

## Supporting Information

# Palladium-catalyzed aminations of aryl halides with phosphine-functionalized imidazolium ligands

Ji-cheng Shi,<sup>1, †, ‡</sup> Pengyu Yang,<sup>‡</sup> Qingsong Tong,<sup>†</sup> Li Jia<sup>†</sup>

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## General procedure

All reactions and manipulations involving air- and/or moisture-sensitive compounds were carried out using standard Schlenk technique under nitrogen. NMR spectra were recorded on a BRUKER DRX 400 MHz or Varian INOVA 400 MHz (<sup>1</sup>H 400 MHz; <sup>13</sup>C 100 MHz; <sup>31</sup>P 162 MHz) spectrometers. Chemical shifts are reported in ppm relative to TMS. Elemental analyses were obtained on an Elementar Vario EI analyzer. High-resolution mass spectra (HRMS, ESI) were obtained on a Micromass Q-ToF Micro (Micromass Inc., Manchester, England). GC analyses were performed on a BF-2002 spectrometer fitted with 50 m AT. SE-30 column. All amines, aryl bromides and chlorides (Aldrich or Acros) were used as received. Pd(OAc)<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub> were purchased from Acros chemical Company. 1,4-Dioxane, toluene and THF were distilled from sodium benzophenone ketyl under nitrogen. Anhydrous DMF was freshly distilled from calcium hydride. KOH was ground to a fine powder using a mortar and a pestle and dried in a vacuum oven prior to use. Cs<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KF, NaOBu<sup>t</sup>, K<sub>3</sub>PO<sub>4</sub> and NaOH were used as received.

**General Procedure for Aminations of Aryl halides.** *Representative Procedure:* An oven-dried round-bottom flask was cooled in vacuo, back-filled with nitrogen, and

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charged with Pd(OAc)<sub>2</sub>, imidazolium salts, and NaO<sup>t</sup>Bu (were weighed in air). Then the flask was evacuated, and back-filled with nitrogen (three times), and dioxane was added under nitrogen. The mixture was stirred at 50 °C for 0.5 h. After cooling to room temperature, the aryl halide and amine were added, and placed in an oil bath. The reaction was monitored by TLC or GC. After complete consumption of starting materials, the reaction mixture was allowed to cool to room temperature, filtered through a layer of Celite with the aid of ethyl acetate. The filtrate was concentrated in vacuo and the crude product was purified chromatographically and the products were identified by <sup>1</sup>H NMR.

**Cross-coupling products:**

**4-(4-Tolyl)morpholine**<sup>2</sup> The general procedure afforded 170mg (96%) of the title compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.87 (s, 4H), 3.71 (s, 3H), 3.86 (s, 4H), 6.84 (d, *J* = 7.6Hz, 2H), 7.09 (d, *J* = 8.0Hz, 2H).

**4-(4-Methoxyphenyl)morpholine**<sup>3</sup> The general procedure afforded 172mg (89%) of the title compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.00 (s, 4H), 3.71 (s, 3H), 3.80 (s, 4H), 6.78-6.80 (m, 4H).

**N-[4-(trifluoromethyl)phenyl]morpholine**<sup>4</sup> The general procedure afforded 201mg (87%) of the title compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.24 (t, *J* = 4.4Hz, 4H), 3.87 (t, *J* = 4.4Hz, 4H), 6.93 (d, *J* = 8.4Hz, 2H), 7.50 (d, *J* = 8.4Hz, 2H).

**N-(2-Pyridyl)morpholine**<sup>5</sup> The general procedure afforded 154mg (94%) of the title compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.46 (t, *J* = 5.2Hz, 4H), 3.78 (t, *J* = 4.8Hz, 4H), 6.59-6.64 (m, 2H), 7.44-7.48 (m, 1H), 8.18-8.19 (m, 1H).

**N-(2-Methylphenyl)morpholine**<sup>6</sup> The general procedure afforded 165mg (93%) of the title compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.30 (s, 3H), 2.88 (t, *J* = 4.8Hz, 4H), 3.82 (t, *J* = 4.8Hz, 4H), 6.98-7.01 (m, 2H), 7.14-7.18 (m, 2H).

**N-(4-Methylphenyl)phenylamine**<sup>5</sup> The general procedure afforded 106mg (58%) of the title compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.29 (s, 3H), 5.57 (br, 1H), 6.87 (t, *J* = 7.2Hz, 1H), 6.98-7.08 (m, 6H), 7.22 (t, *J* = 7.6Hz, 2H).

**N-phenyl-morpholine**<sup>7</sup> The general procedure afforded 156mg (96%) of the title

compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.10 (t,  $J = 5.2\text{Hz}$ , 4H), 3.80 (t,  $J = 4.8\text{Hz}$ , 4H), 6.81-6.87 (m, 2H), 7.19-7.24 (m, 2H).

***N*-Hexyl-4-methylaniline**<sup>7</sup> The general procedure in argon afforded 159mg (83%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.90 (t,  $J = 6.4\text{Hz}$ , 3H), 1.26-1.42 (m, 6H), 1.60-1.66 (m, 2H), 2.10 (s, 3H), 3.12 (t,  $J = 7.2\text{Hz}$ , 2H), 6.58-6.64 (dd,  $J_1 = 7.8\text{Hz}$ ,  $J_2 = 10.0\text{Hz}$ , 1H), 7.02 (d,  $J = 7.2\text{Hz}$ , 1H), 7.10 (t,  $J = 7.6\text{Hz}$ , 1H).

***N,N*-Dibutyl-4-methylbenzamine**<sup>7</sup> The general procedure afforded 202mg (92%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.84 (t,  $J = 7.6\text{Hz}$ , 6H), 1.21-1.26 (m, 4H), 1.41-1.48 (m, 4H), 2.13 (s, 2H), 3.12 (t,  $J = 7.6\text{Hz}$ , 4H), 6.48 (d,  $J = 8.0\text{Hz}$ , 2H), 6.91 (d,  $J = 8.4\text{Hz}$ , 2H).

***N*-(2-Methoxyphenyl)morpholine**<sup>7</sup> The general procedure afforded 169mg (90%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.08 (s, 4H), 3.87-3.90 (m, 7H), 6.87-7.02 (m, 4H).

***N*-(4-Methylphenyl)piperidine**<sup>7</sup> The general procedure afforded 163mg (93%) of the title compound.

***N*-(2,6-Dimethylphenyl)morpholine**<sup>7</sup> The general procedure afforded 138mg (72%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.85 (d,  $J = 3.2\text{Hz}$ , 6H), 2.86 (t,  $J = 4.8\text{Hz}$ , 4H), 3.82 (t,  $J = 4.8\text{Hz}$ , 4H), 6.90-7.00 (m, 3H).

***N*-Hexyl-2-methylaniline**<sup>7</sup> The general procedure afforded 170mg (89%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.87-0.91 (m, 3H), 1.26-1.43 (m, 6H), 1.58-1.65 (m, 2H), 3.23 (m, 2H), 4.6 (br, 1H), 6.36 (d,  $J = 8.4\text{Hz}$ , 1H), 6.54 (dd,  $J_1 = 1.2\text{Hz}$ ,  $J_2 = 5.6\text{Hz}$ , 1H), 7.38-7.42 (m, 1H), 8.06 (d,  $J = 5.2\text{Hz}$ , 1H).

**4-(4-Imidazol-1-yl-3,5-dimethylphenyl)morpholine** The general procedure afforded 183mg (71%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.00 (s, 6H), 3.20 (t,  $J = 4.8\text{ Hz}$ , 4H), 3.87 (t,  $J=4.8\text{Hz}$ , 4H), 6.66 (s, 2H), 6.90 (s, 1H), 7.24 (s, 1H), 7.46 (s, 1H).

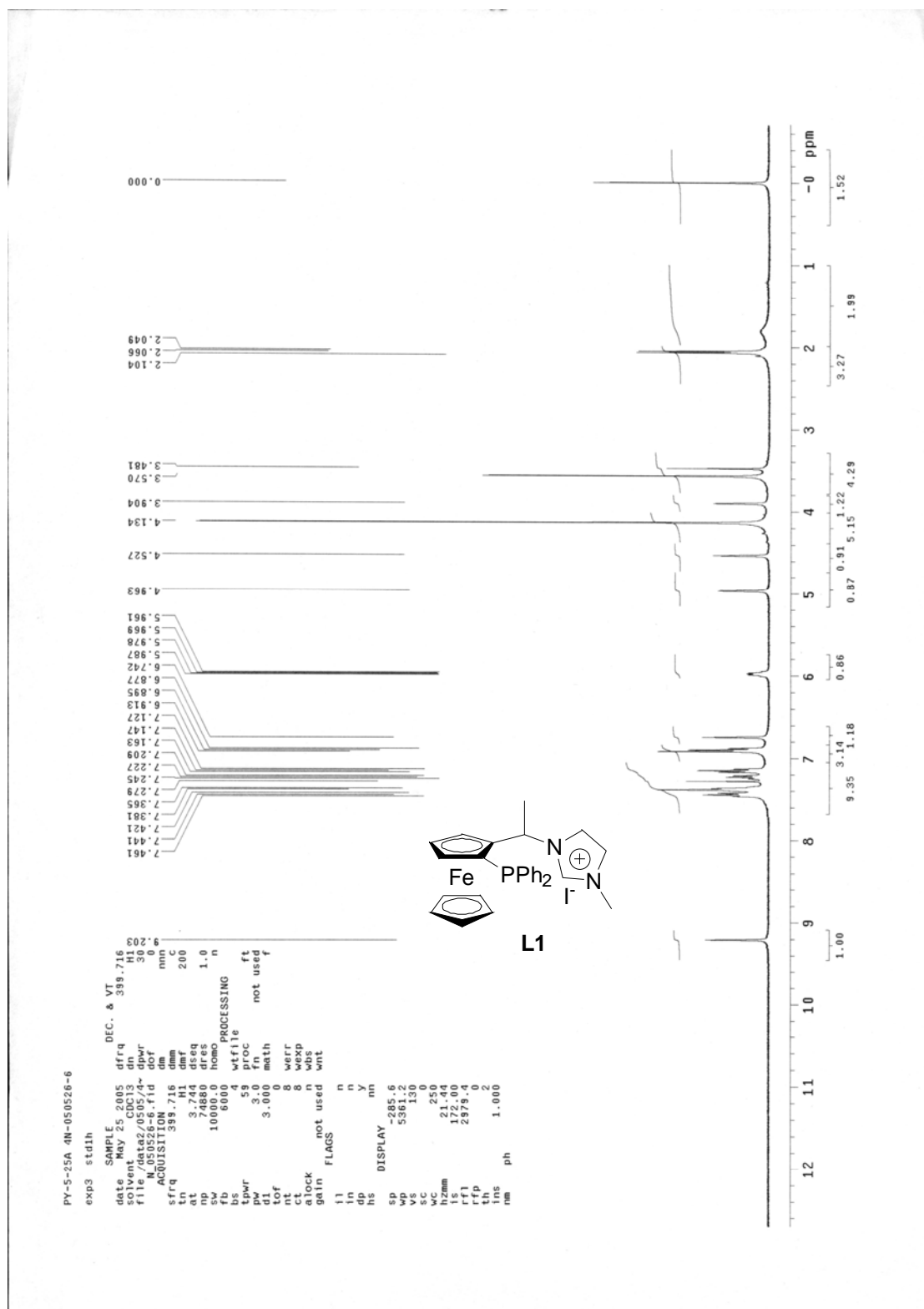
**1-(4-Imidazol-1-yl-3,5-dimethylphenyl)-4-(3,5-dimethylphenyl)piperazine** The general procedure afforded 344mg (78%) of the title compound.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.97 (s, 12H), 3.35 (s, 8H), 6.69 (s, 4H), 6.87 (s, 2H), 7.21 (s, 2H), 7.43 (s, 2H).

**1-(4-Imidazol-1-yl-3,5-dimethylphenyl)piperazine** The general procedure afforded 151mg (59%) of the title compound.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 1.97 (s, 6H), 3.03 (t,  $J = 5.2\text{Hz}$ , 4H), 3.18 (t,  $J = 4.8\text{Hz}$ , 4H), 6.66 (s, 2H), 6.87 (s, 1H), 7.20 (s, 1H), 7.41 (s, 1H).

**1,4-Di-p-tolyl-piperazine**<sup>7</sup> The general procedure afforded 234mg (88%) of the title compound.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.28 (s, 6H), 3.29 (s, 8H), 6.91 (d,  $J = 8.4\text{Hz}$ , 4H).

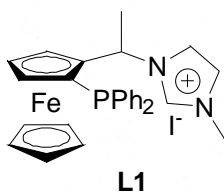
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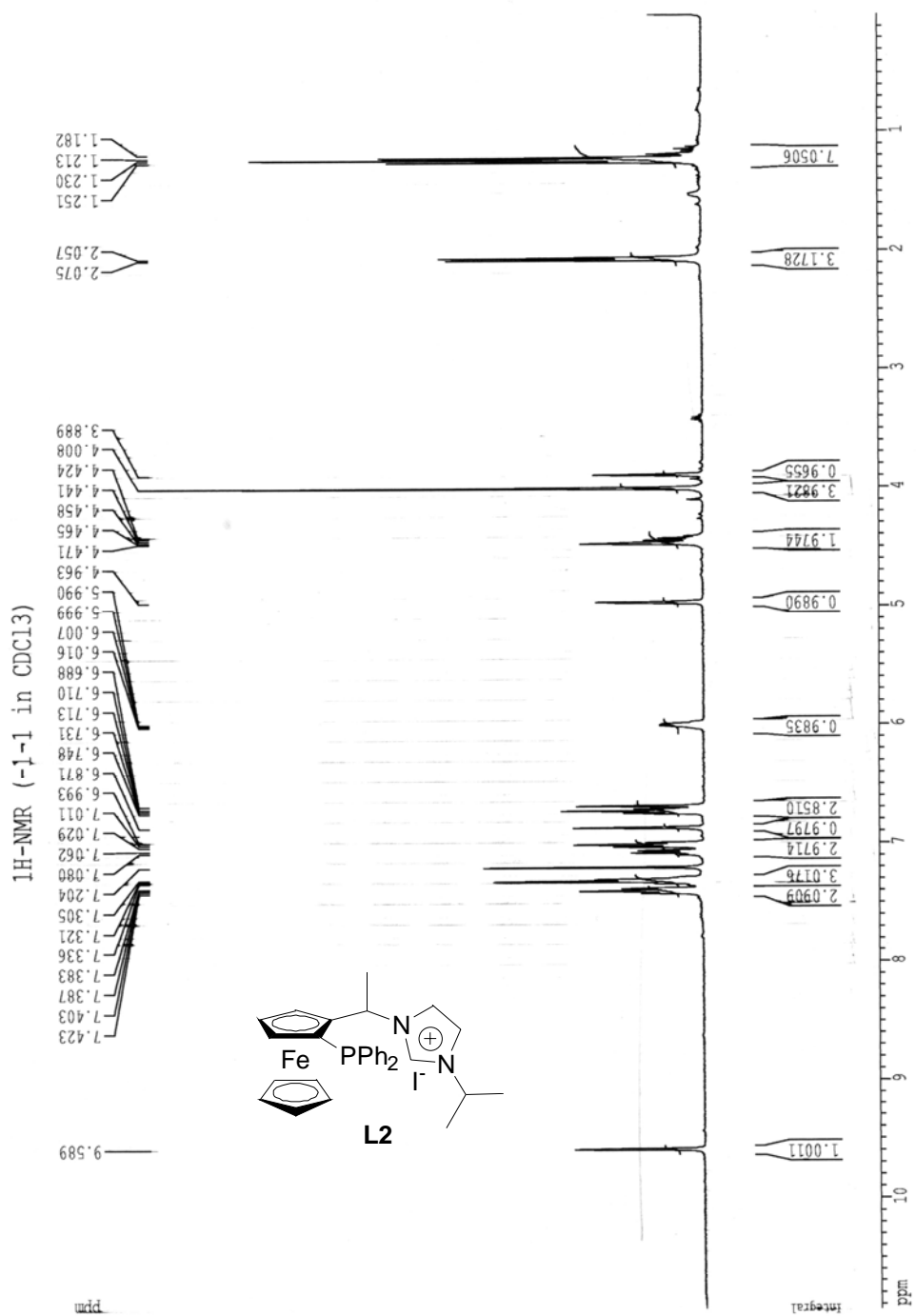
- (1) Seo, H.; Kim, J. H.; Kim, B. Y.; Lee, H. J.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618-620.
- (2) Tsuji, Y.; Huh, K. T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365-1370.
- (3) Old, D.W.; Wolfe, J.P.; Buchwald, S.L. *J. Am. Chem. Soc.*, **1998**, *120*, 9722-9723.
- (4) Kamikawa, K.; Sugimoto, S.; Uemura, M. *J. Org. Chem.*, **1998**, *63*, 8407-8410.
- (5) Barluenga, J.; Aznar, F.; Fernandez, M. *Chem. Eur. J.* **1997**, *3*, 1629-1637.
- (6) Desmarets, C.; Schneider, R.; Fort, Y. *Tetrahedron Lett.*, **2000**, *41*, 2875-2879.
- (7) Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6054-6058.



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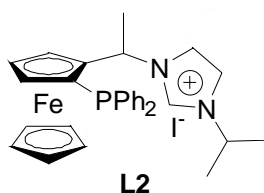


$^{13}\text{C}$  NMR ( $\sim 1-1$  in  $\text{CDCl}_3$ )

29.542  
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22.357  
21.542

90.103  
77.217  
76.899  
76.582  
72.687  
70.906  
70.202  
70.018  
56.328  
56.228  
52.747

138.840  
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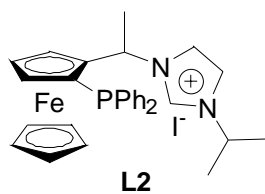
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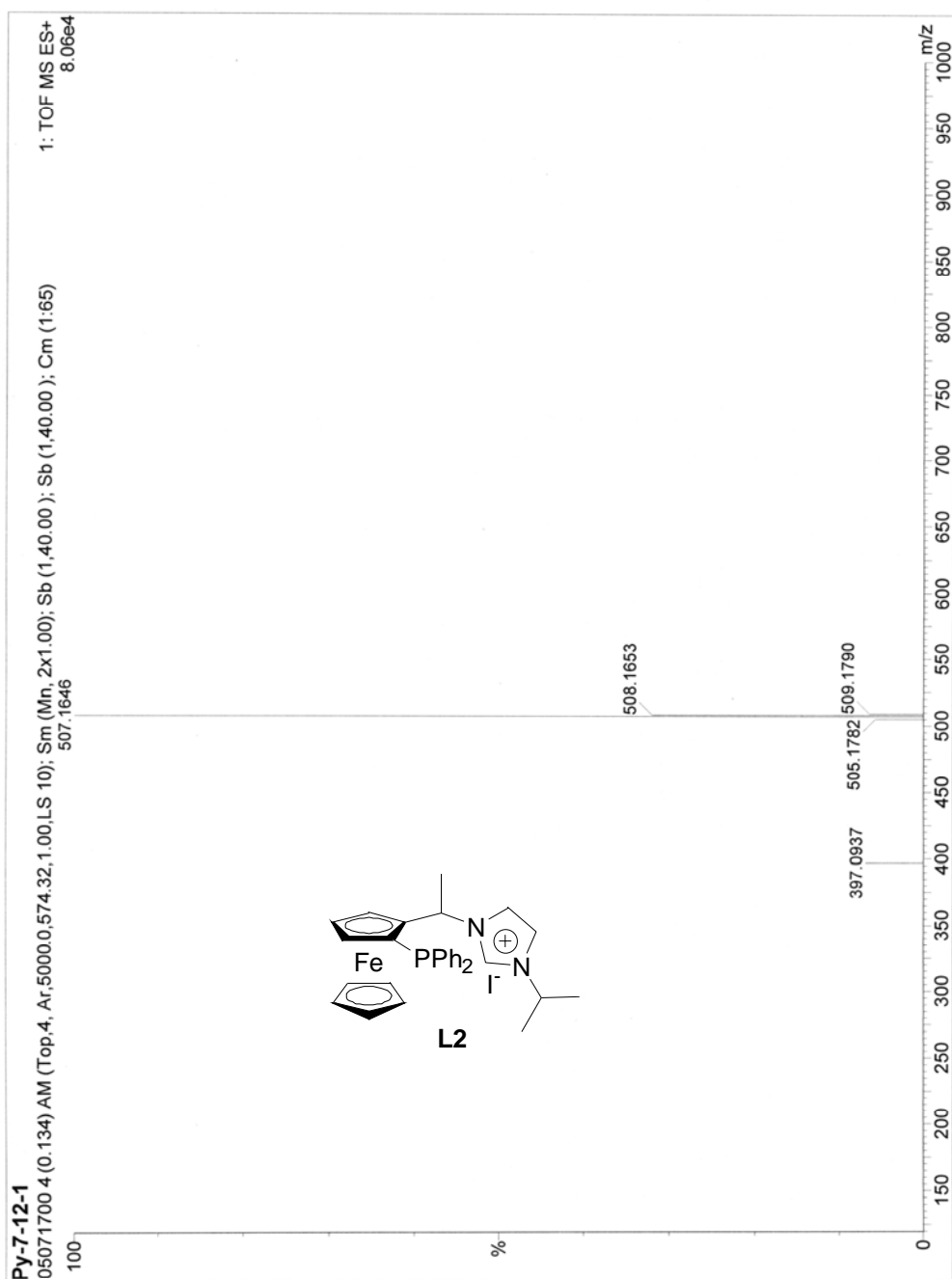
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31 P NMR (-1-1 in CDCl<sub>3</sub>)

27.702





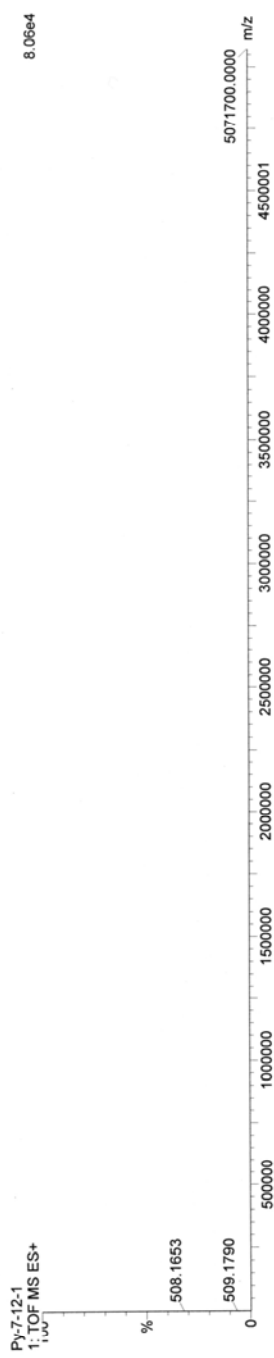
## Elemental Composition Report

Page 1

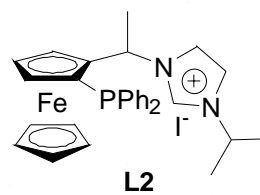
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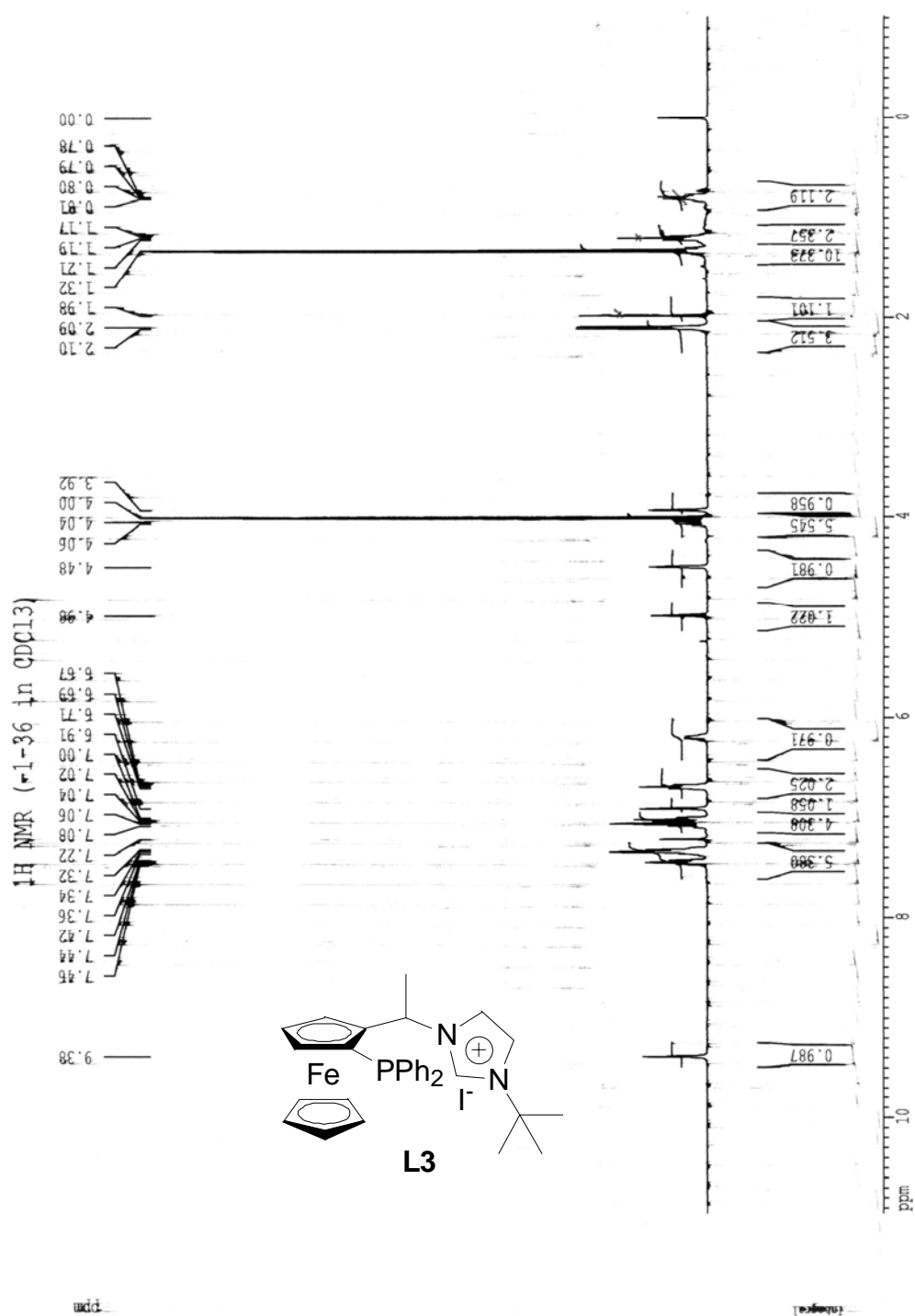
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Monoisotopic Mass, Odd and Even Electron Ions  
57 formula(e) evaluated with 1 results within limits (up to 6 closest results for each mass)

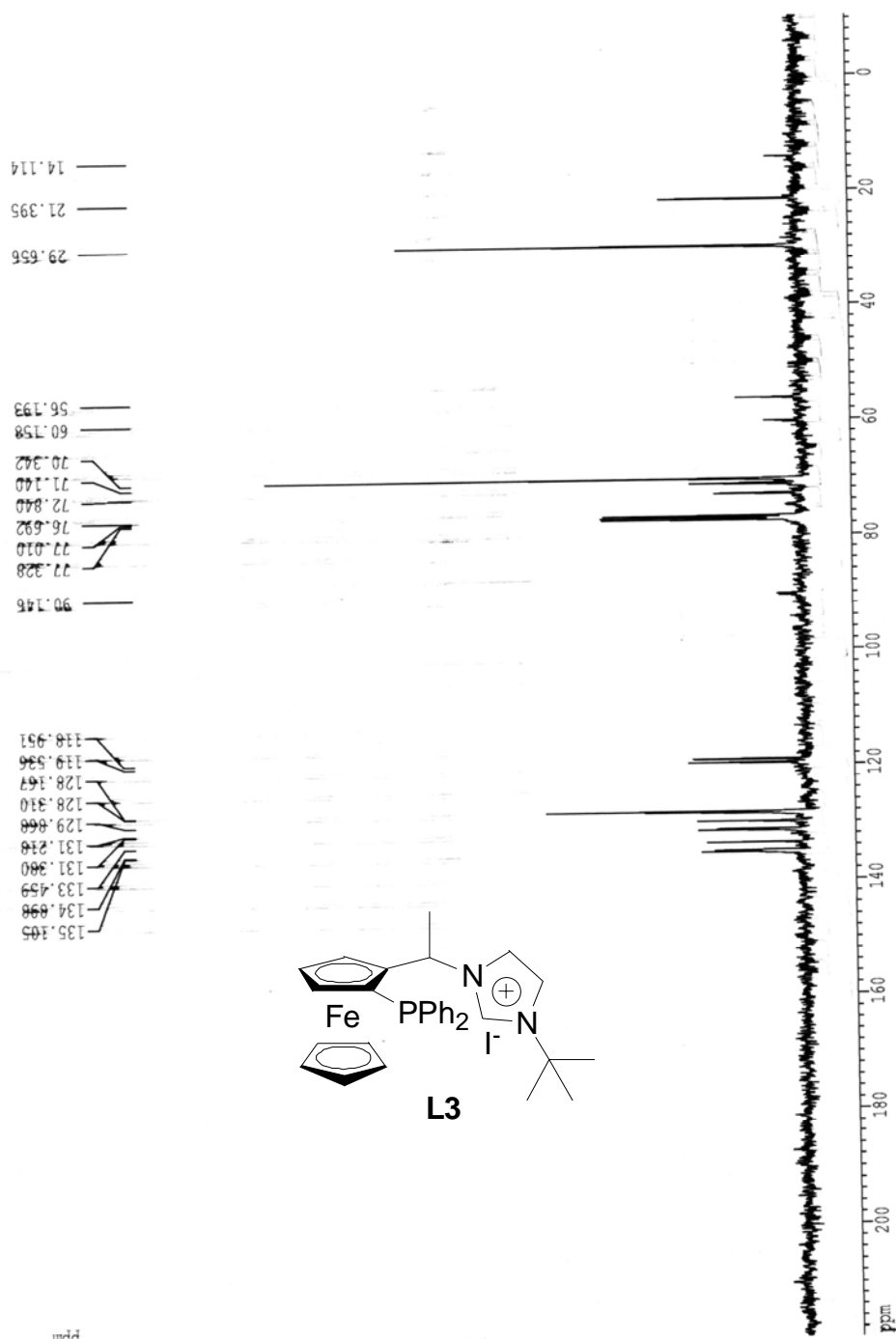


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| Maximum: | 60.0     |            |          |     |      |     |      |     |      |       |   |         |                 |
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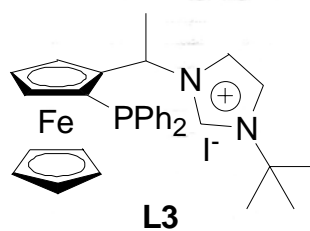
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acid

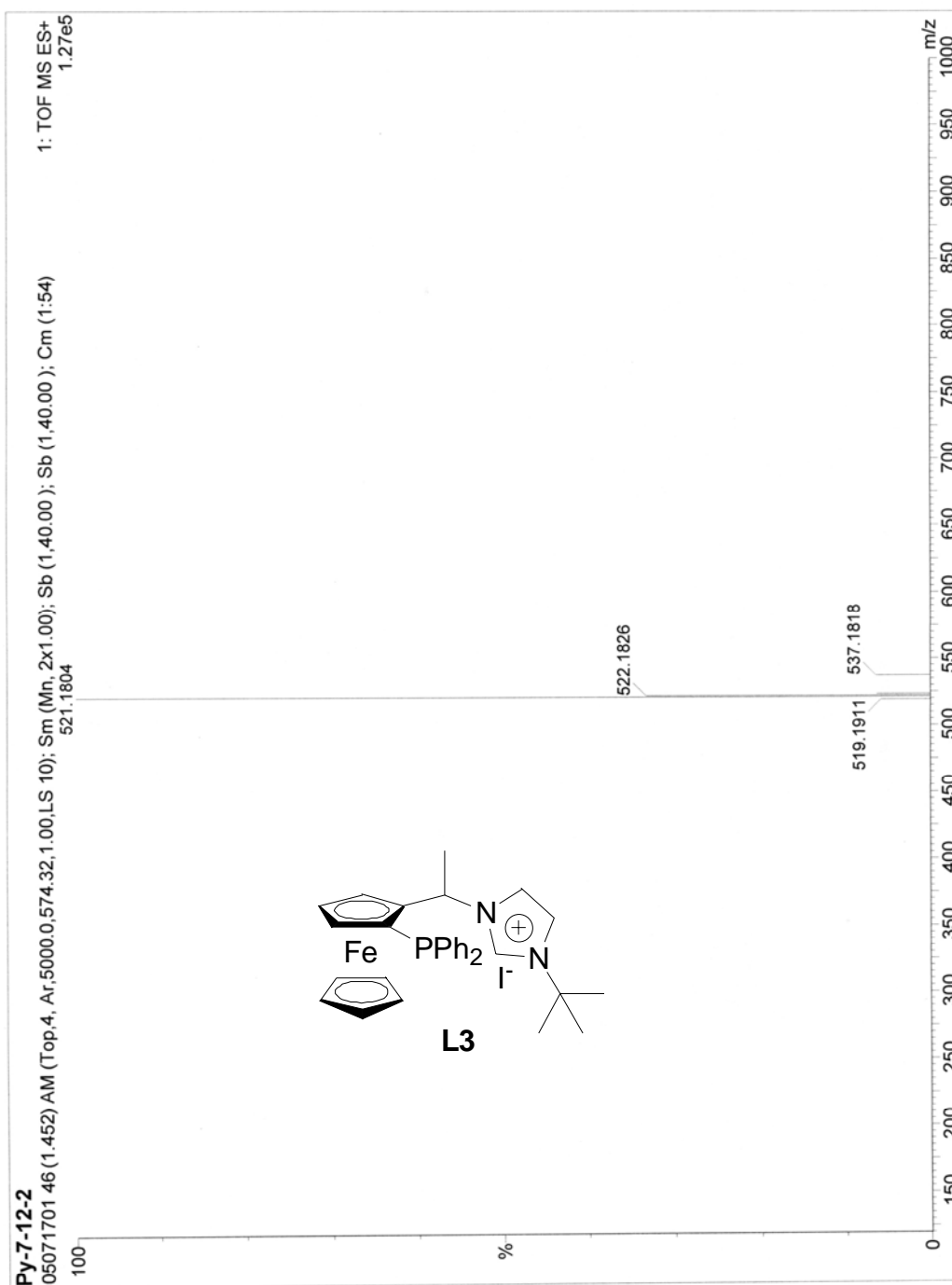
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650.12



ucd





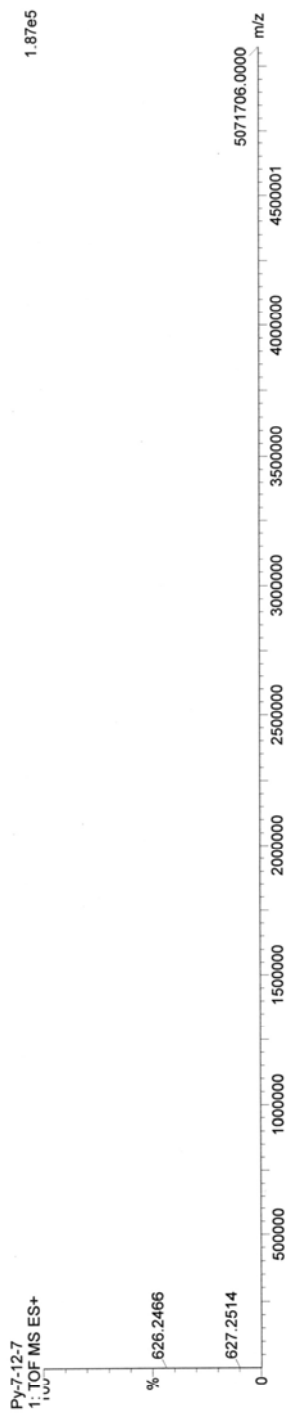
## Elemental Composition Report

Page 1

### Single Mass Analysis

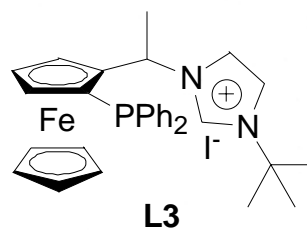
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57 formula(e) evaluated with 1 results within limits (up to 6 closest results for each mass)

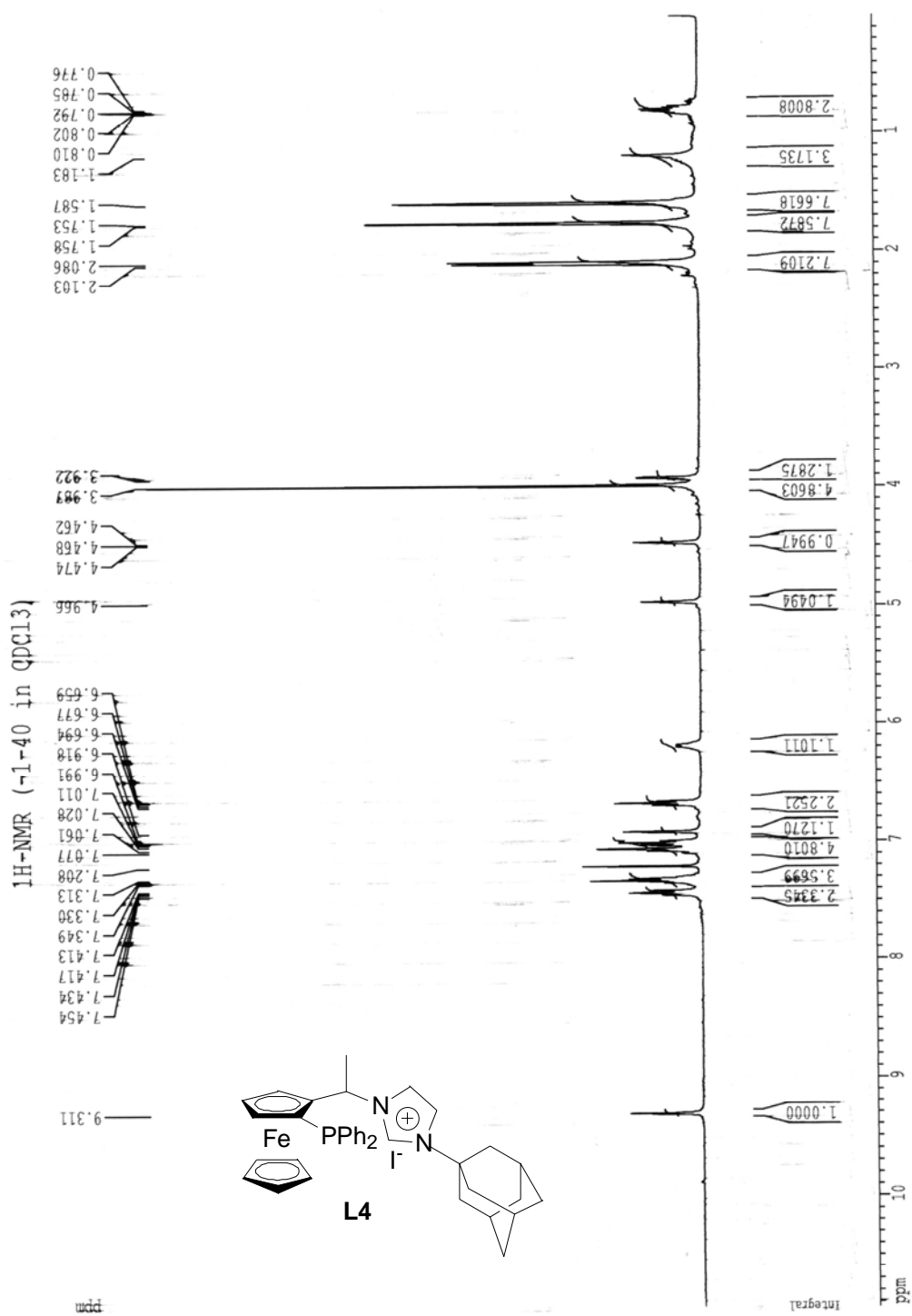


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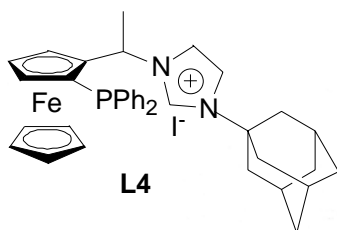
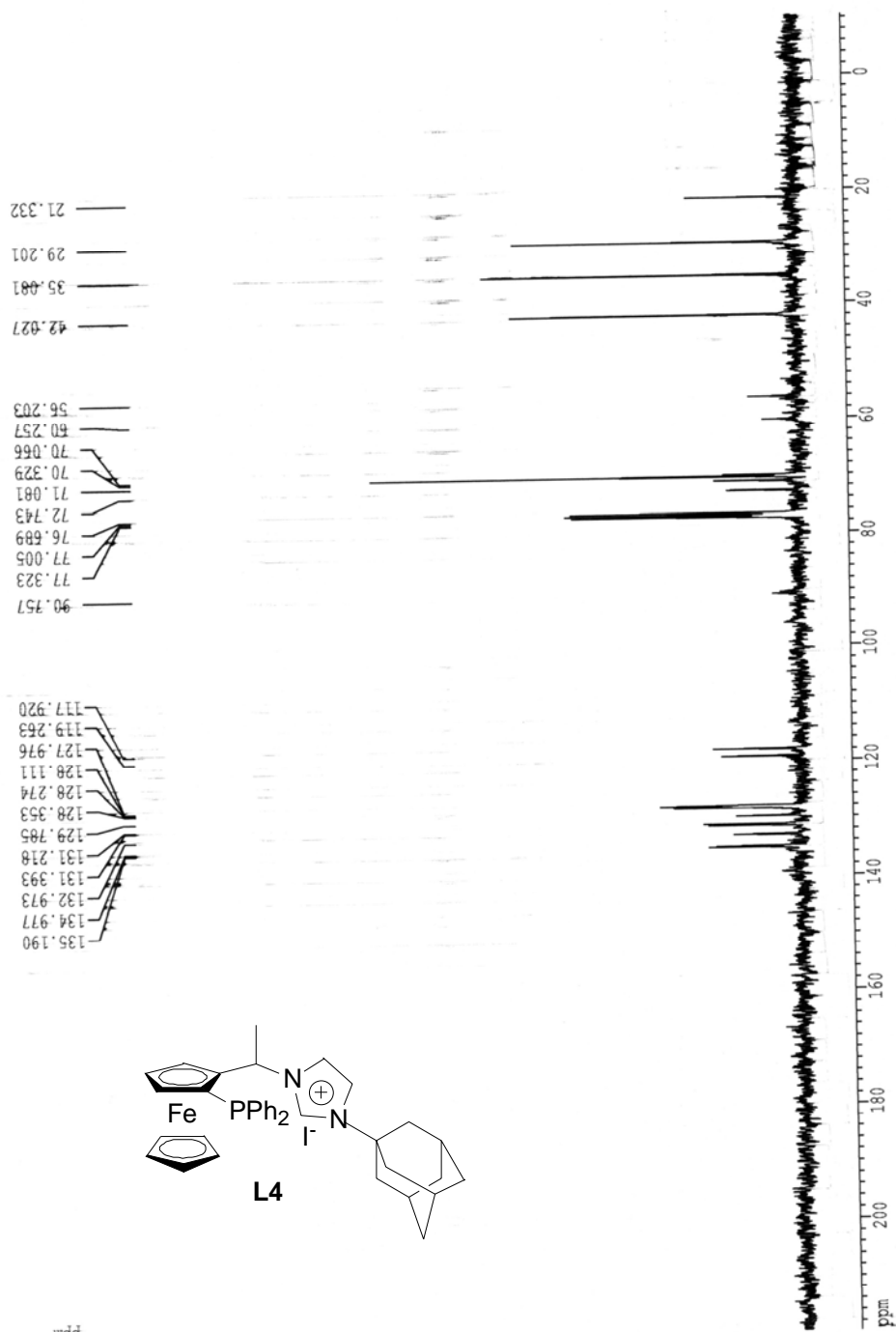
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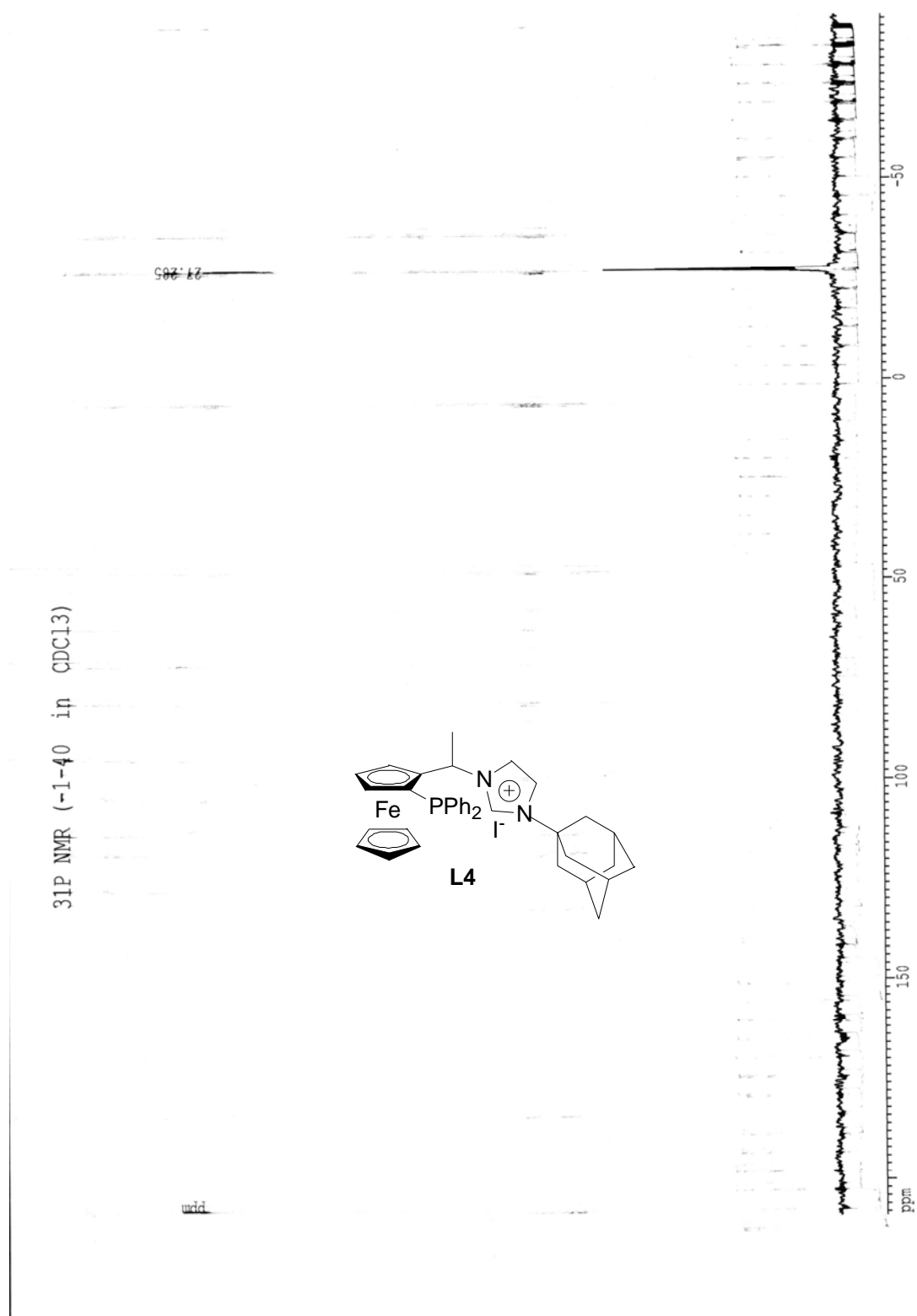


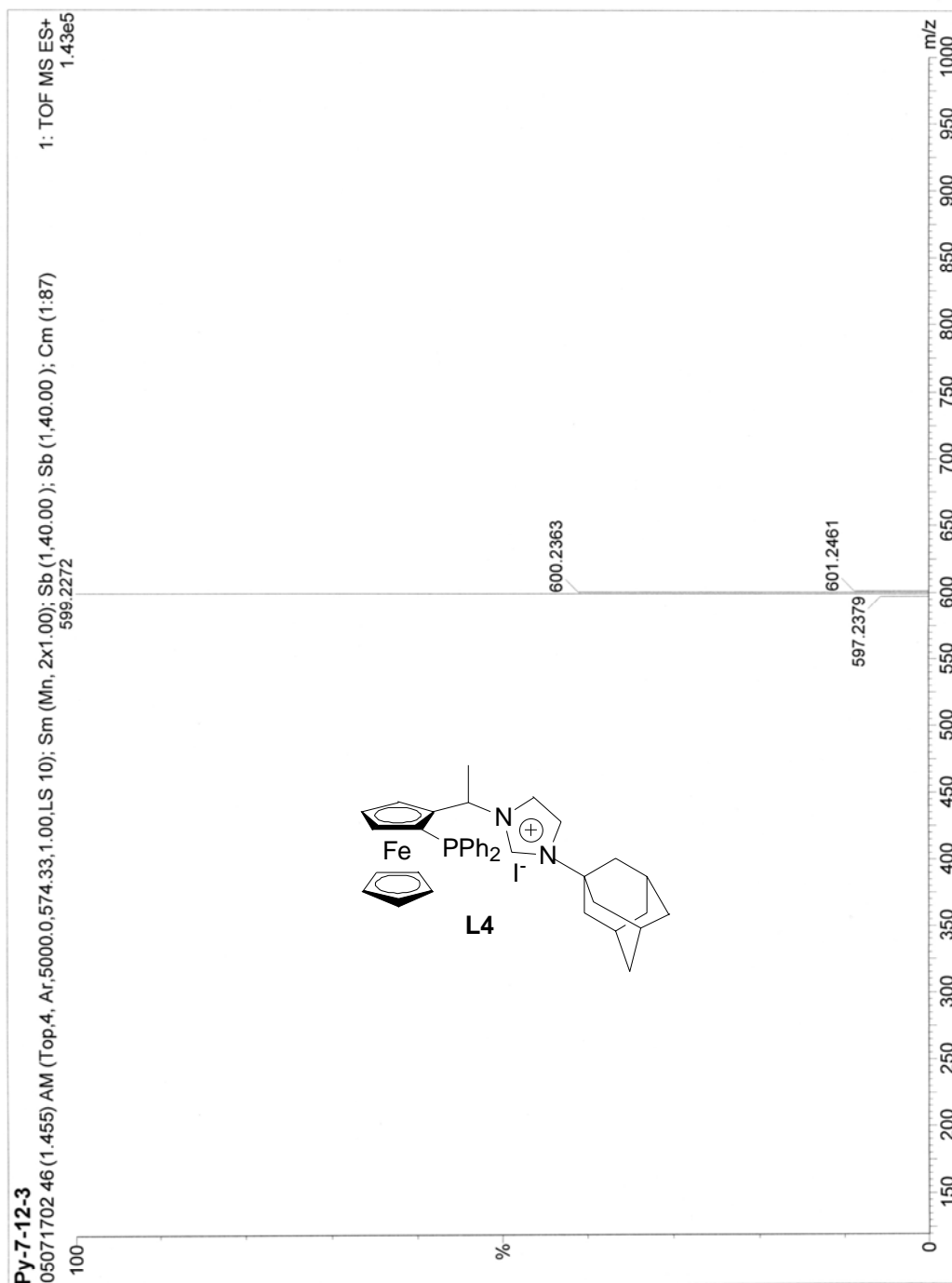


$^{13}\text{C}$  NMR (-1-40 in  $\text{CDCl}_3$ )



wci



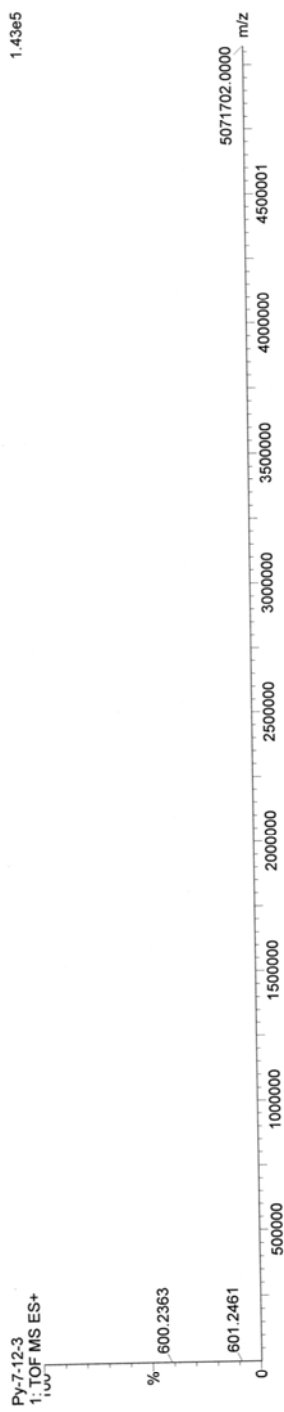


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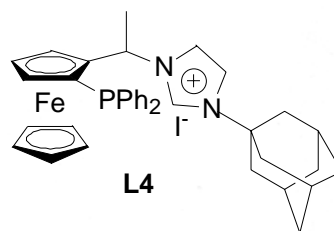
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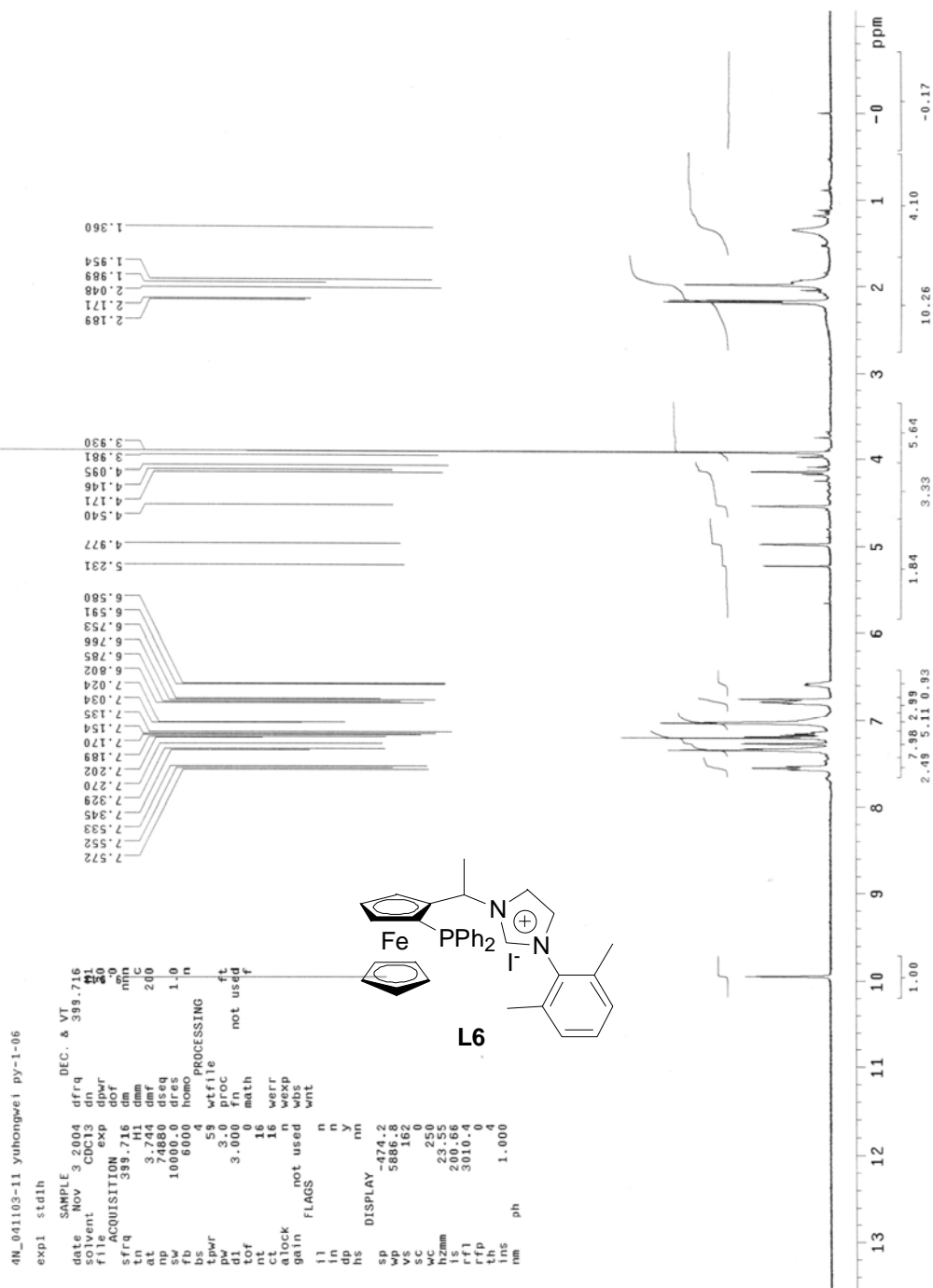


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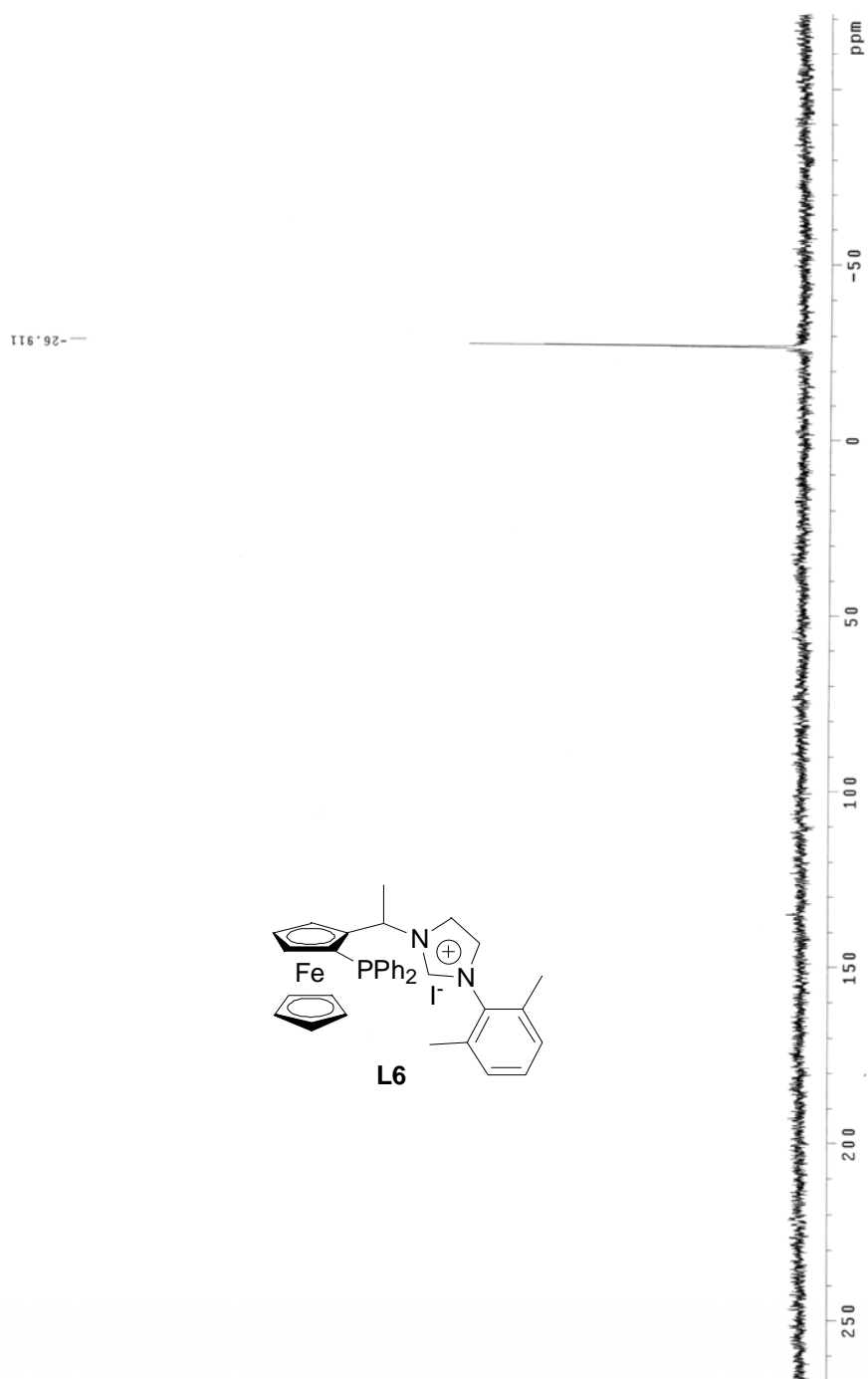
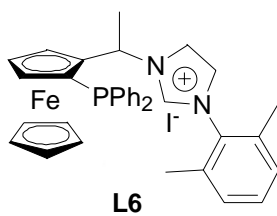
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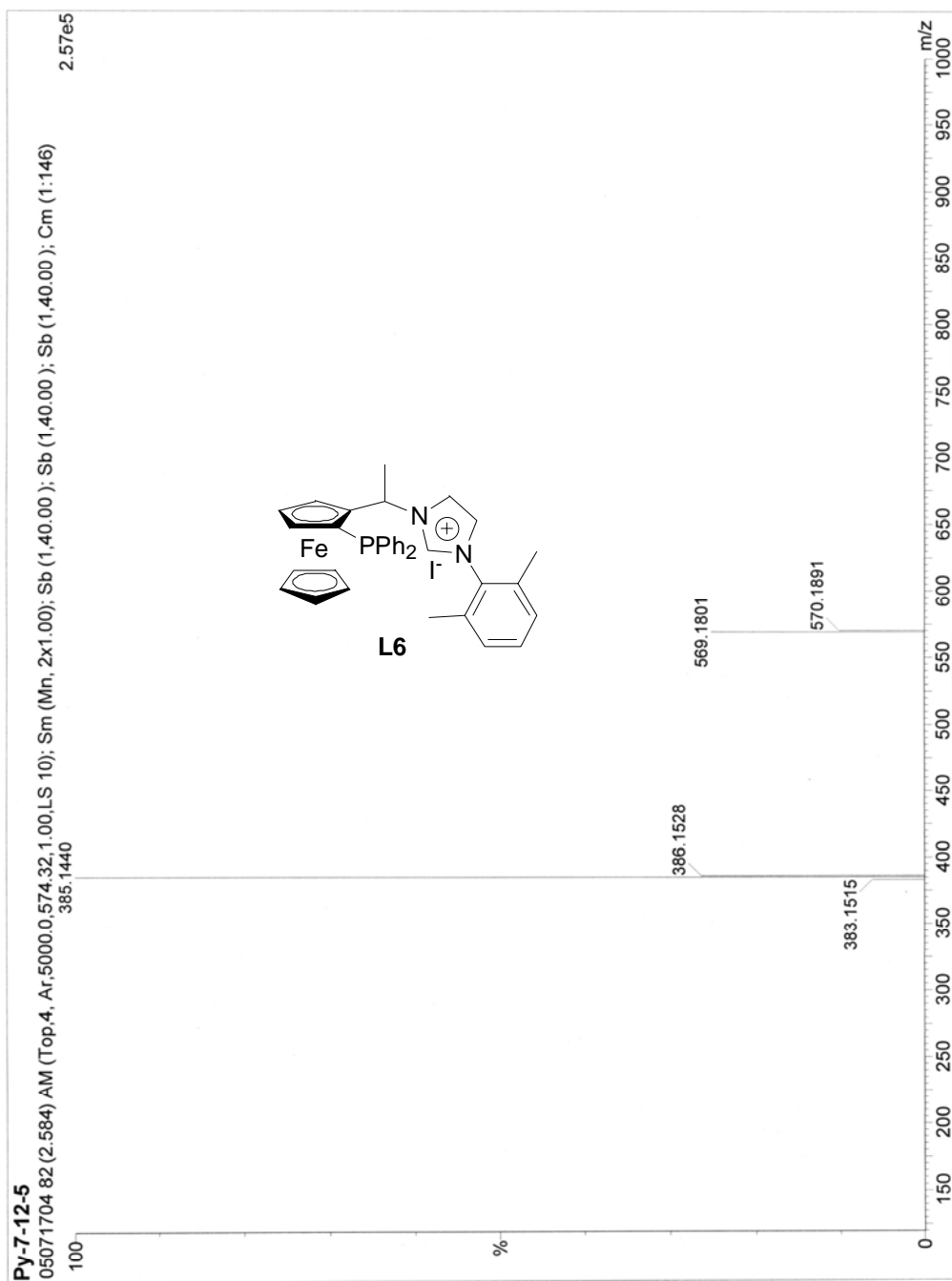
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## Elemental Composition Report

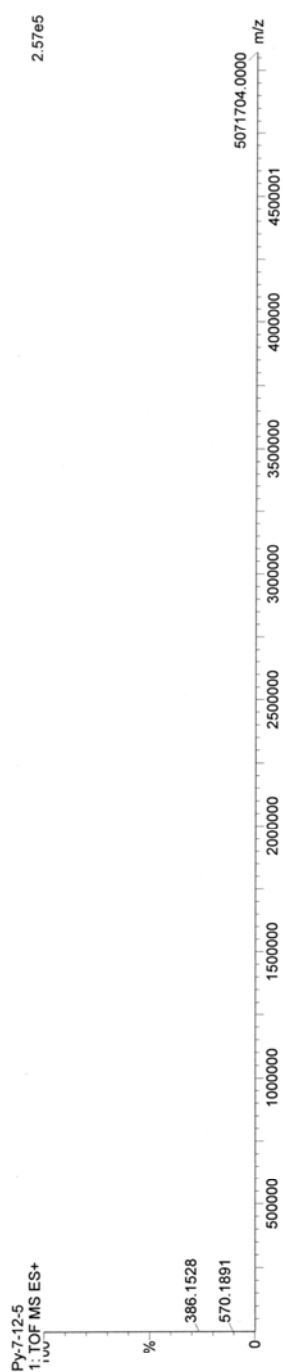
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### Single Mass Analysis

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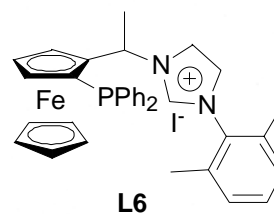
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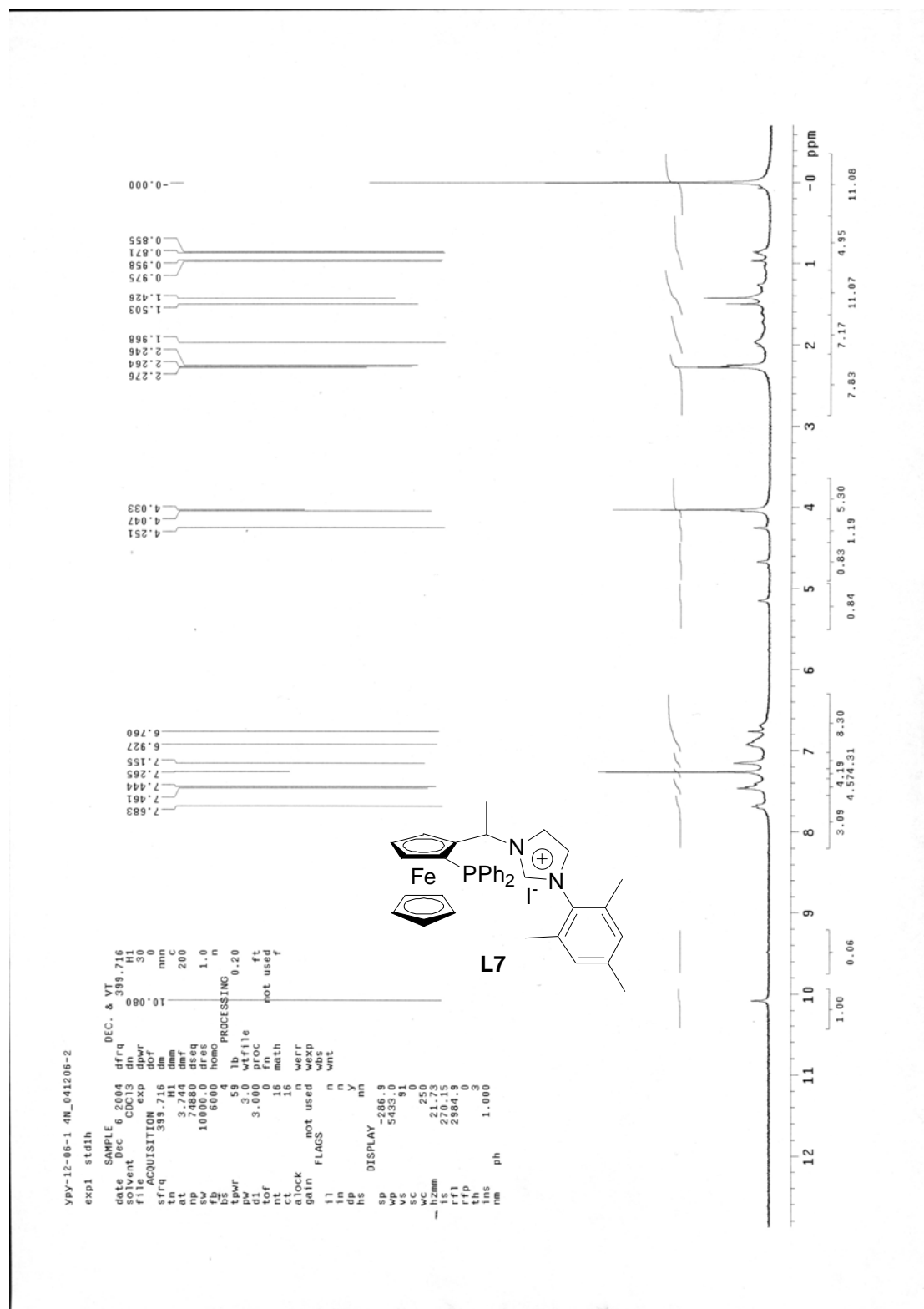
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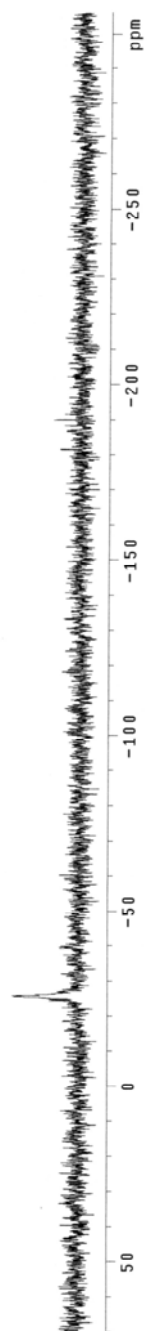
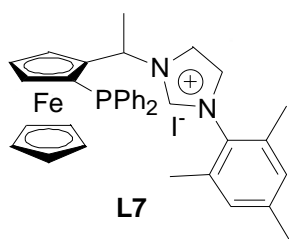
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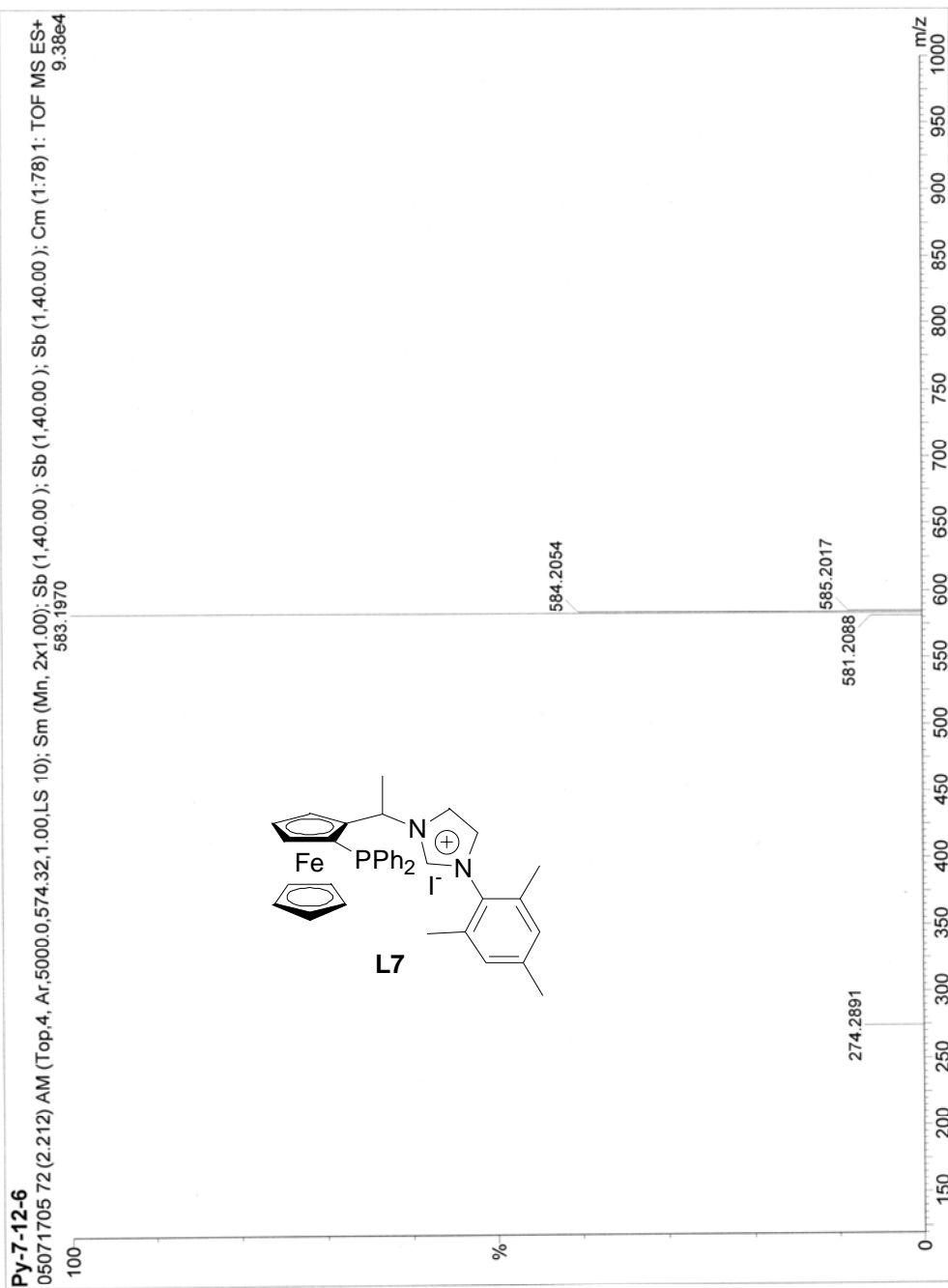




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### Elemental Composition Report

Page 1

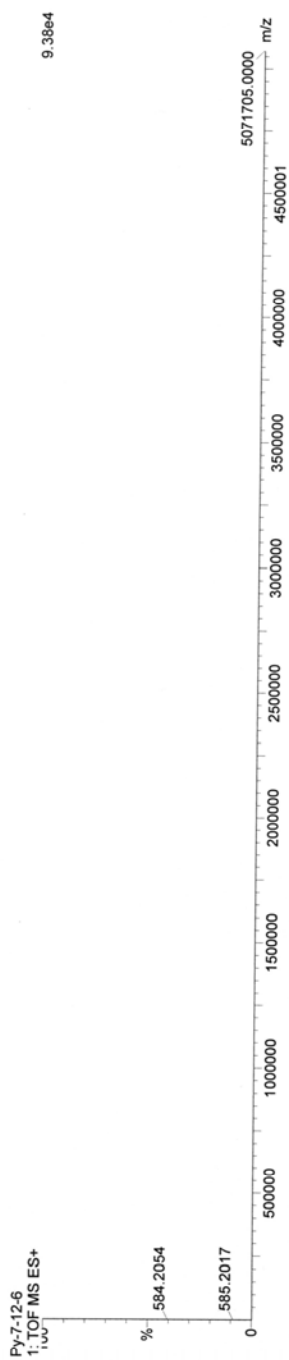
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Monoisotopic Mass, Odd and Even Electron Ions

57 formula(e) evaluated with 1 results within limits (up to 6 closest results for each mass)

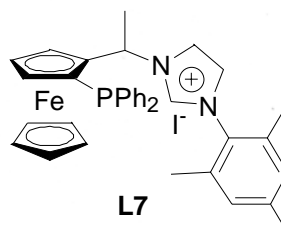


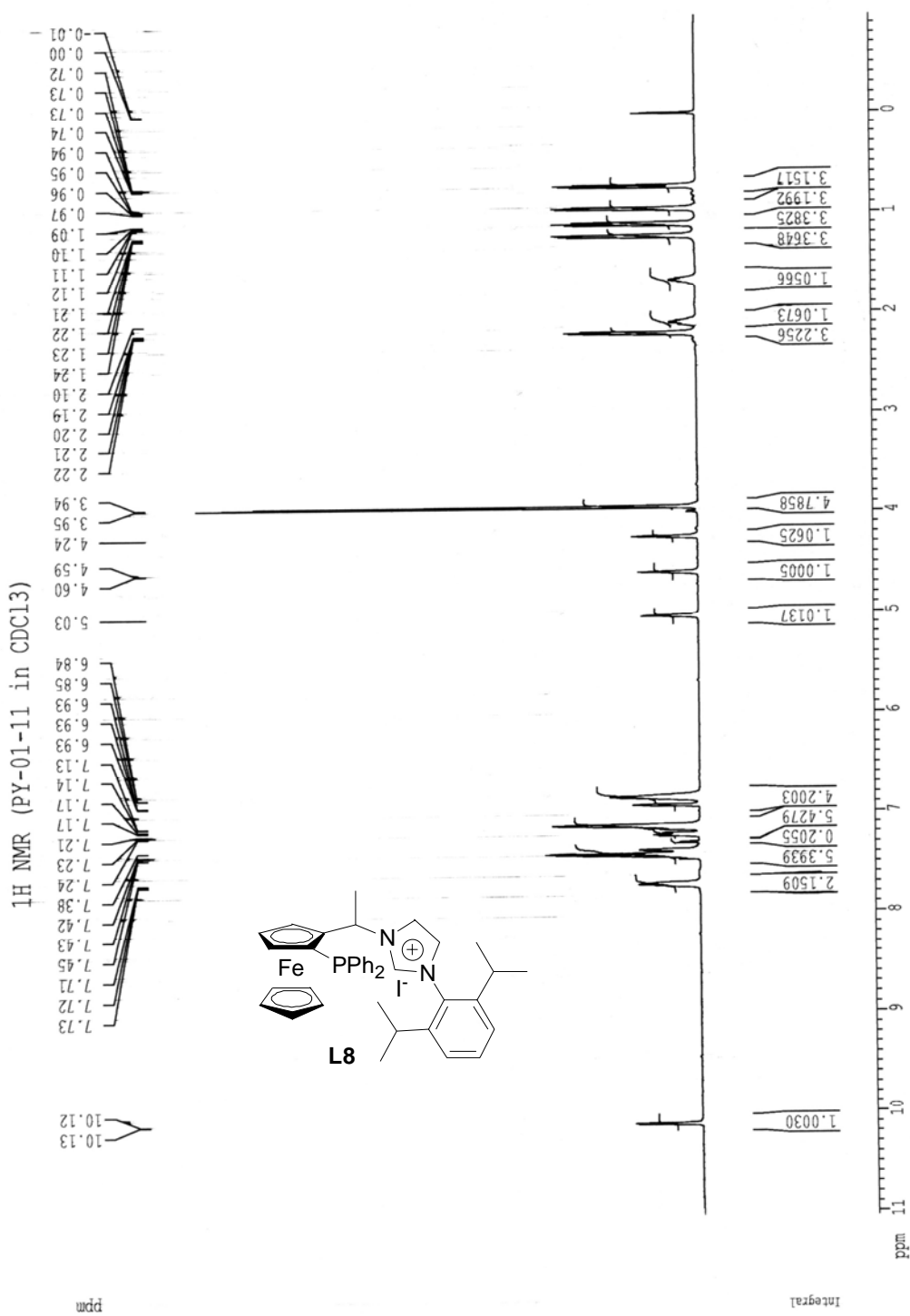
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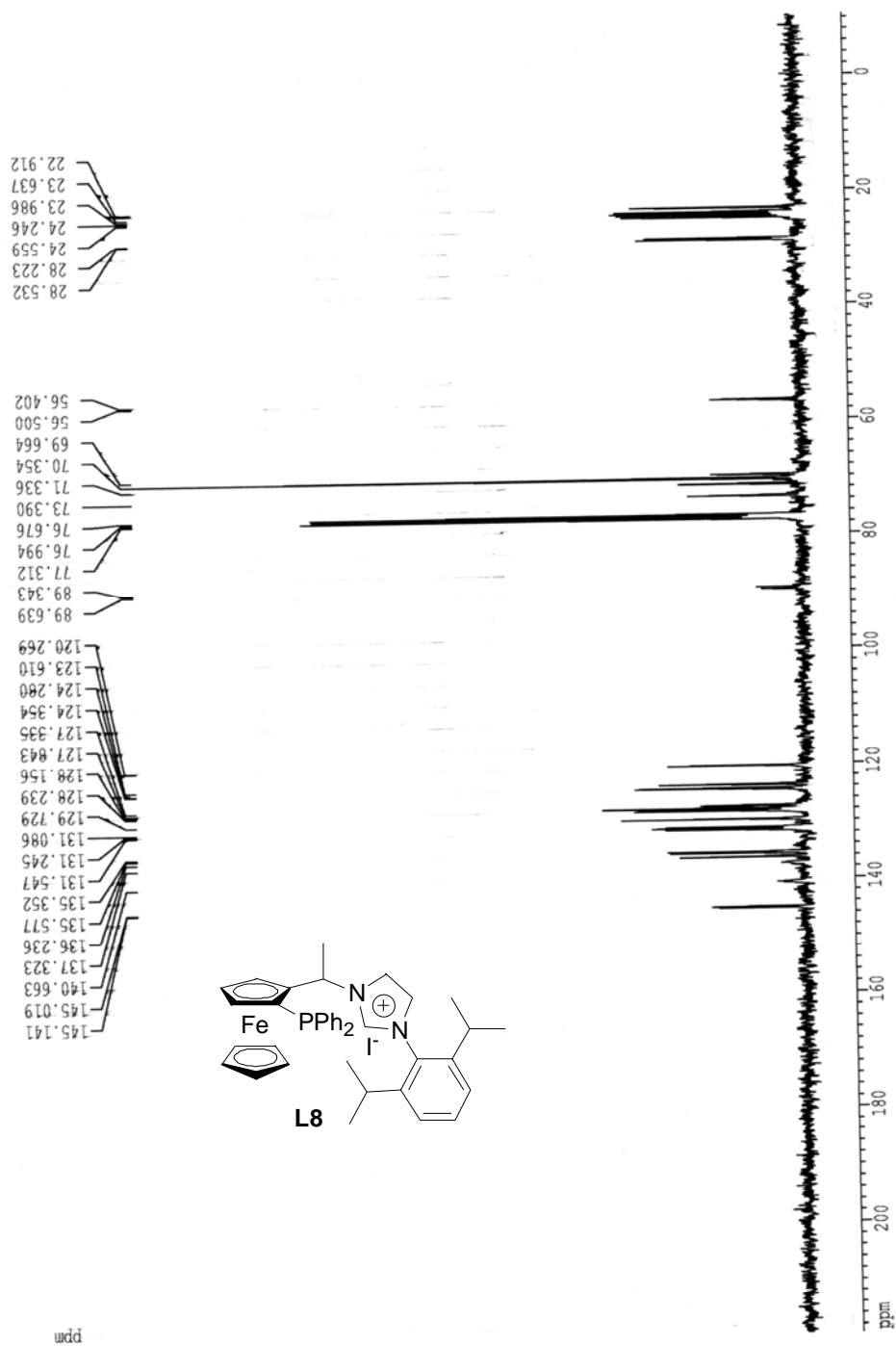
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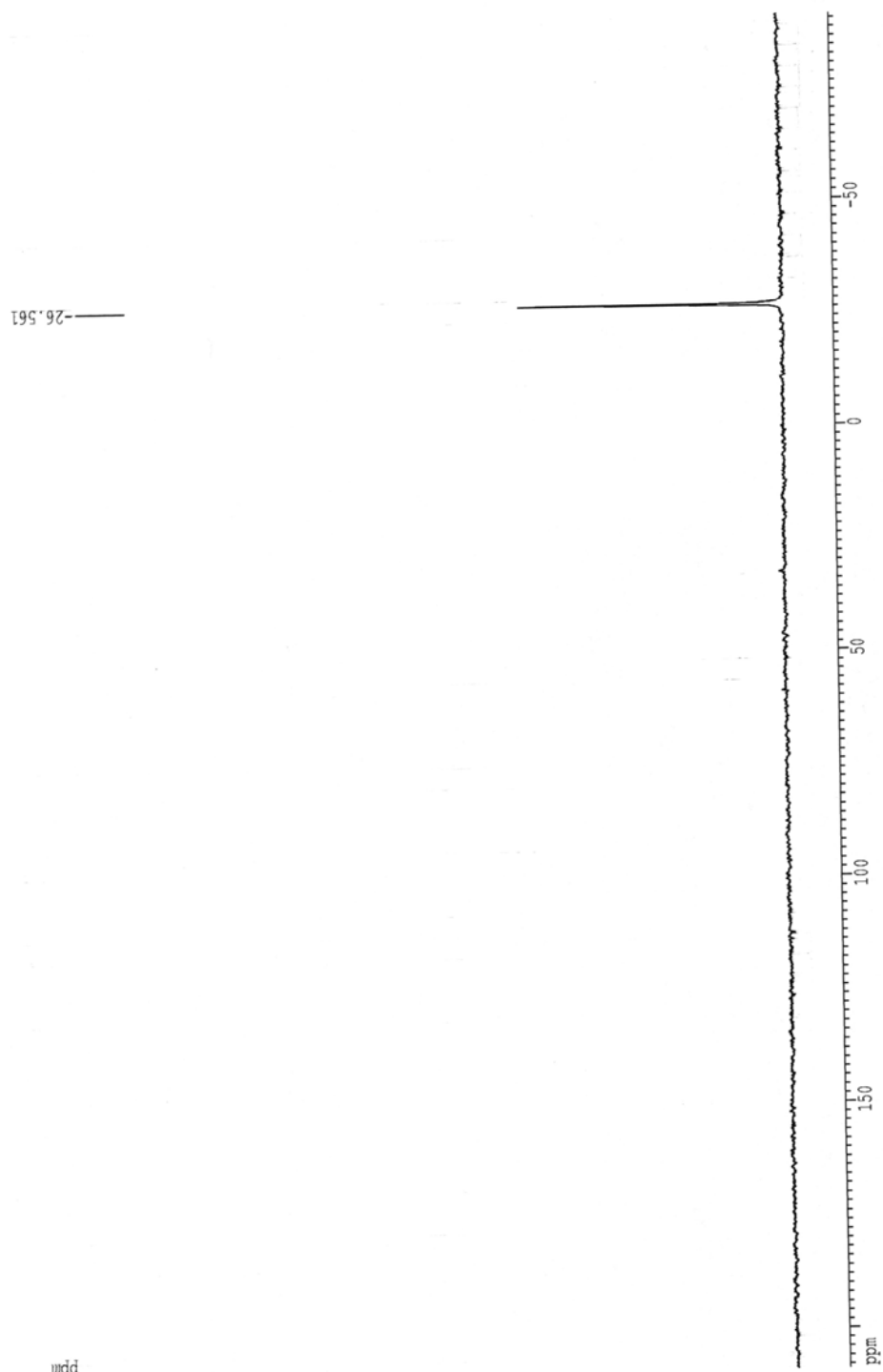




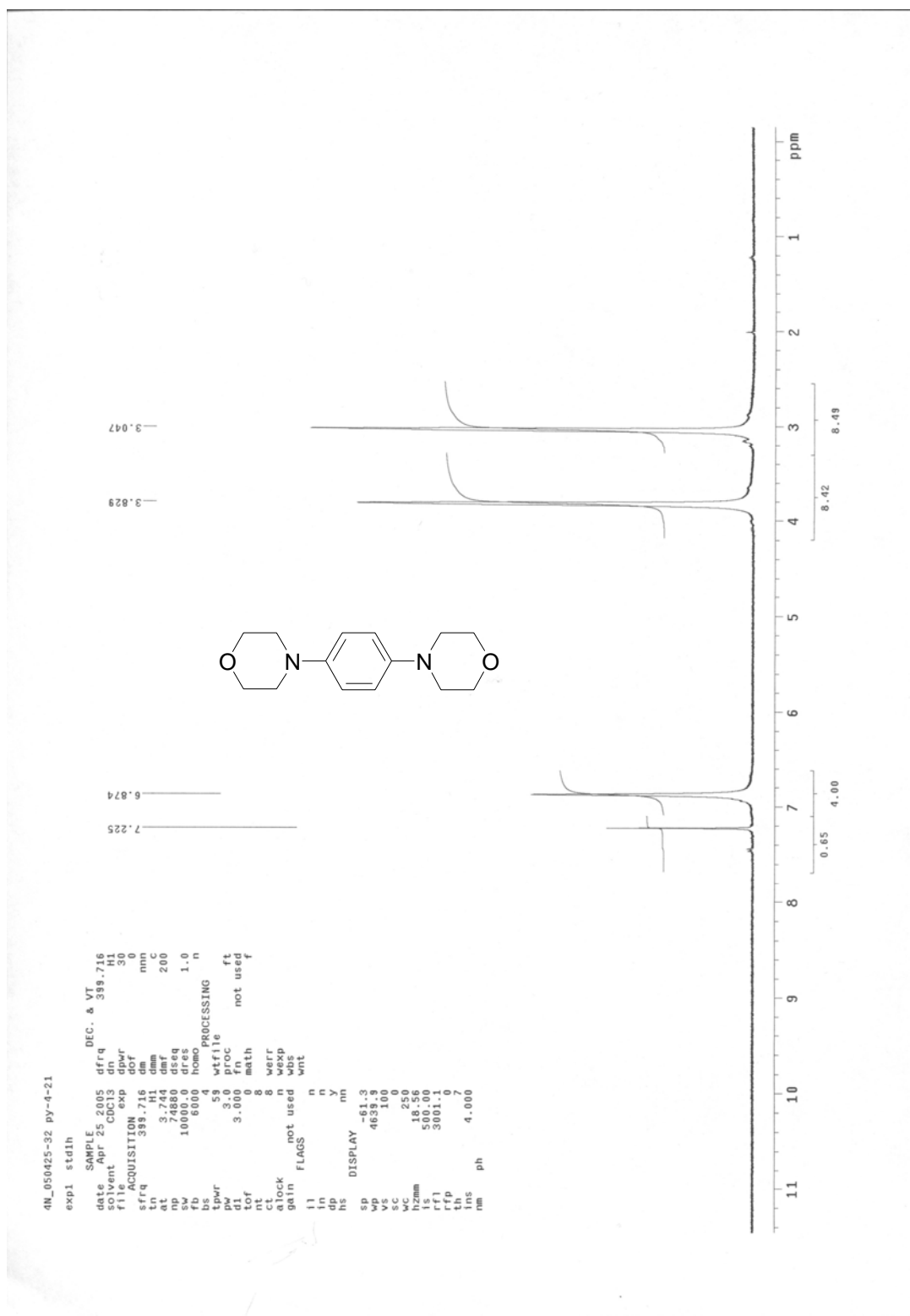
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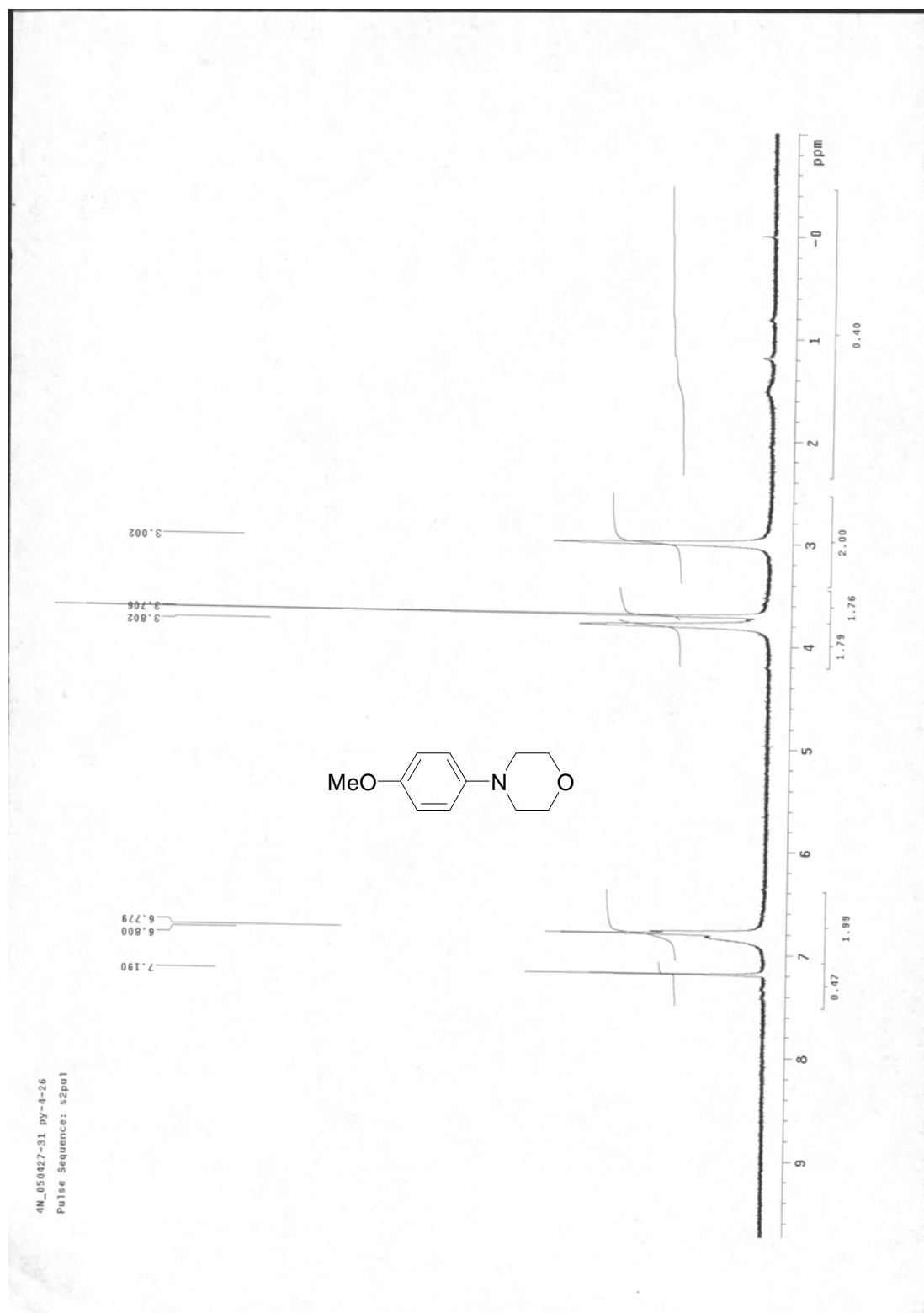


31P NMR (PY-01-11 in CDCl3)

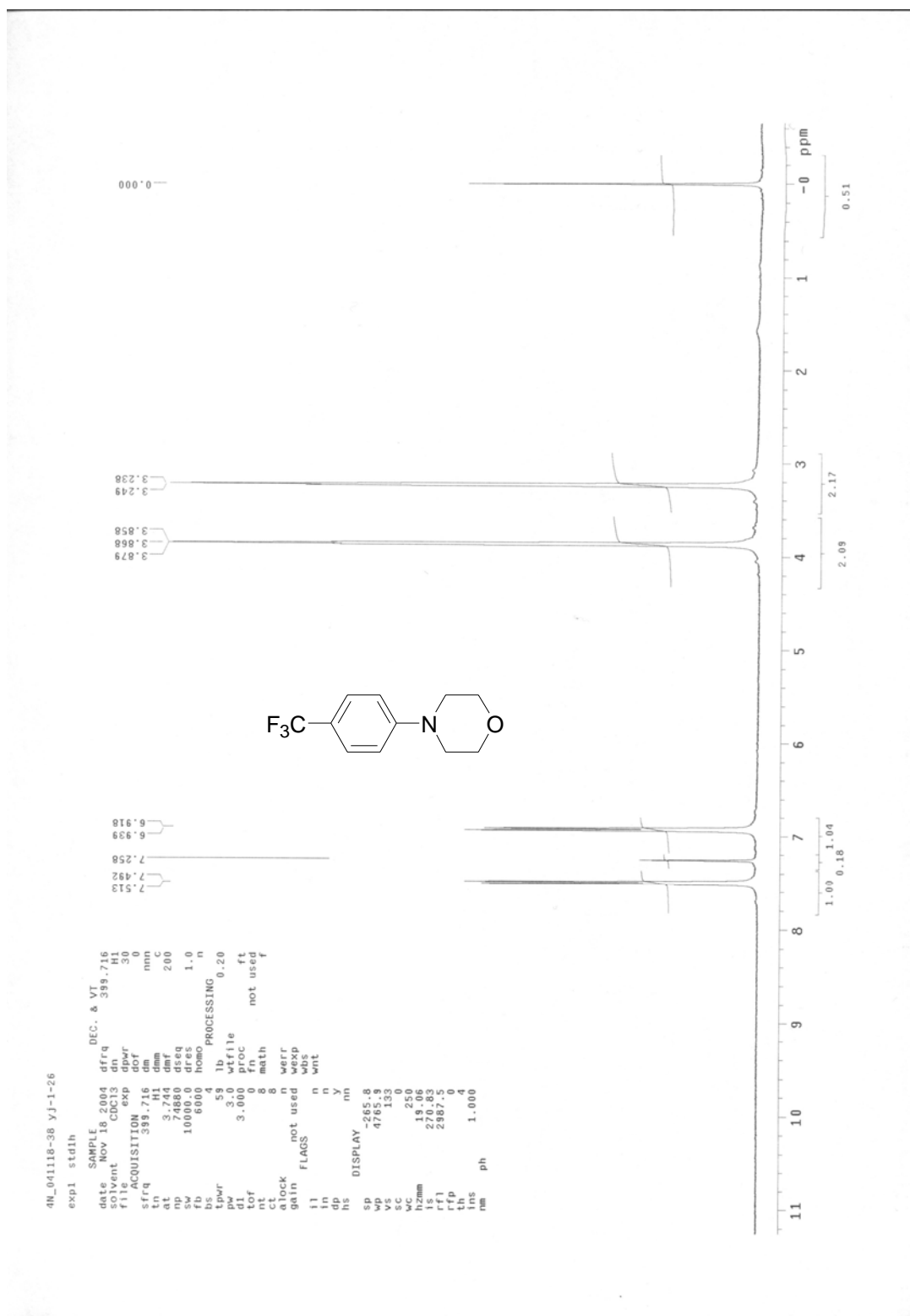


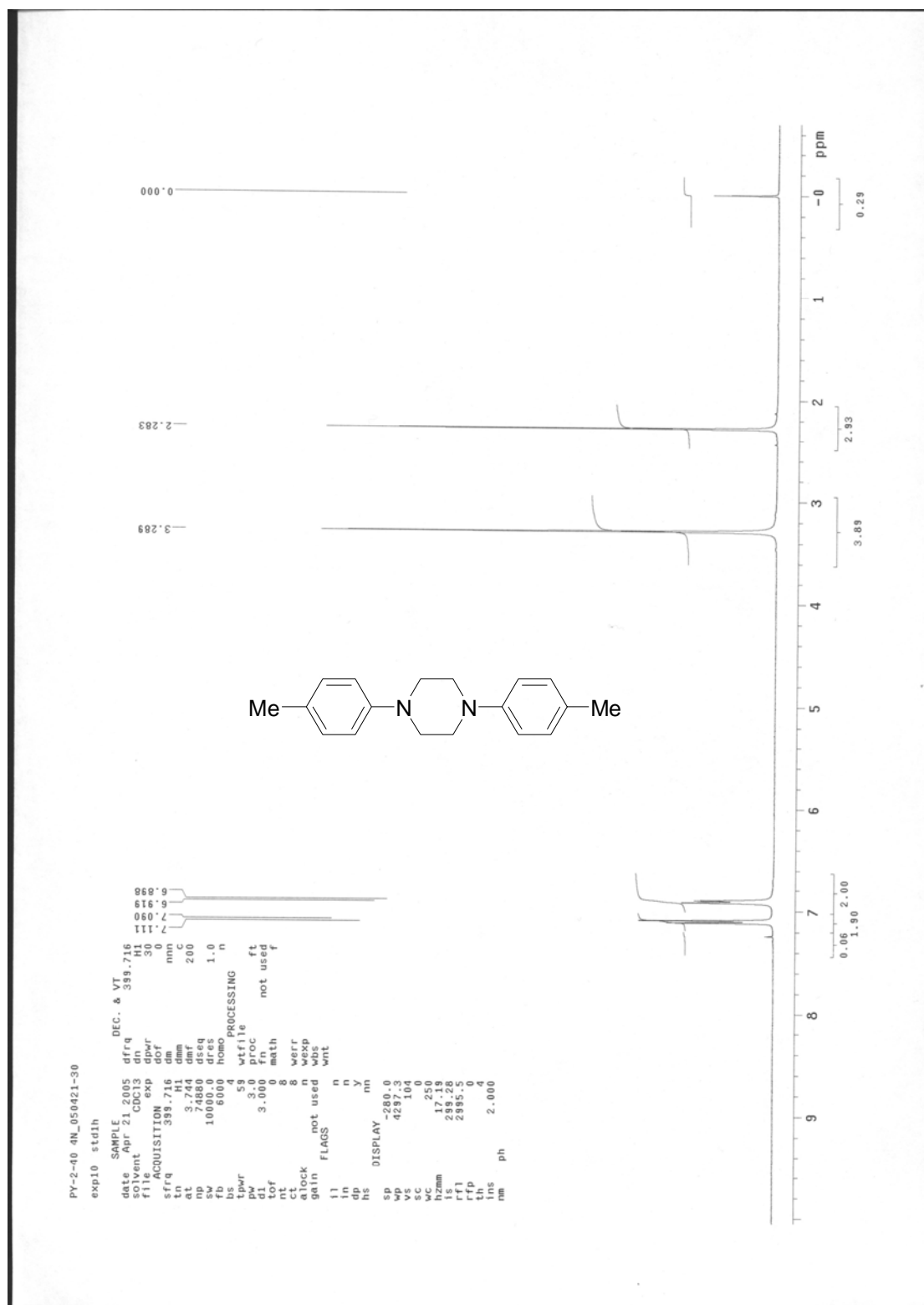


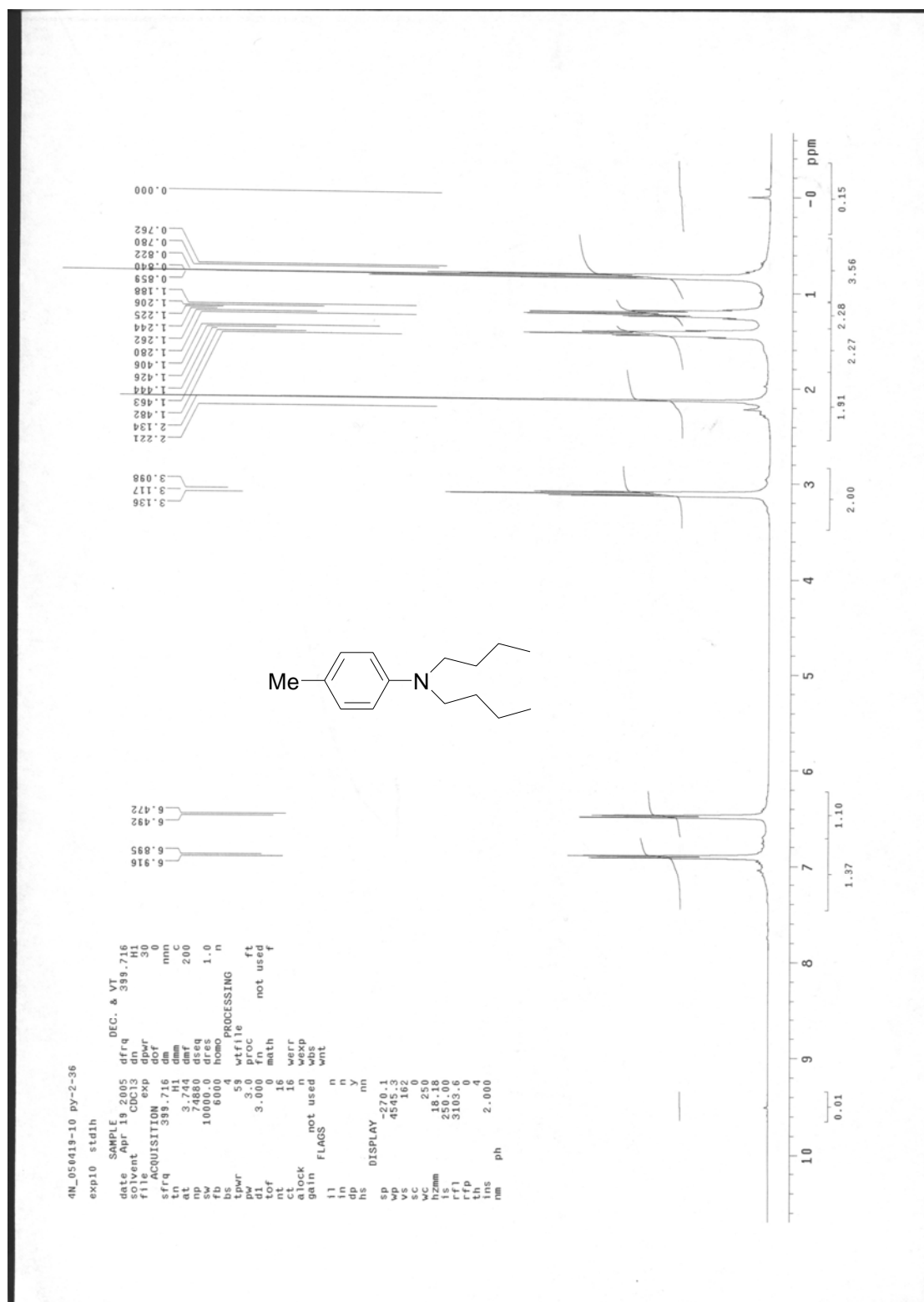


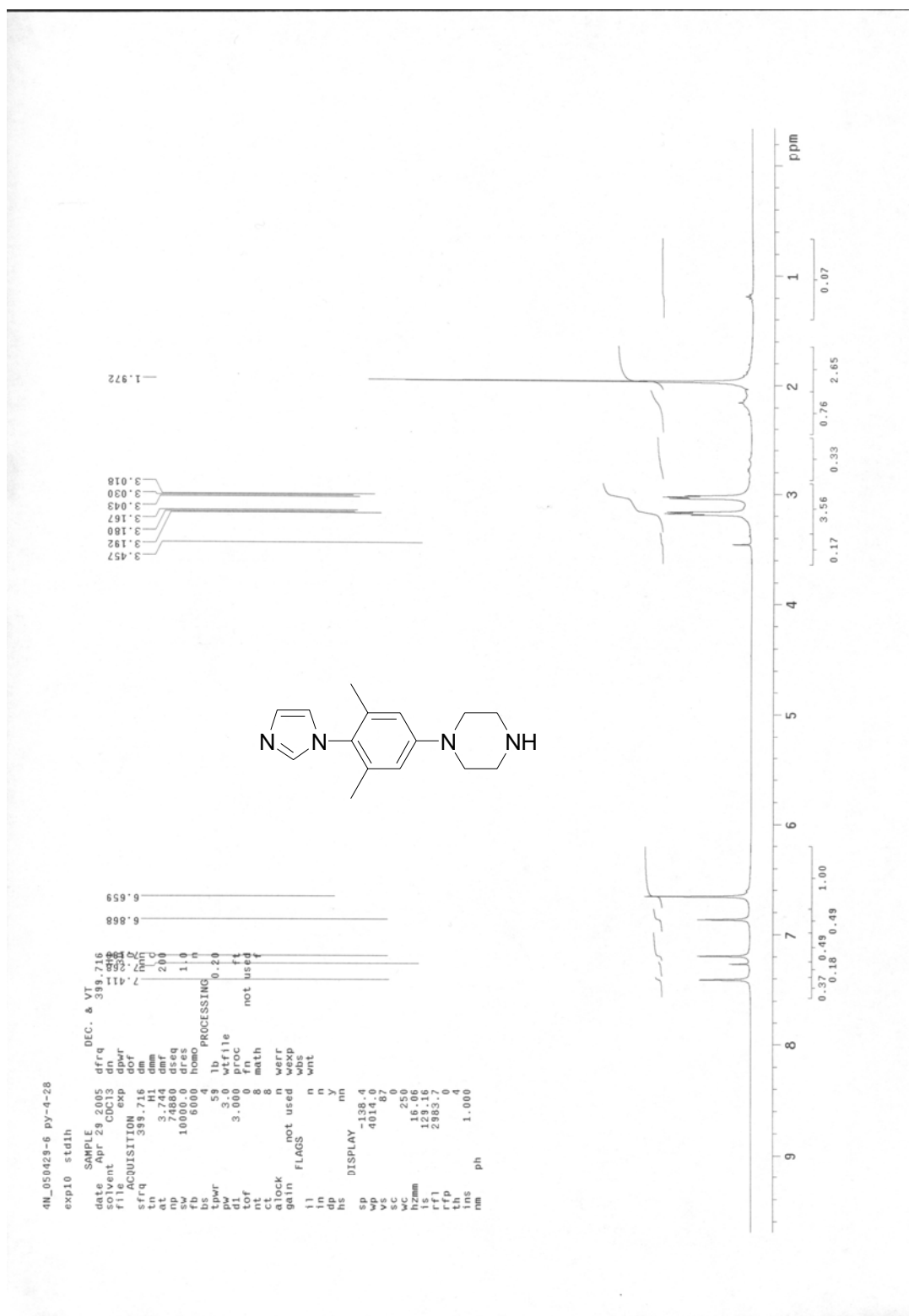


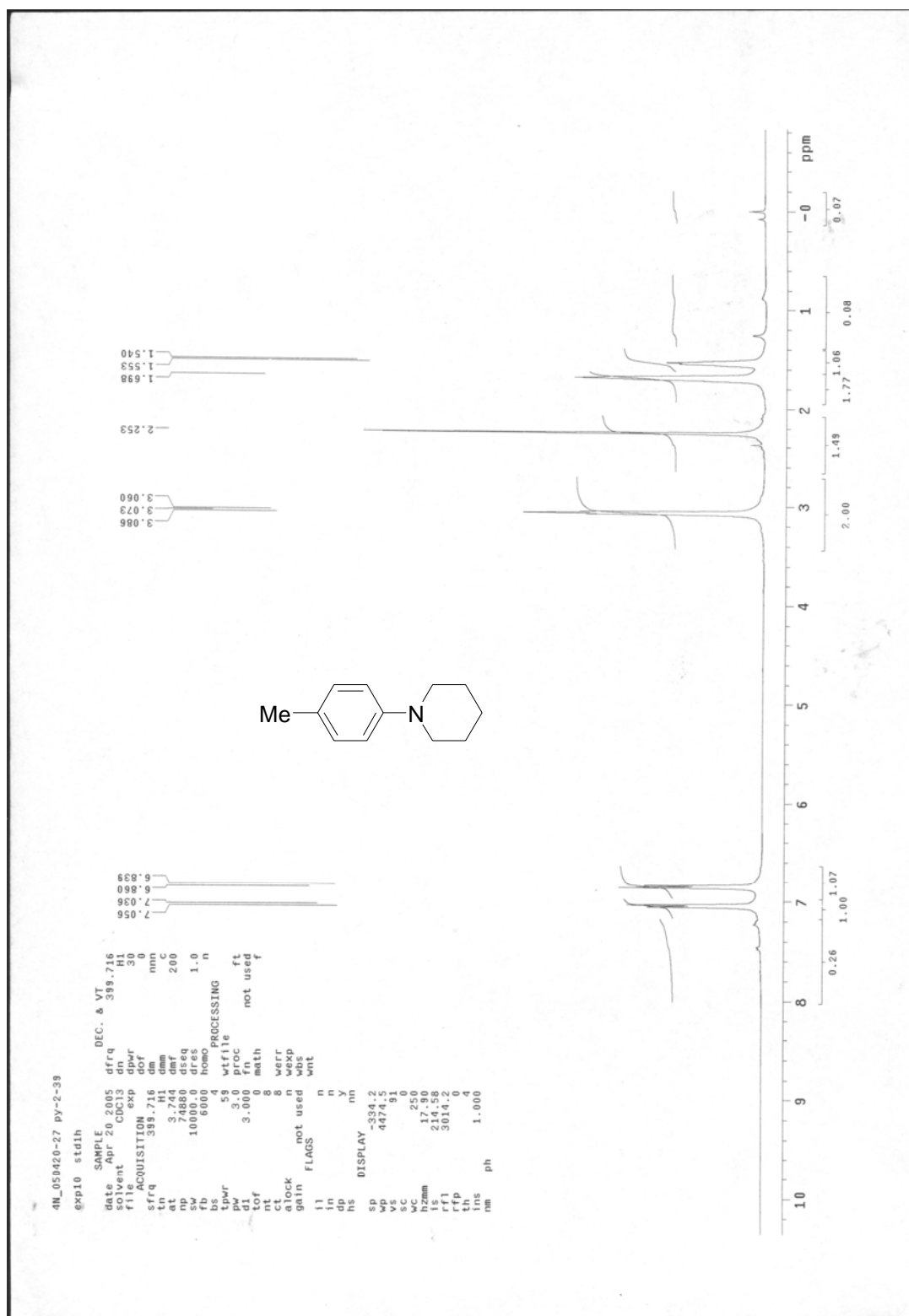




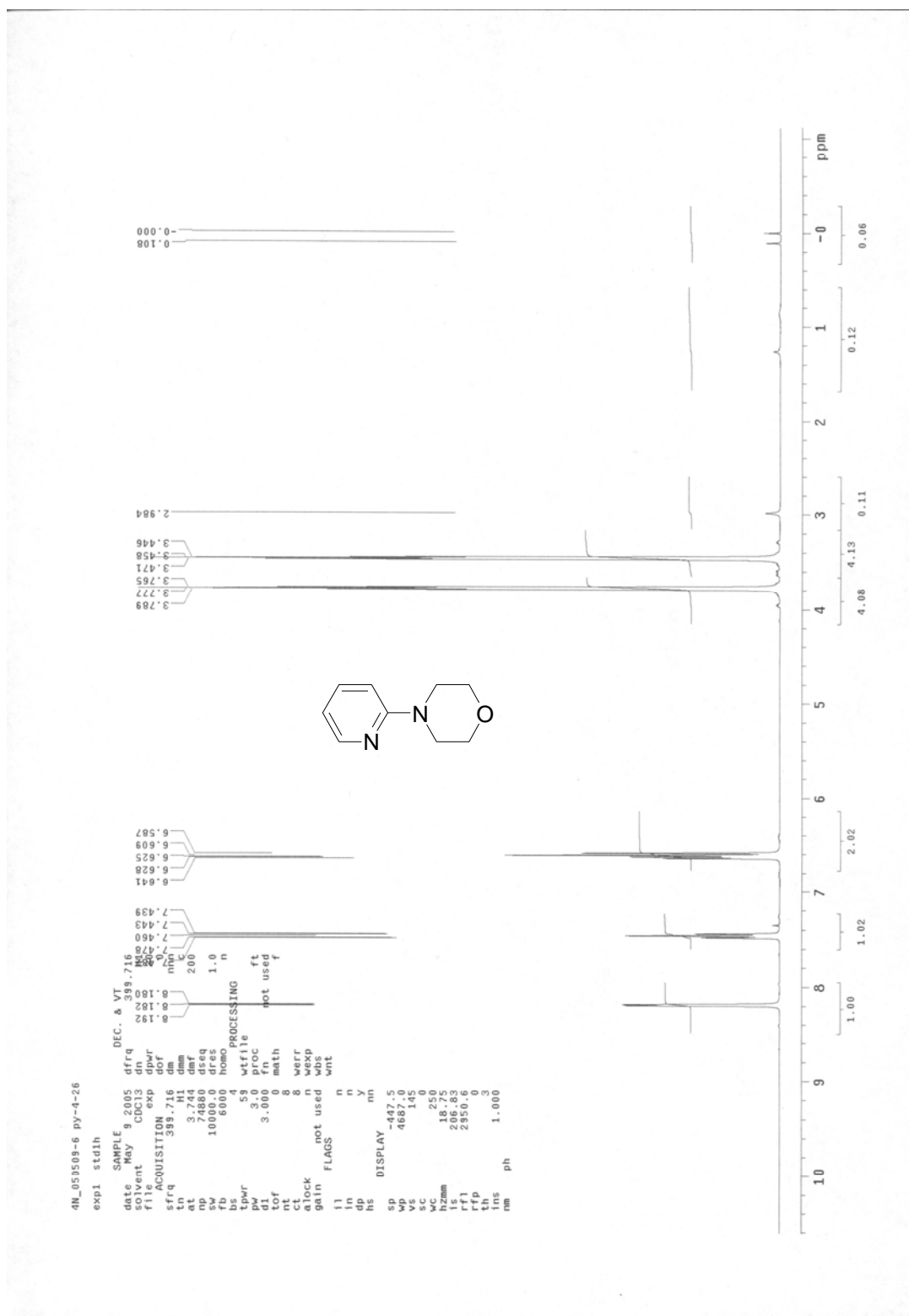


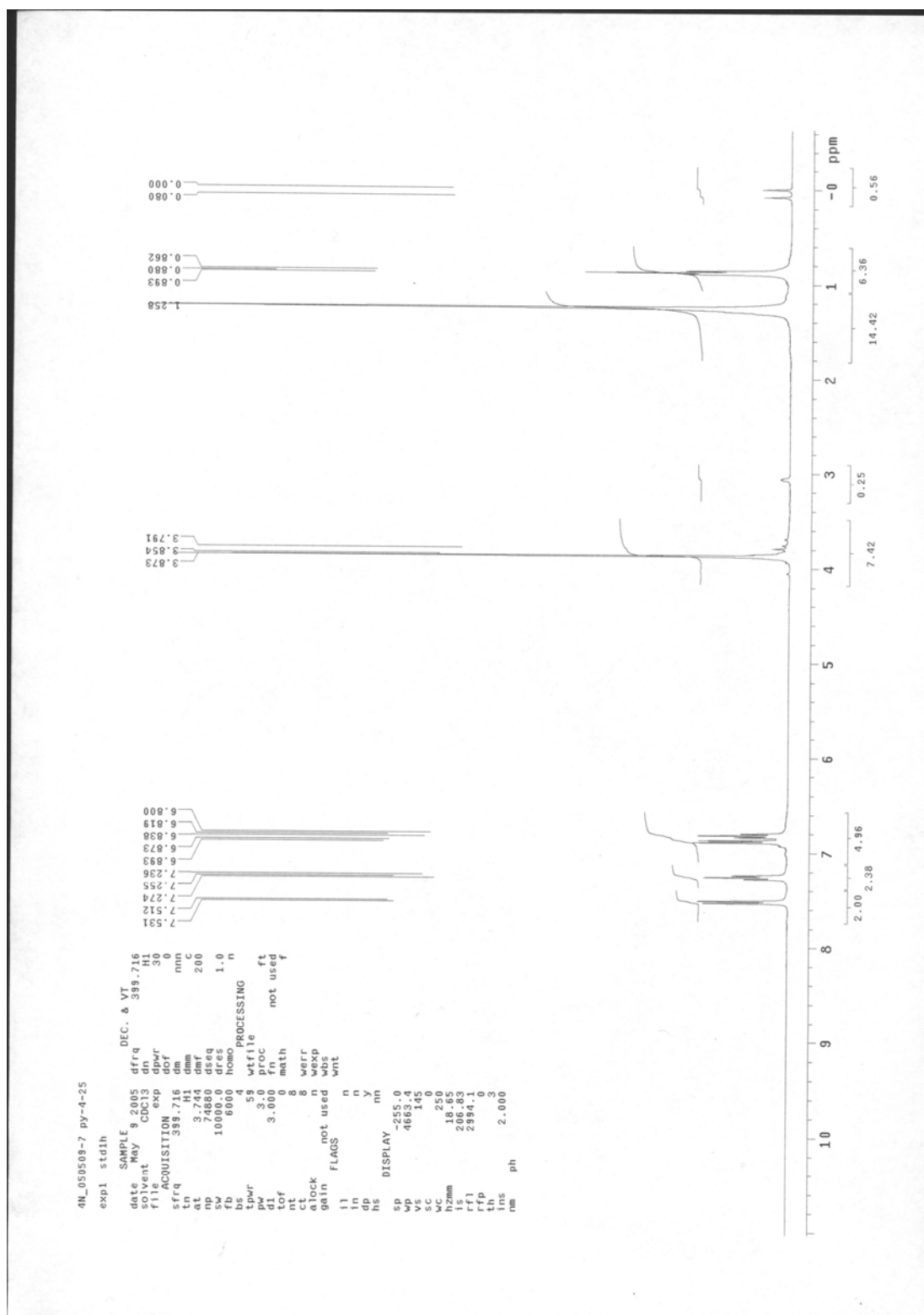


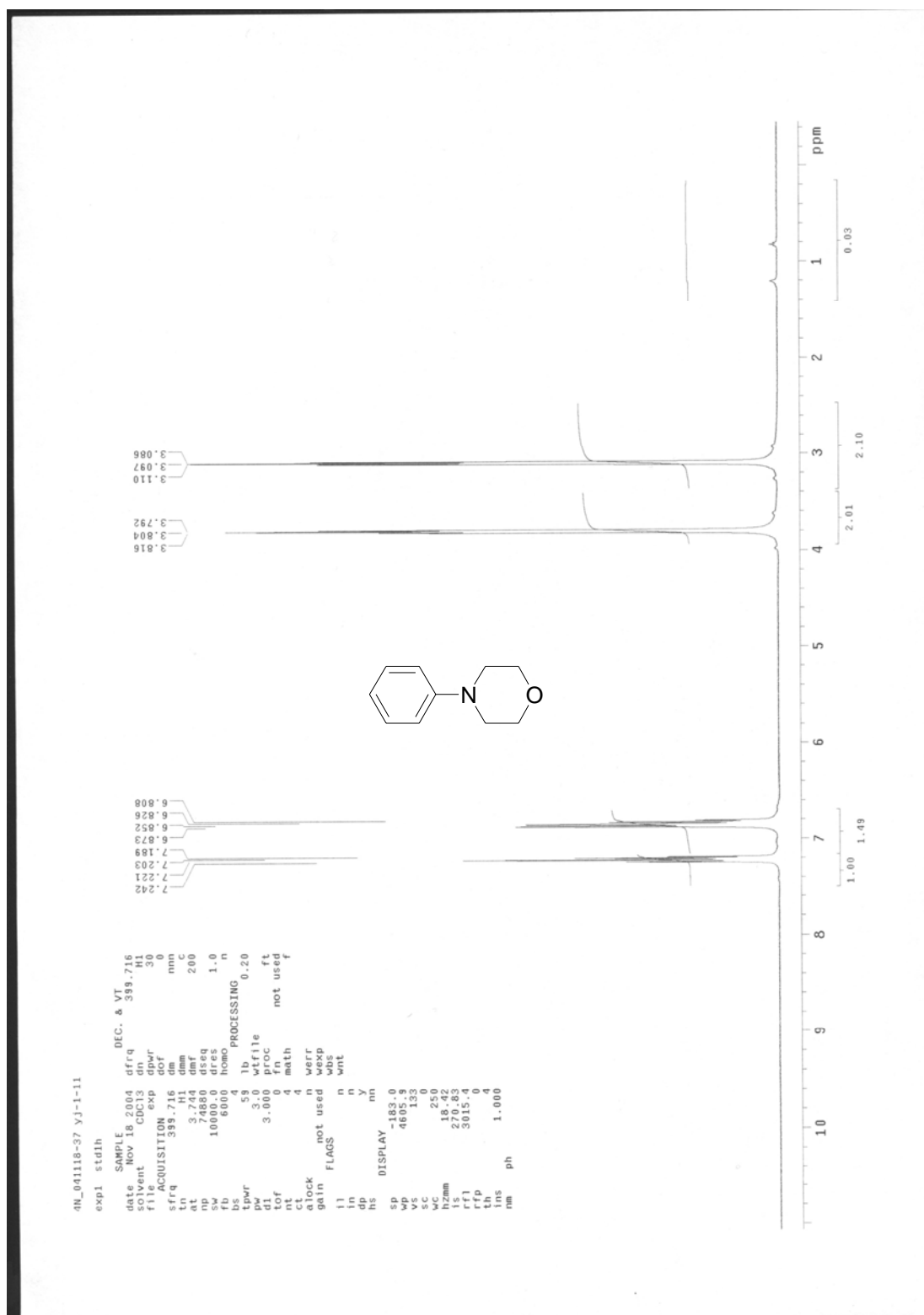


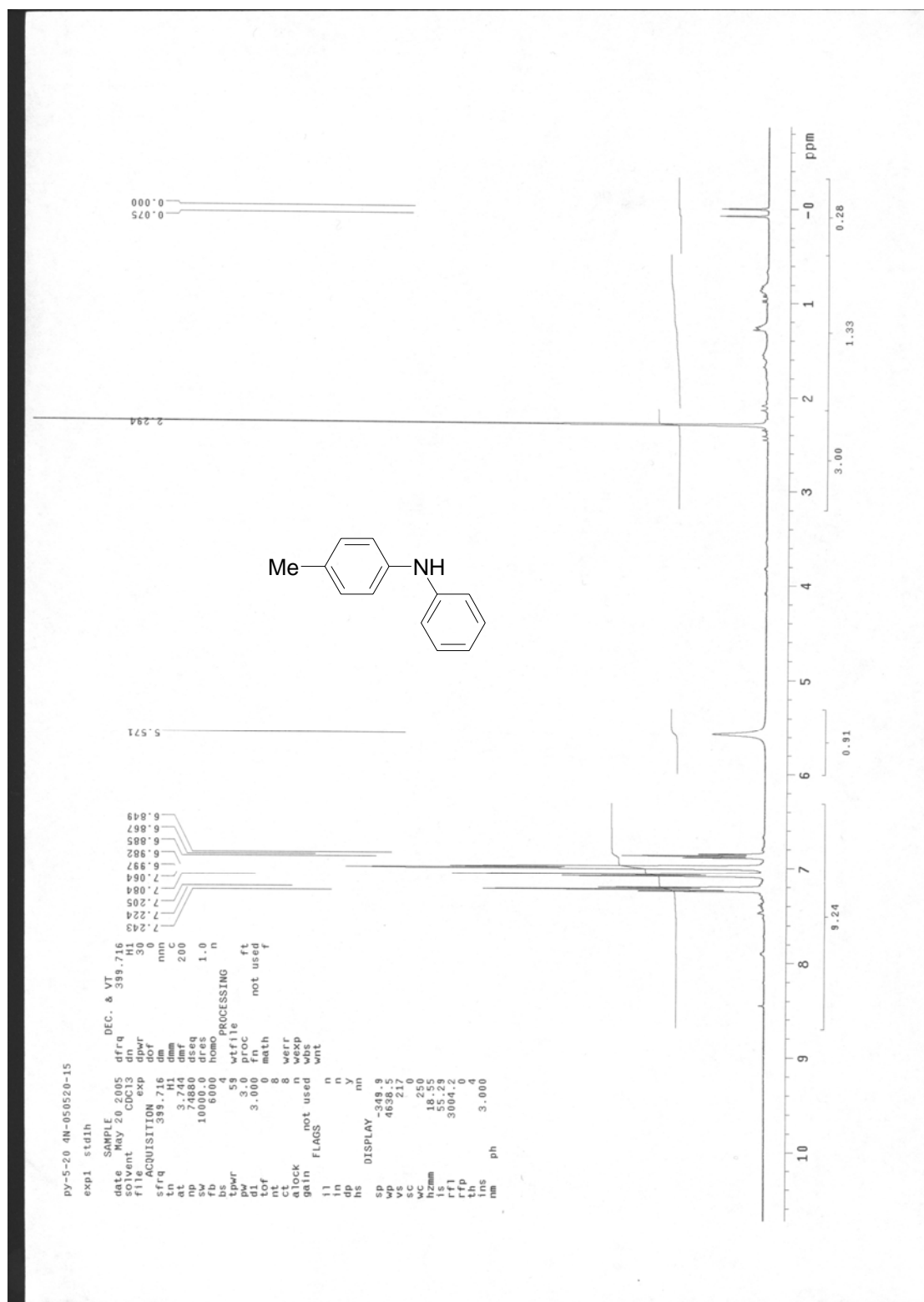


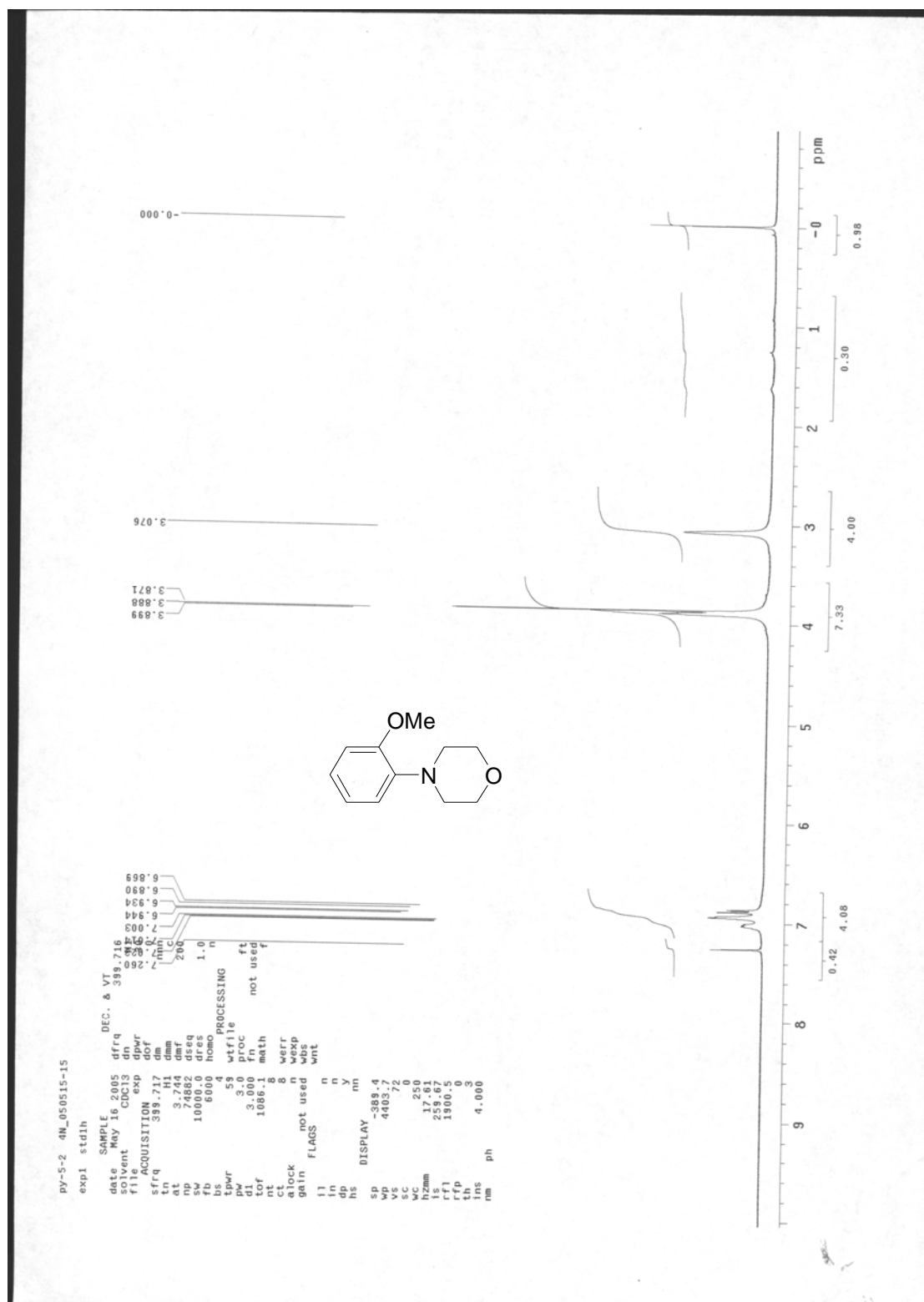


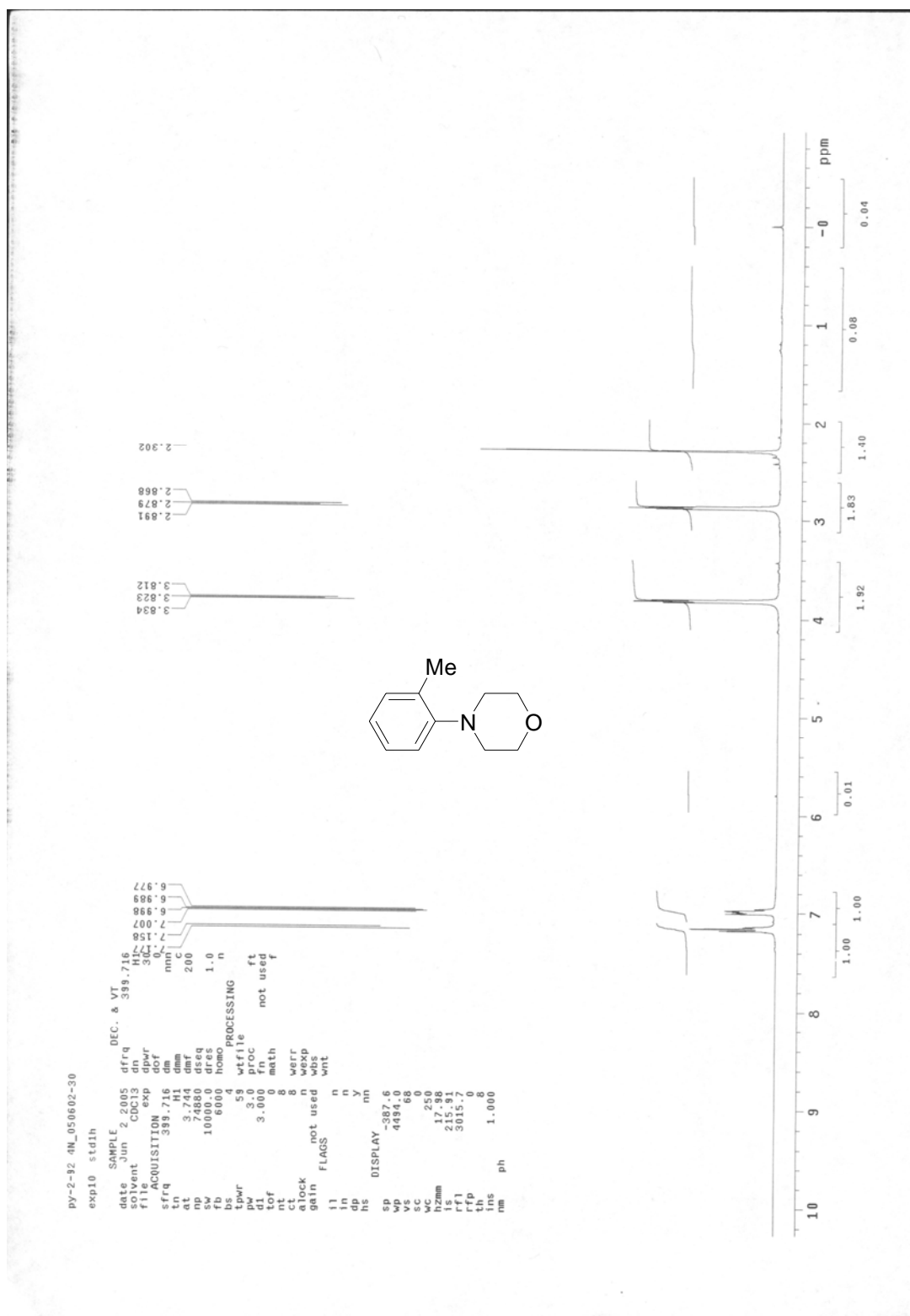


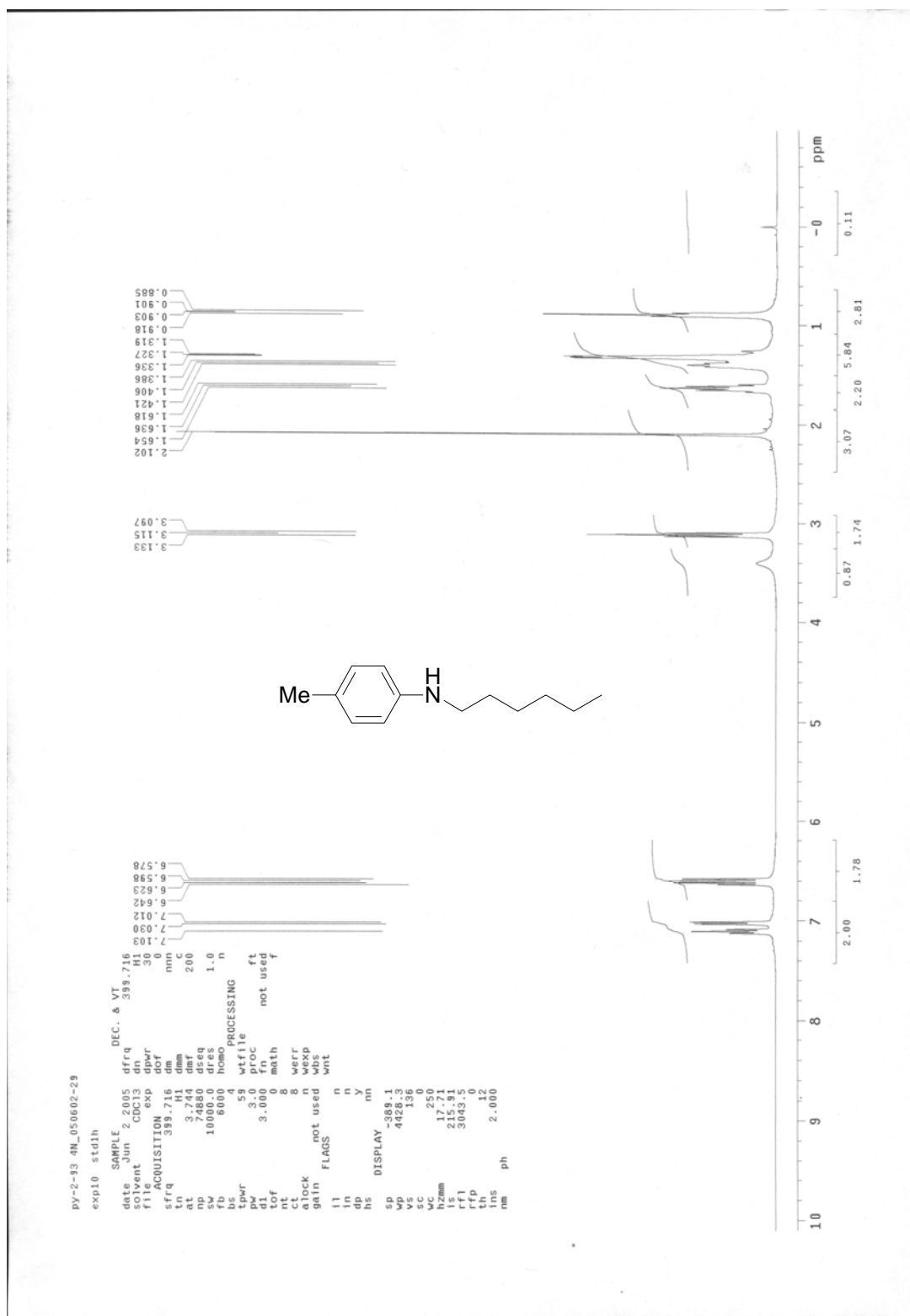


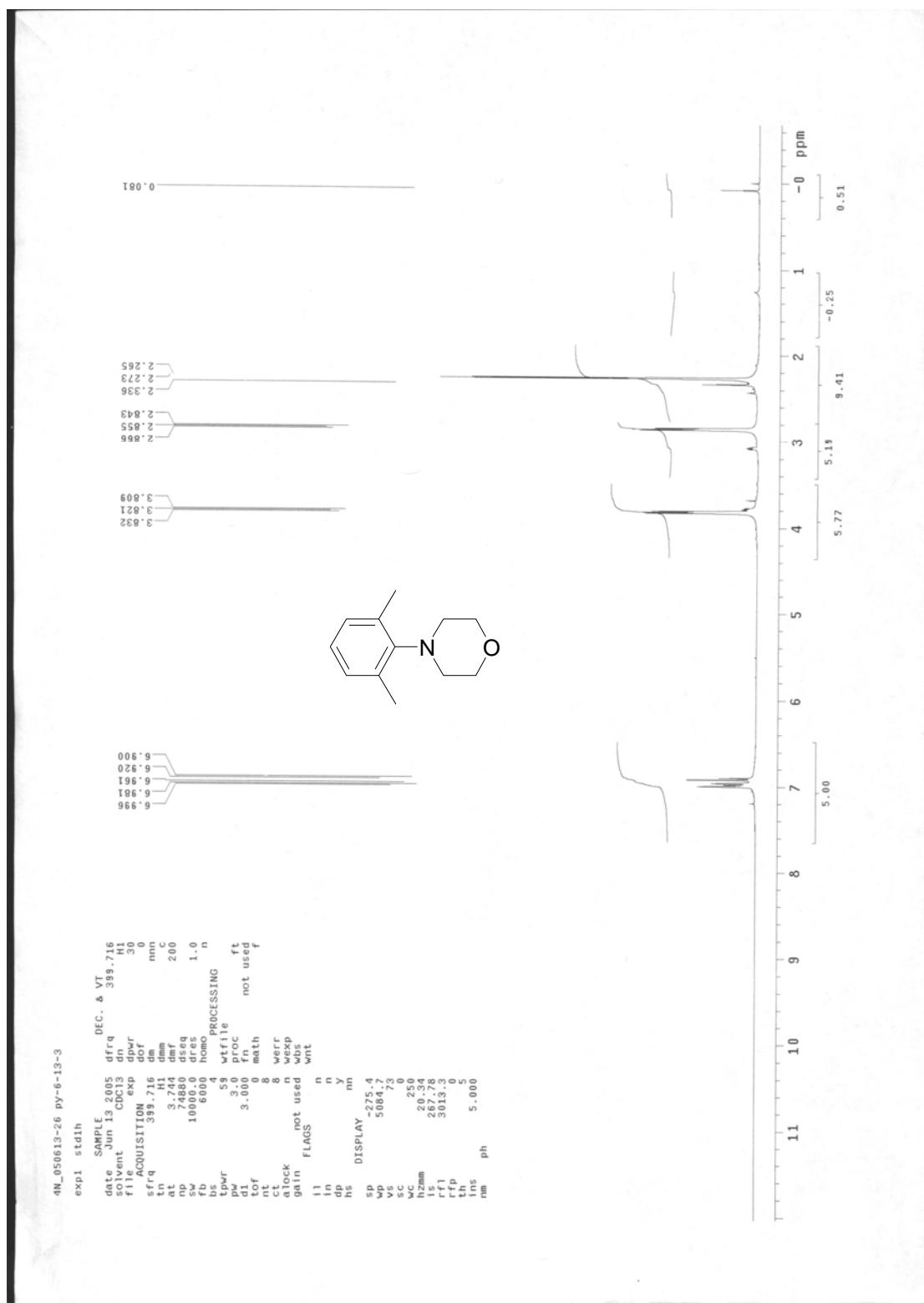
















### Elemental Composition Report

#### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 60.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

56 formula(e) evaluated with 1 results within limits (up to 6 closest results for each mass)

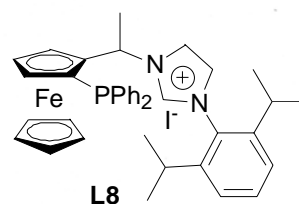
Py7-12-7  
1: TOF MS ES+

1.87e5

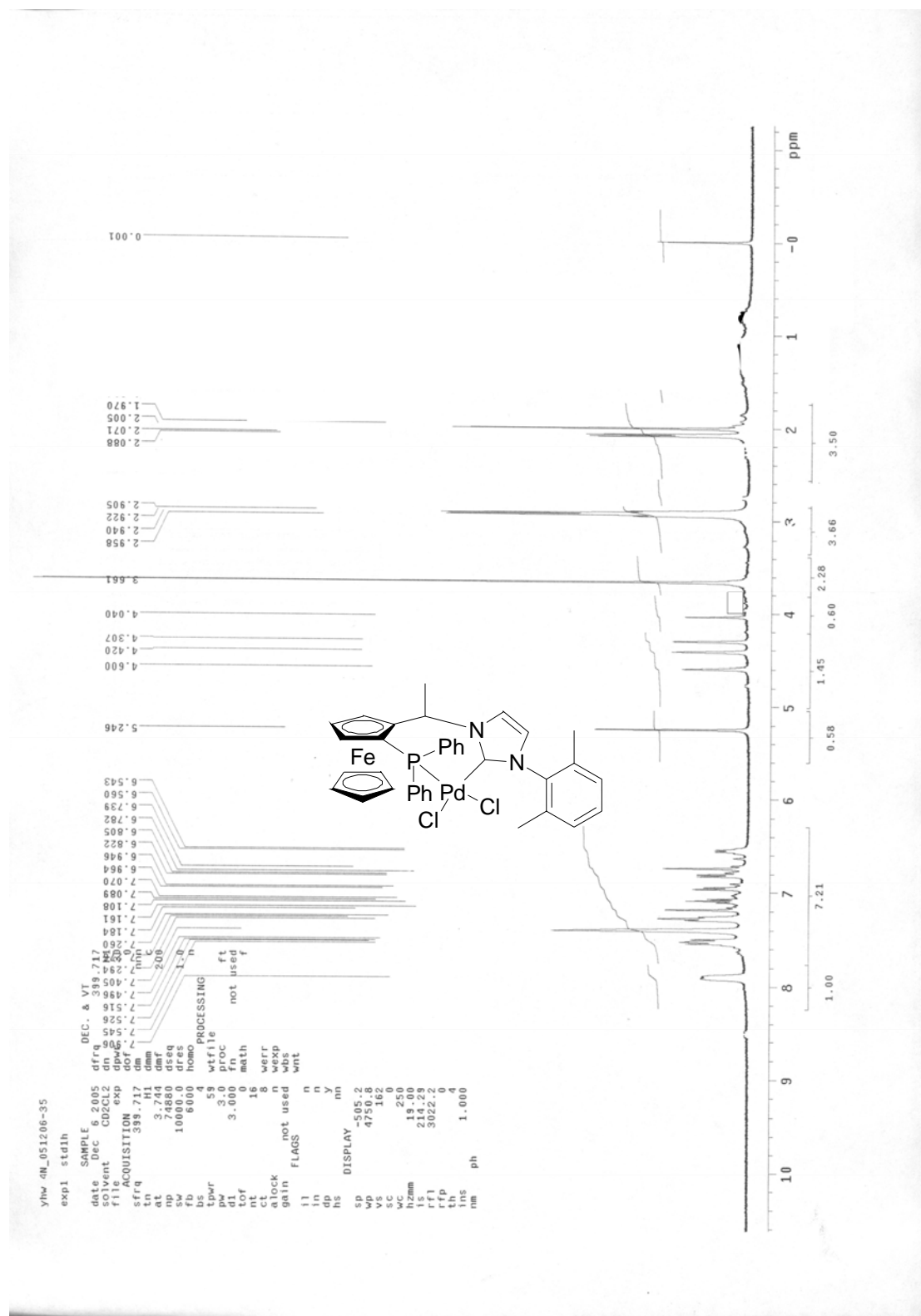


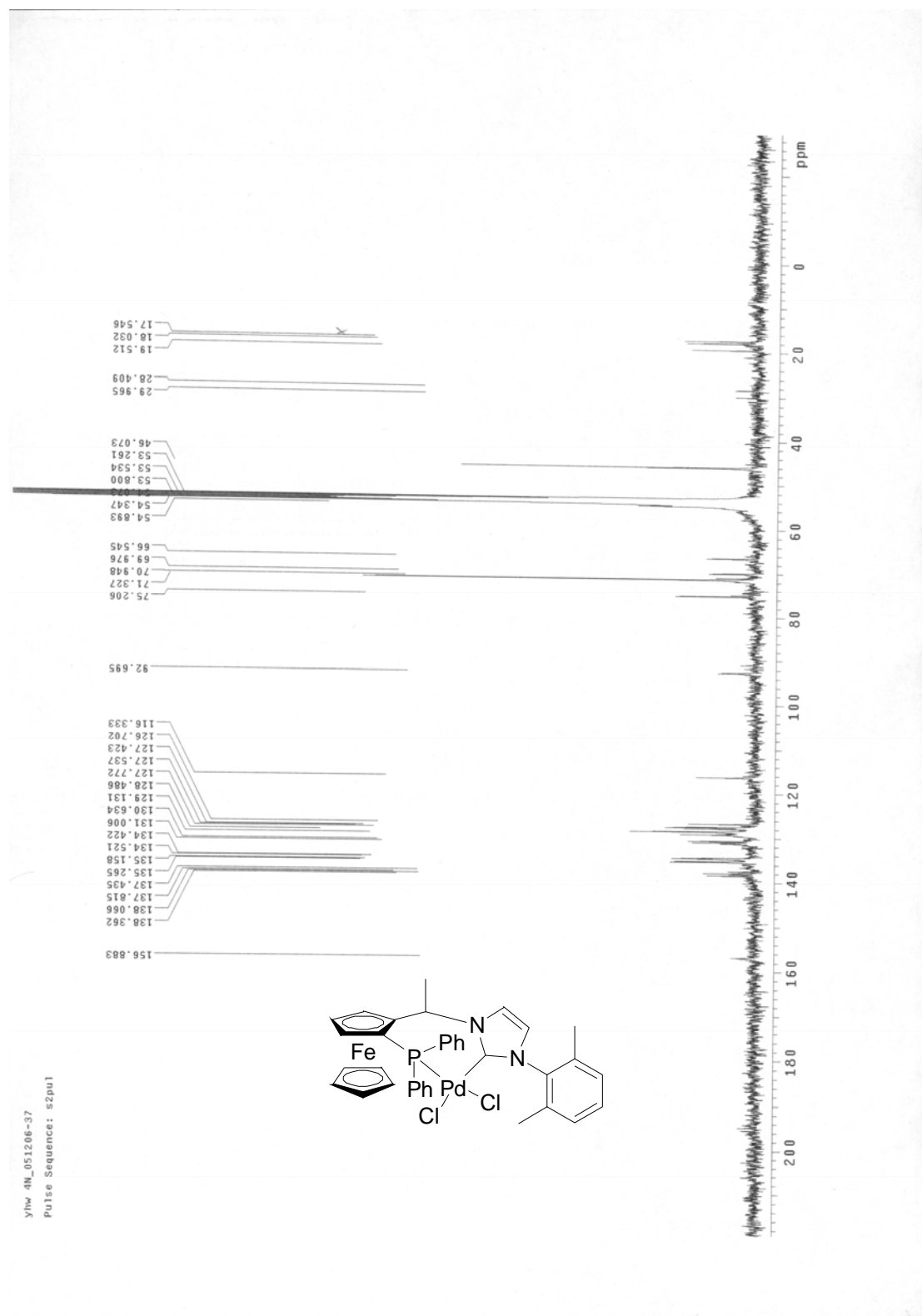
Minimum: -1.5  
Maximum: 60.0

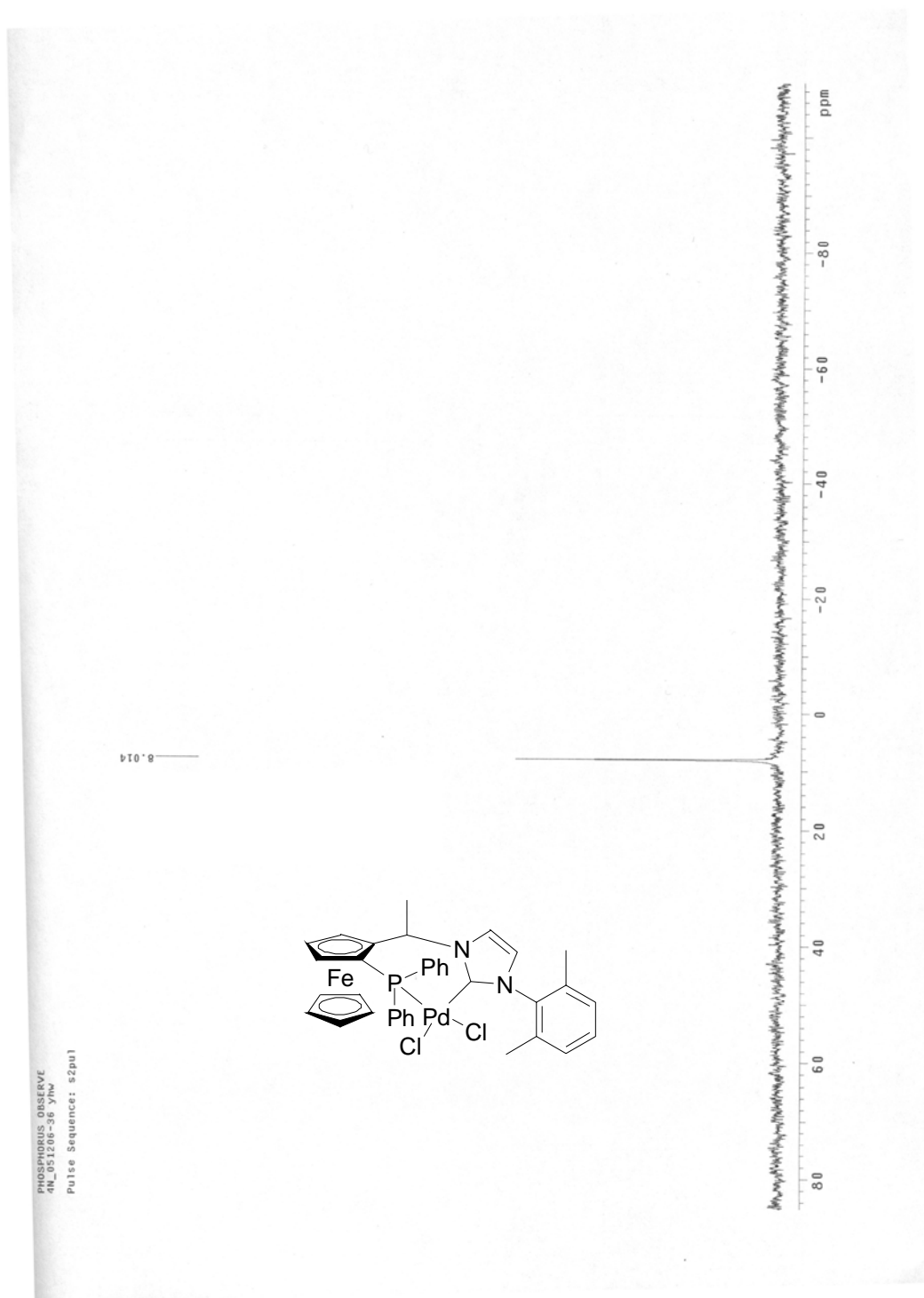
| Mass     | Calc. Mass | mDa  | FPM  | DBE  | Score | Formula         |
|----------|------------|------|------|------|-------|-----------------|
| 625.2429 | 625.2435   | -0.6 | -1.0 | 20.5 | 1     | C39 H42 N2 Fe P |

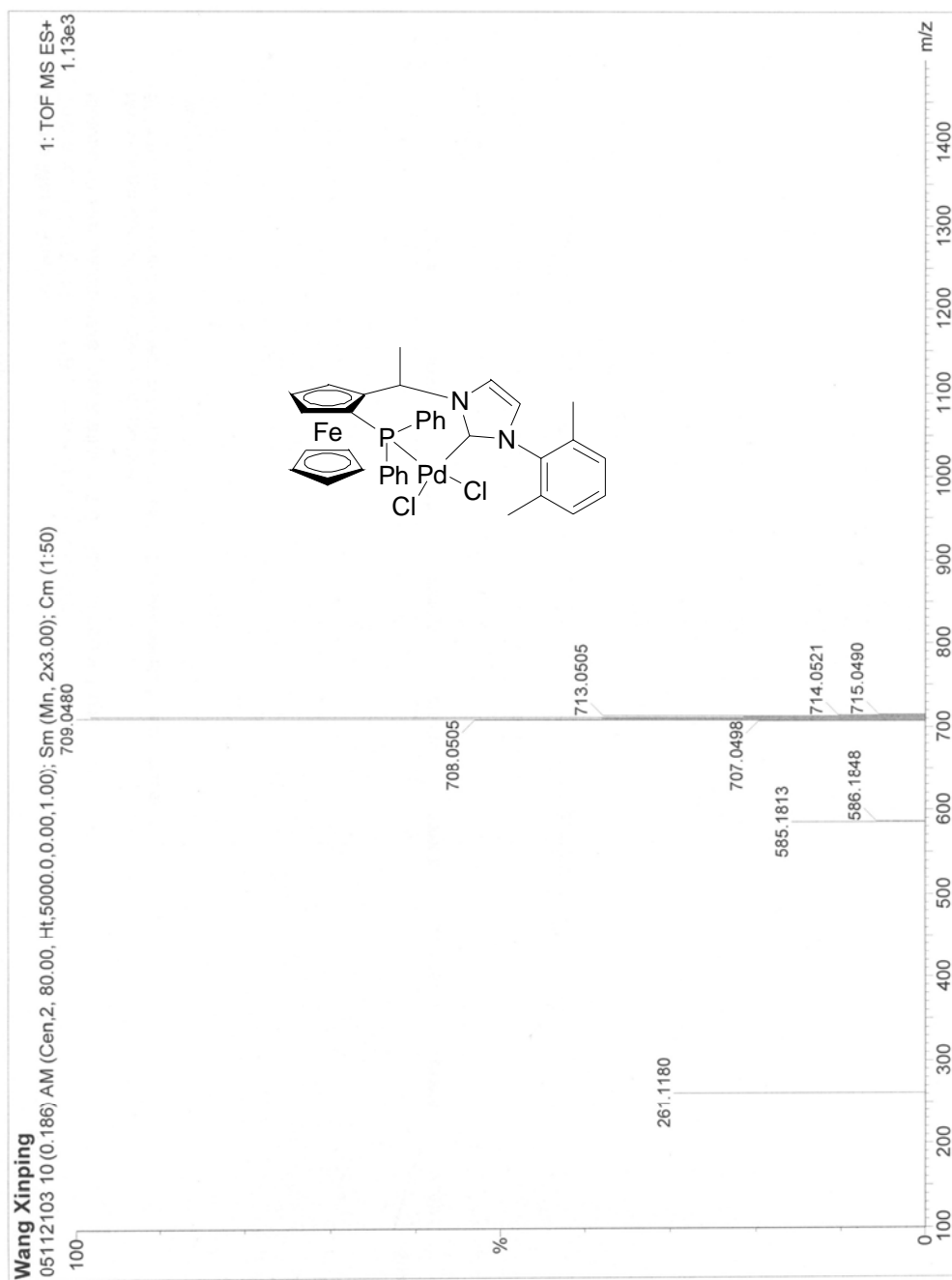


L8









## Elemental Composition Report

Page 4

### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 60.0

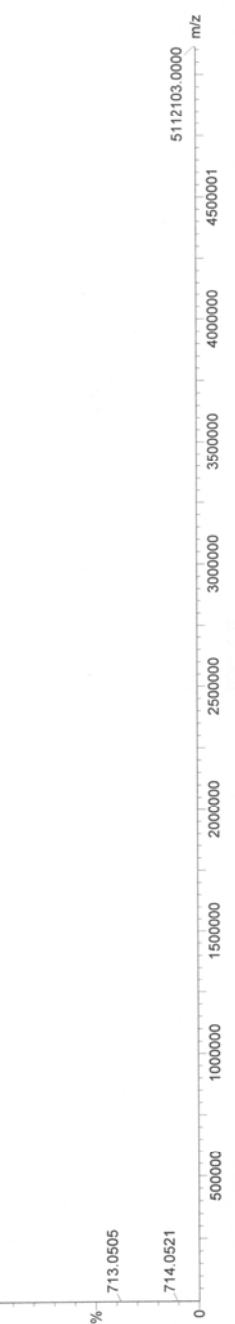
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

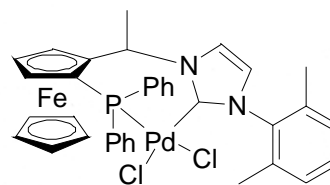
57 formula(e) evaluated with 2 results within limits (up to 10 closest results for each mass)

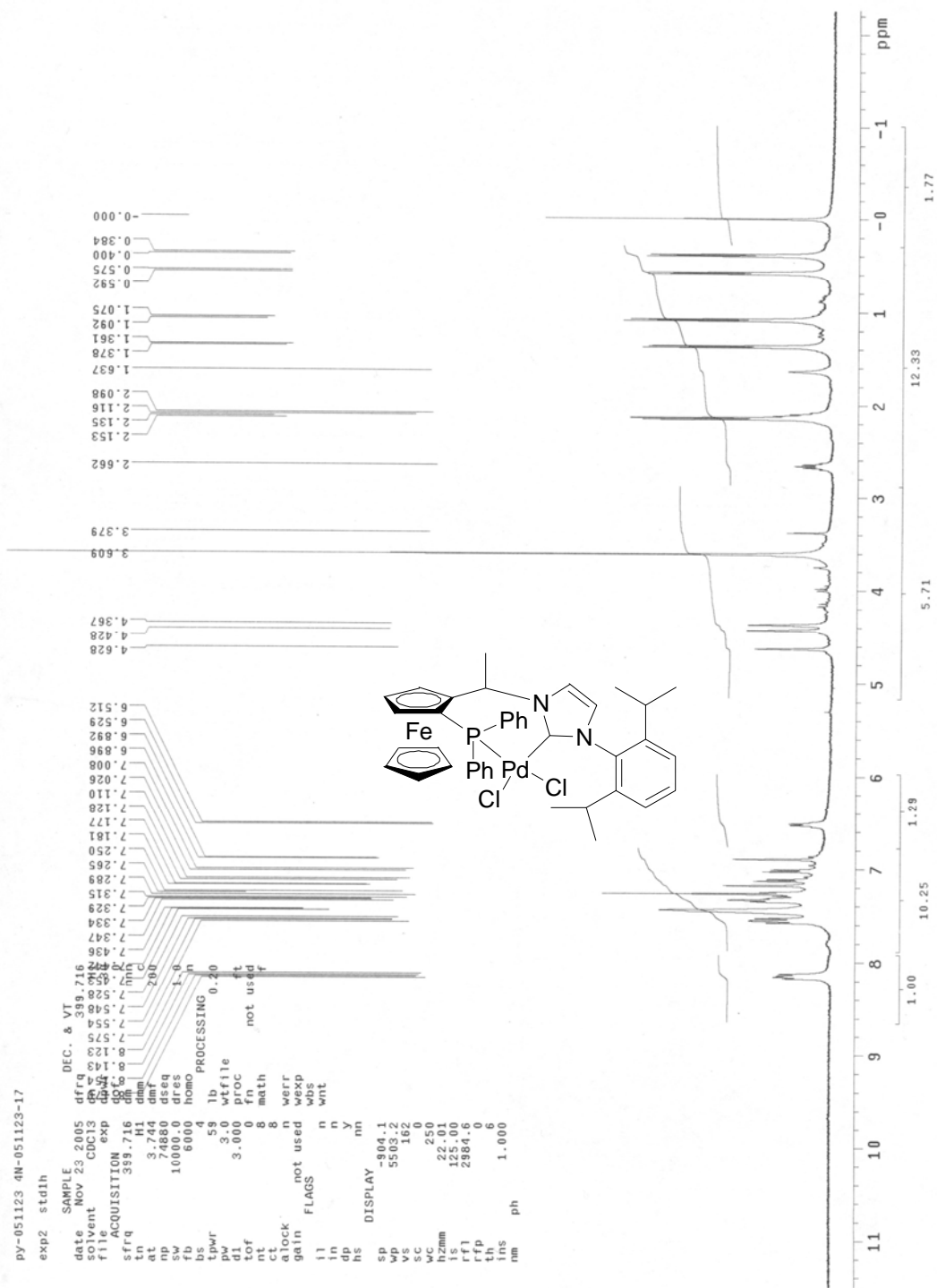
Wang Xinping  
1: TOF MS ES+

1.13e3

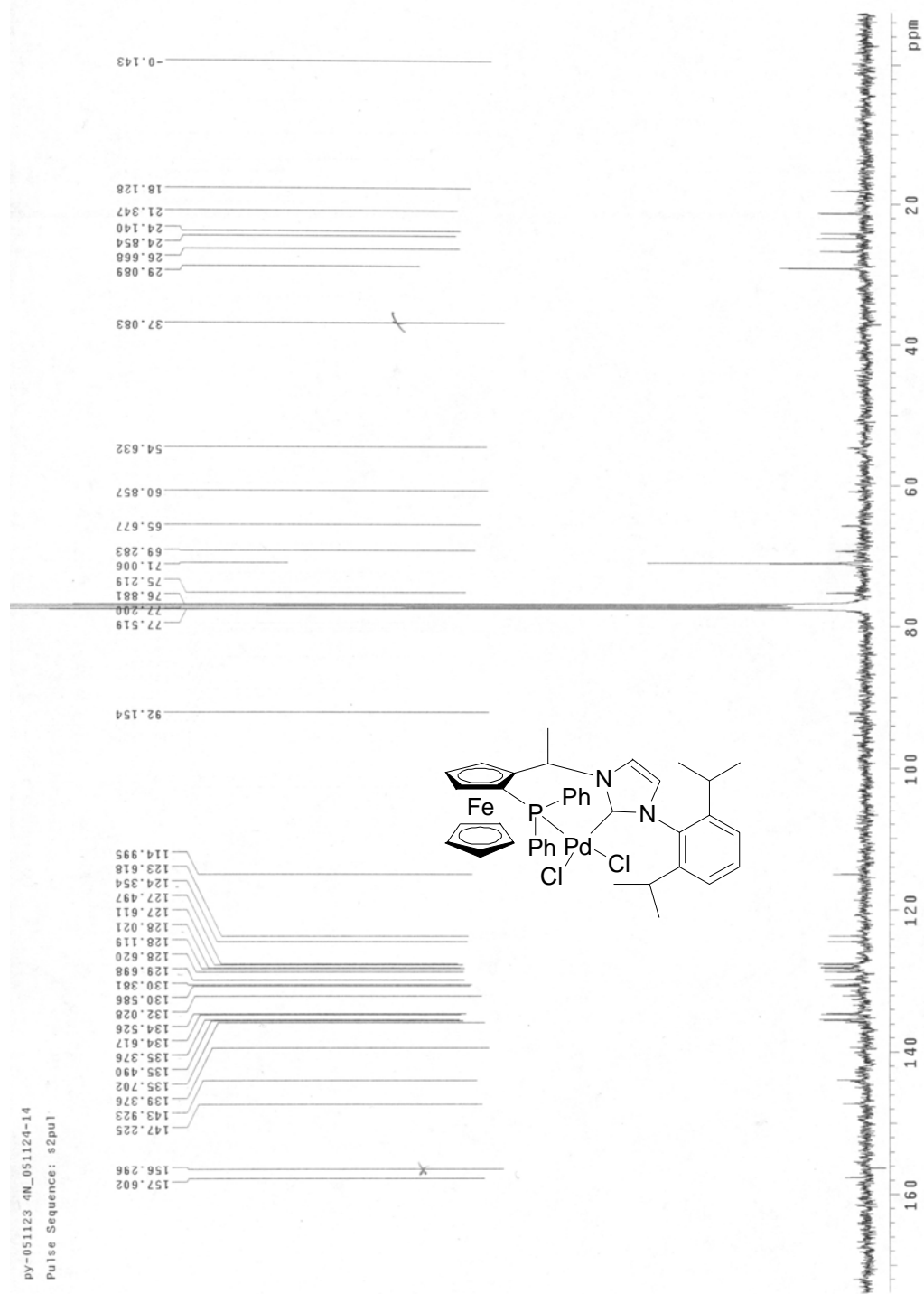


| Mass     | Calc. Mass | mDa  | FPM  | DBE  | Score | Formula               |
|----------|------------|------|------|------|-------|-----------------------|
| 709.0480 | 709.0454   | 2.6  | 3.7  | 20.5 | 1     | C35 H33 N2 Pd P Fe Cl |
| 709.0513 | 709.0513   | -3.3 | -4.6 | 17.0 | 2     | C27 H31 N9 Pd P Fe Cl |

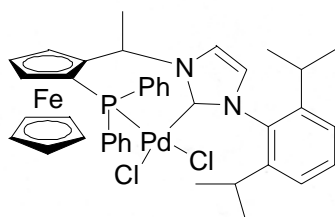




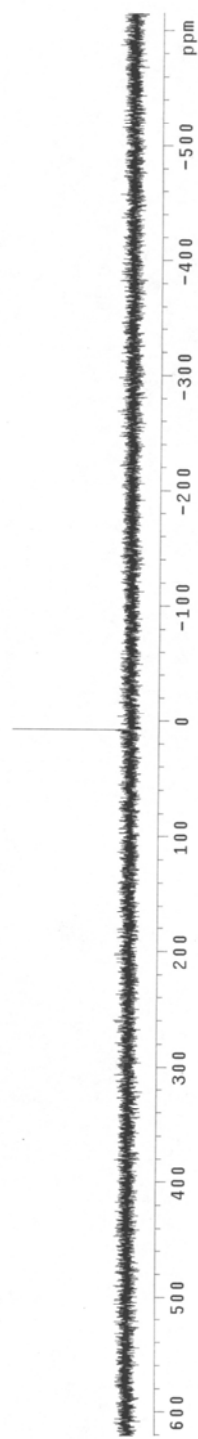


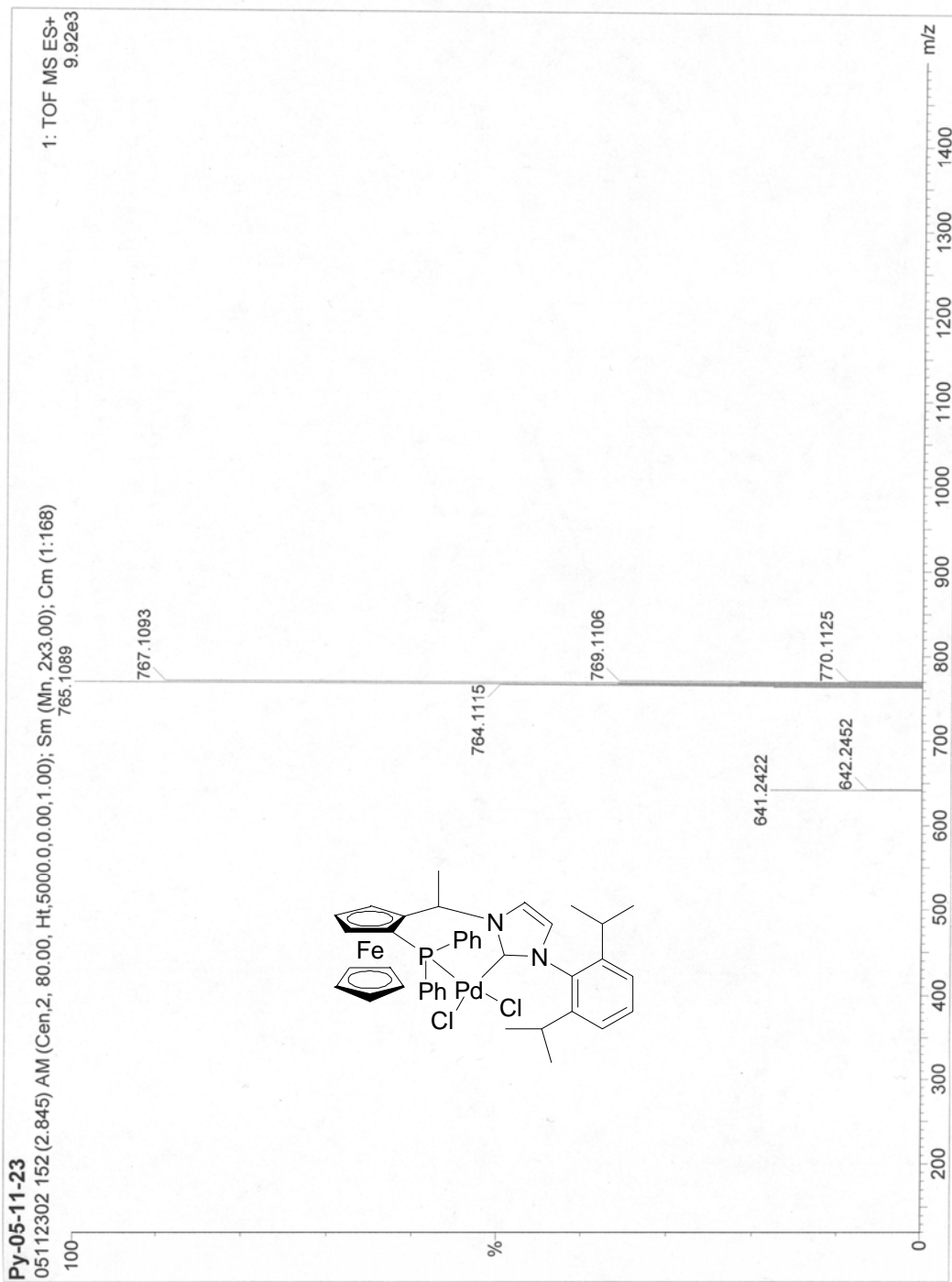


PHOSPHORUS OBSERVE  
py-051123\_4N\_051123-18  
Pulse Sequence: s2pu1



7.674





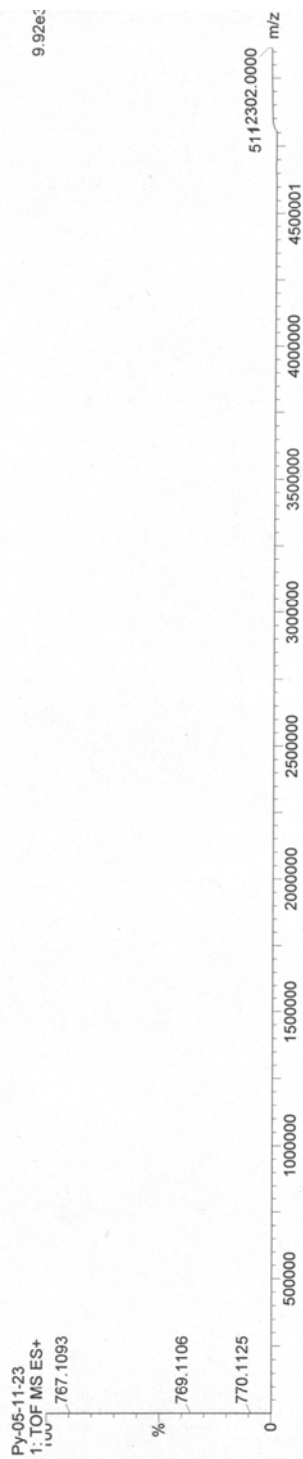
### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 60.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

56 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)



Minimum:  
Maximum:

-1.5  
60.0

DBE

200.0

5.0

PPM

Score

Formula

Mass

Calc. Mass

mDa

0.9

1.2

20.5

1

C39 H41 N2 Pd P Fe Cl

765.1089

765.1080

0.9

1.2

20.5

1

C39 H41 N2 Pd P Fe Cl

