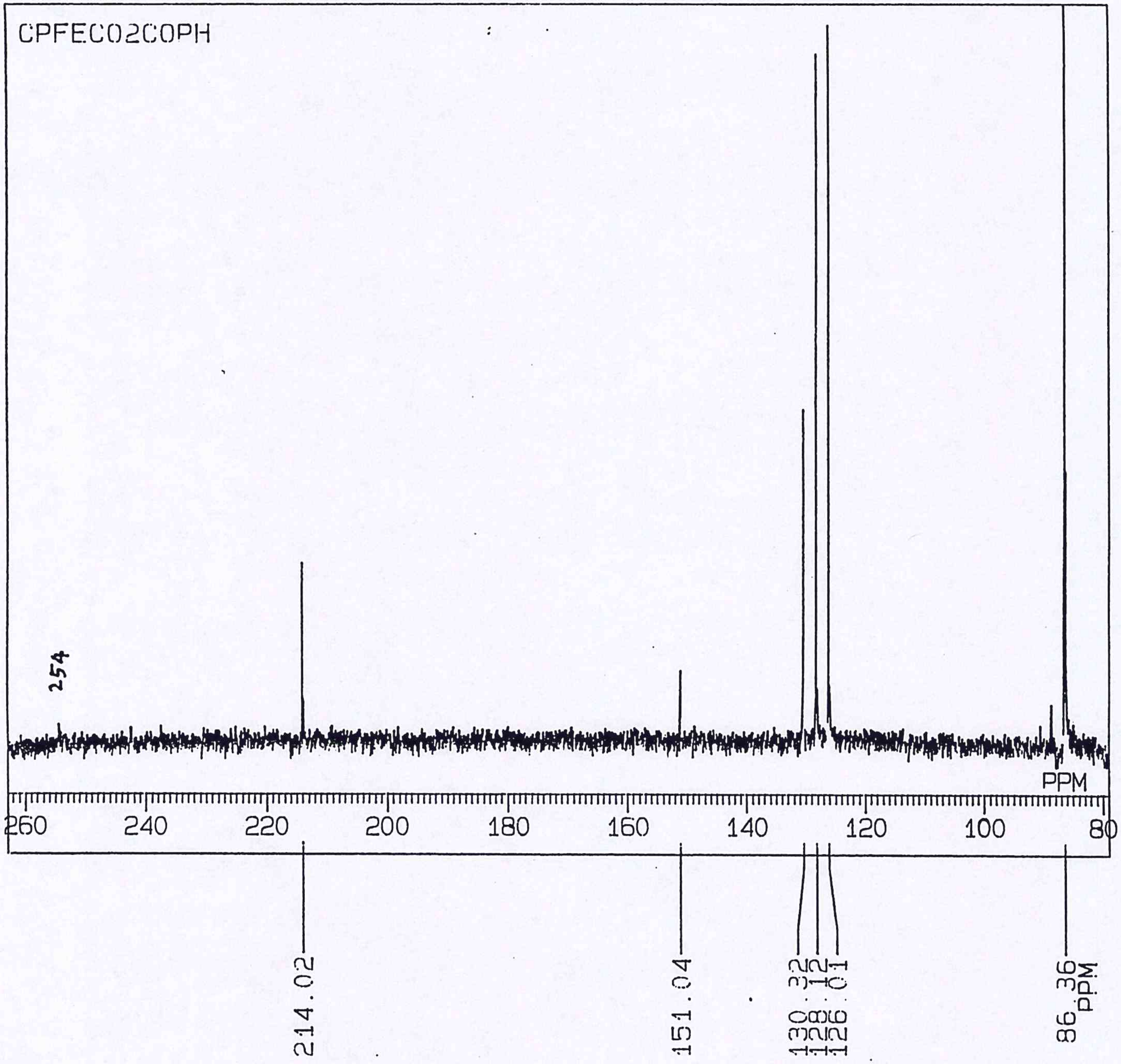

CPF-270
LA TECH

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FILTR        .9050 Hz
SCANS        10000
ACQTM        0.908 sec
PD           0.800 sec
PW1            2.5 us
ADBIT     12
IRNUC 1H
IRSET       112.00 kHz
IRFIN       5400.0 Hz
IRATN           32
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TEMP     27.0 c
SPEED           15 Hz
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EXREF         0.00 ppm
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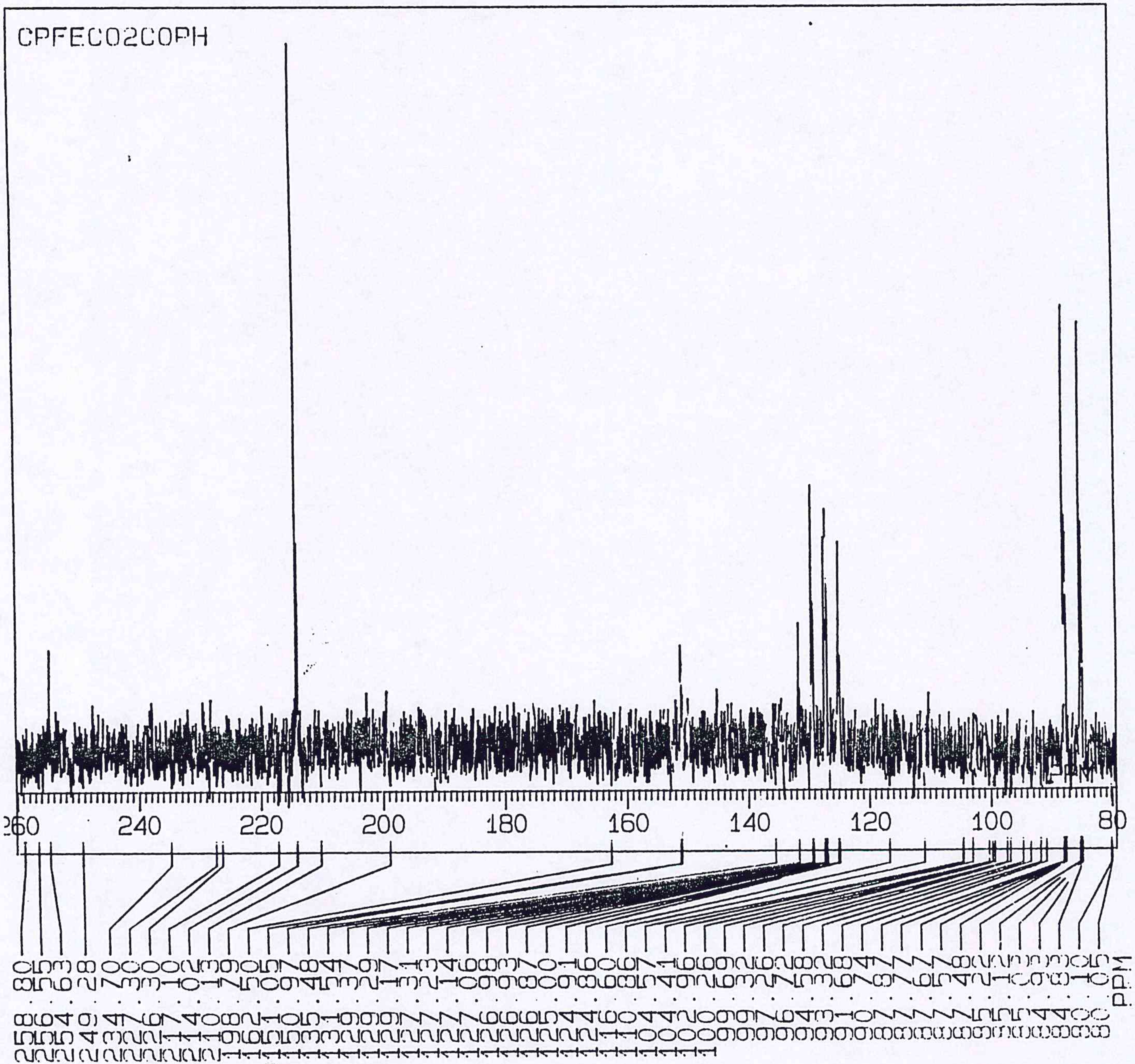
CPF-270
LA TECH



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FILTR	9050	Hz
SCANS	20000	
ACQTM	0.908	sec
PD	0.800	sec
PW1	2.5	us
ADBIT	12	
IRNUC	1H	
IRSET	112.00	kHz
IRFIN	5400.0	Hz
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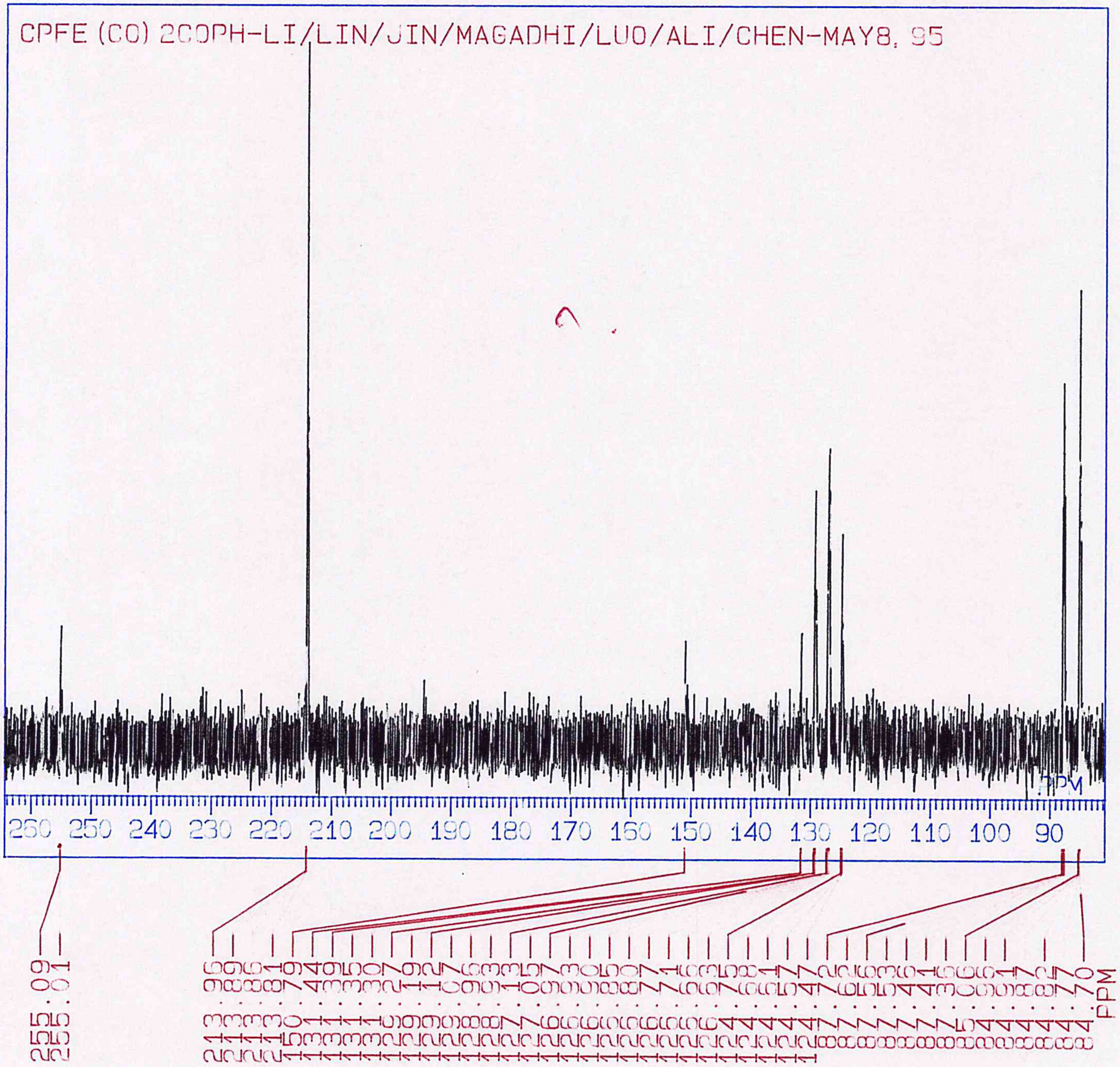

CPF-270
LA TECH

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FREQU        18050.5 Hz
FILTR           9050 Hz
SCANS          45263
ACQTM          0.908 sec
PD             0.800 sec
PW1              2.5 us
ADBIT     12
IRNUC 1H
IRSET         112.00 kHz
IRFIN         5400.0 Hz
IRATN             32
IRRPW             27 us
TEMP.   27.0 c
SPEED             15 Hz
SLVNT CDCL3
EXREF          77.00 ppm
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