Supplementary Information

# Two new Types of π-Conjugation between a Fullerene Sphere and an Addend.

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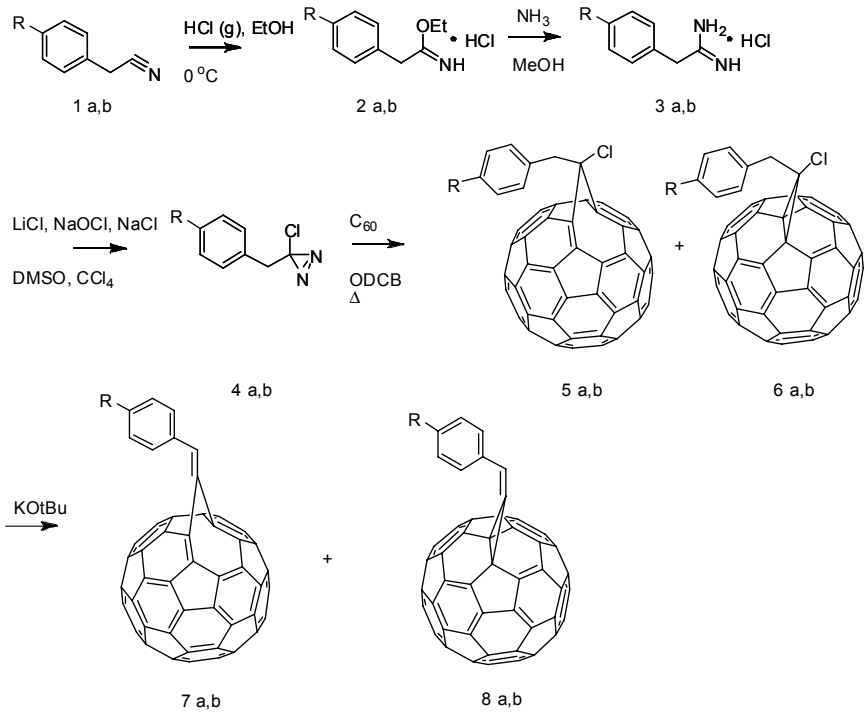


**Figure 1: General Synthetic Scheme (a: R=H, b: R=NO2)**

## General Procedure for Diazirine addition:

A flame-dried three-necked flask equiped with thermometer, condensor, $N_2$-inlet, and stirring egg was charged with a solution of $C_{60}$ in ODCB (20 mg/ml). This solution was thoroughly degassed by 3 $N_2$/vacuum purges. The diazirine (5 eq.) was added at once to this solution. The resulting reaction mixture was heated to 60 °C. The reaction was followed by HPLC and stopped at the following conversion: $C_{60}$ : 50%, [6,6]-adduct : 32 % and [5,6]-adduct : 5%. The different products were then isolated by preparative HPLC using a Buckyclutcher column and cyclohexane/toluene (1:1) as the eluent.

## General Procedure for the HCl elimination reaction:

A flame dried flask was charged with a solution of fullerene in ODCB (1mg/ml). This solution was heated to 50 °C and KOtBu (2 eq) was then added at once. The reaction was followed by HPLC. When a conversion of around 85% was reached, the reaction was stopped and the products were purified by the same preparative HPLC procedure as before.

**1-benzyl-1-chlorohomofullerene 5a:** IR (KBr) = ν ($cm^{-1}$): 3425 (s), 3060 (m), 3028 (s), 2923 (s), 2851 (m), 1722 (m), 1601 (m), 1495 (s), 1454 (s), 1433 (s), 1380 (m), 1260 (w), 1174 (w), 1033 (m), 747 (s), 697 (s), 527 (s). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 537, 602. Mass m/z calcd. for $C_{68}H_7Cl$: 858.02. Found: 858.8

**1-(*p*-nitrobenzyl)-1-chlorohomofullerene 5b:** UV/Vis (toluene/cyclohexane 1:1); λ (nm): 540, 603. Mass m/z calcd. for $C_{68}H_6ClNO_2$: 903.01, Found: 903.8

**1-benzyl-1-chlorocyclopropafullerene 6a:** IR (KBr) = ν ($cm^{-1}$): 3426 (s), 3026 (w), 1602 (w), 1494 (m), 1465 (m), 1452 (m), 1429 (m), 1385 (w), 1186 (m), 698 (m), 577 (m), 526 (s). $^1$H NMR ($CS_2$ with $D_2O$ insert, 300 MHz); δ (ppm): 7.78 (d, *J* = 6.9 Hz, 2H), 7.47–7.7.56 (m, 3H), 4.67 (s, 2H). $^{13}$C NMR ($D_2O/CS_2$, 300 MHz); δ (ppm): 39.1, 57.3, 78.8, 127.3, 128.4, 129.7, 130.1, 135.2, 137.0, 138.7, 140.6, 140.9, 141.4, 141.7, 141.8, 141.9, 142.7, 142.9, 143.2, 144.0, 144.1, 144.2, 144.4, 144.5, 144.6, 144.7, 144.8, 145.3, 145.6. UV/Vis (toluene/cyclohexane 1:1); λ (nm): 431, 497, 692. Mass m/z calcd. for $C_{68}H_7Cl$: 858.02. Found: 858.6.

**1-(*p*-nitrobenzyl)-1-chlorocyclopropafullerene 6b:** IR (KBr) = ν ($cm^{-1}$): 3424 (s), 1601 (m), 1517 (s), 1430 (m), 1340 (s), 854 (w), 578 (w), 526 (s). $^1$H NMR ($CS_2$ with $D_2O$ insert, 400 MHz); δ (ppm): 8.45 (d, J = 8.8 Hz, 2H) , 8.06 (d, *J* = 8.8 Hz, 2H), 4.58 (s, 2H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 438, 490, 685. Mass m/z calcd. for $C_{68}H_6ClNO_2$: 903.01. Found: 903.3.

**Benzylidenehomofullerene 7a:** UV/Vis (toluene/cyclohexane 1:1); λ (nm): 548, 603, 664. Mass m/z calcd. for $C_{68}H_6$: 822.04. Found: 822.7.

***p*-Nitrobenzylidenehomofullerene 7b:** UV/Vis (toluene/cyclohexane 1:1); λ (nm): 547. Mass m/z calcd. for $C_{68}H_5NO_2$: 867.03. Found: 867.8.

**Benzylidenecyclopropafullerene 8a:** IR (KBr) = ν ($cm^{-1}$): 3026 (s), 1538 (w), 1496 (w), 1466 (m), 1452 (m), 1429 (s), 1259 (m), 1188 (s), 1076 (m), 915 (w), 879 (w), 752 (m), 743 (m), 688 (s), 525 (s), 518 (s). $^1$H NMR ($CS_2$ with $D_2O$ insert, 300 MHz); δ (ppm): 8.1 (d, J = 7.7 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 2H), 7.54–7.58 (m, 1H). 7.47 (s, 1H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 427, 515, 690. Mass m/z calcd. for $C_{68}H_6$: 822.04. Found: 822.7.

***p*-Nitrobenzylidenecyclopropafullerene 8b:** IR (KBr) = ν ($cm^{-1}$): 3446 (s), 1597 (m), 1516 (s), 1429 (m), 1340 (s), 1109 (m), 526 (s). $^1$H NMR ($CS_2$ with $D_2O$ insert, 400 MHz); δ (ppm): 8.49 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 2H), 7.58 (s, 1H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 511. Mass m/z calcd. for $C_{68}H_5NO_2$: 867.03. Found: 867.7.

## UV/VIS spectroscopy

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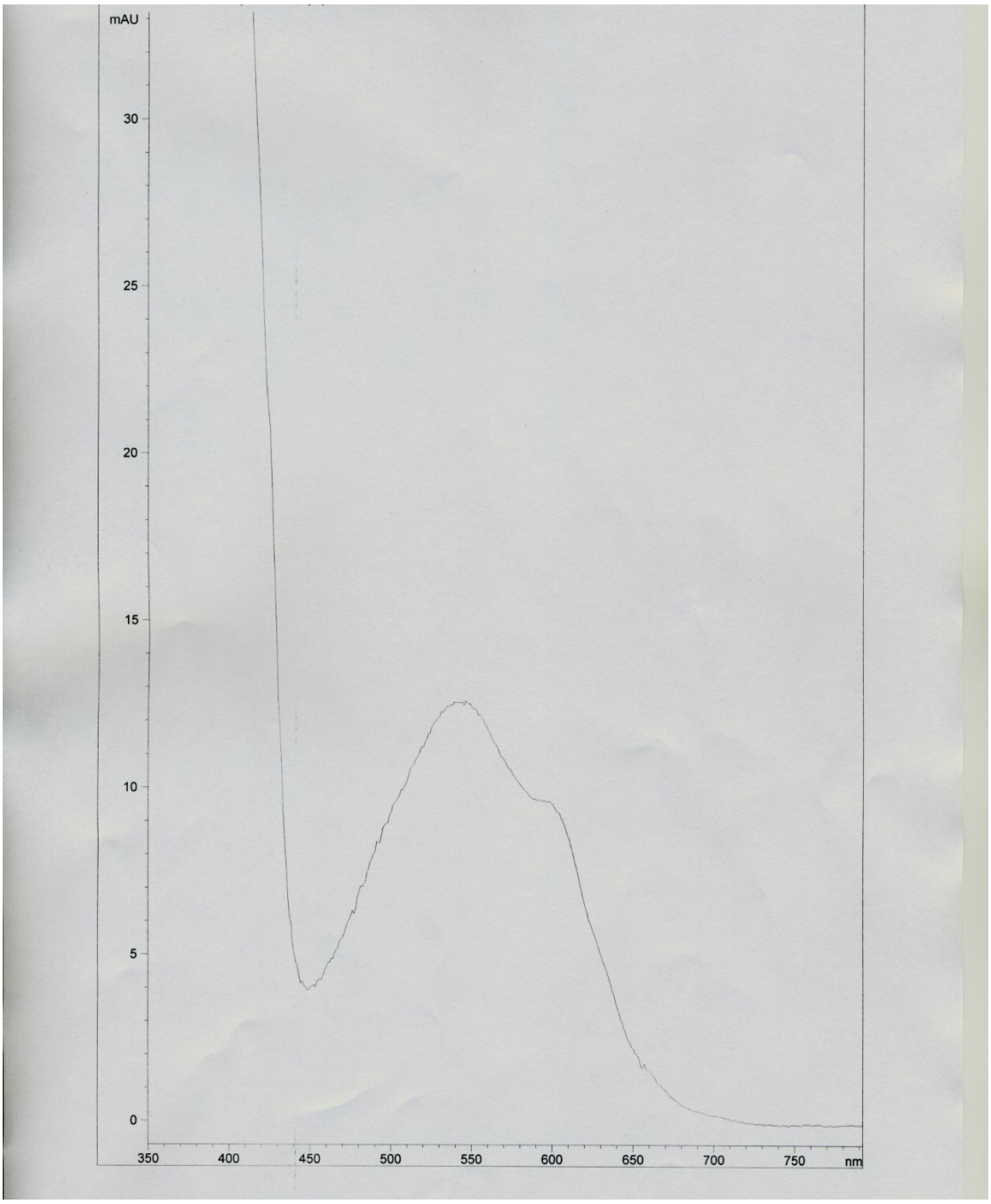

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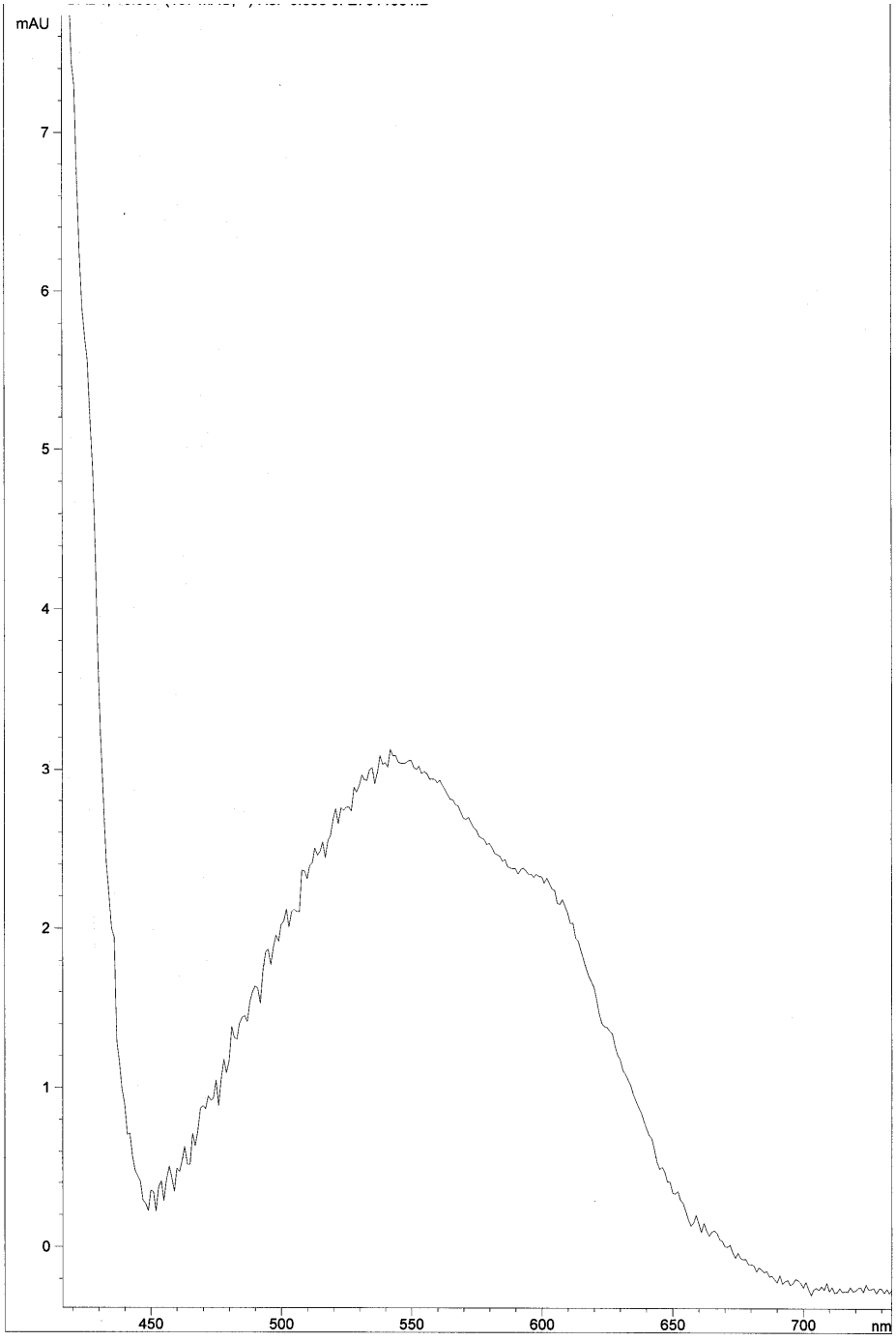

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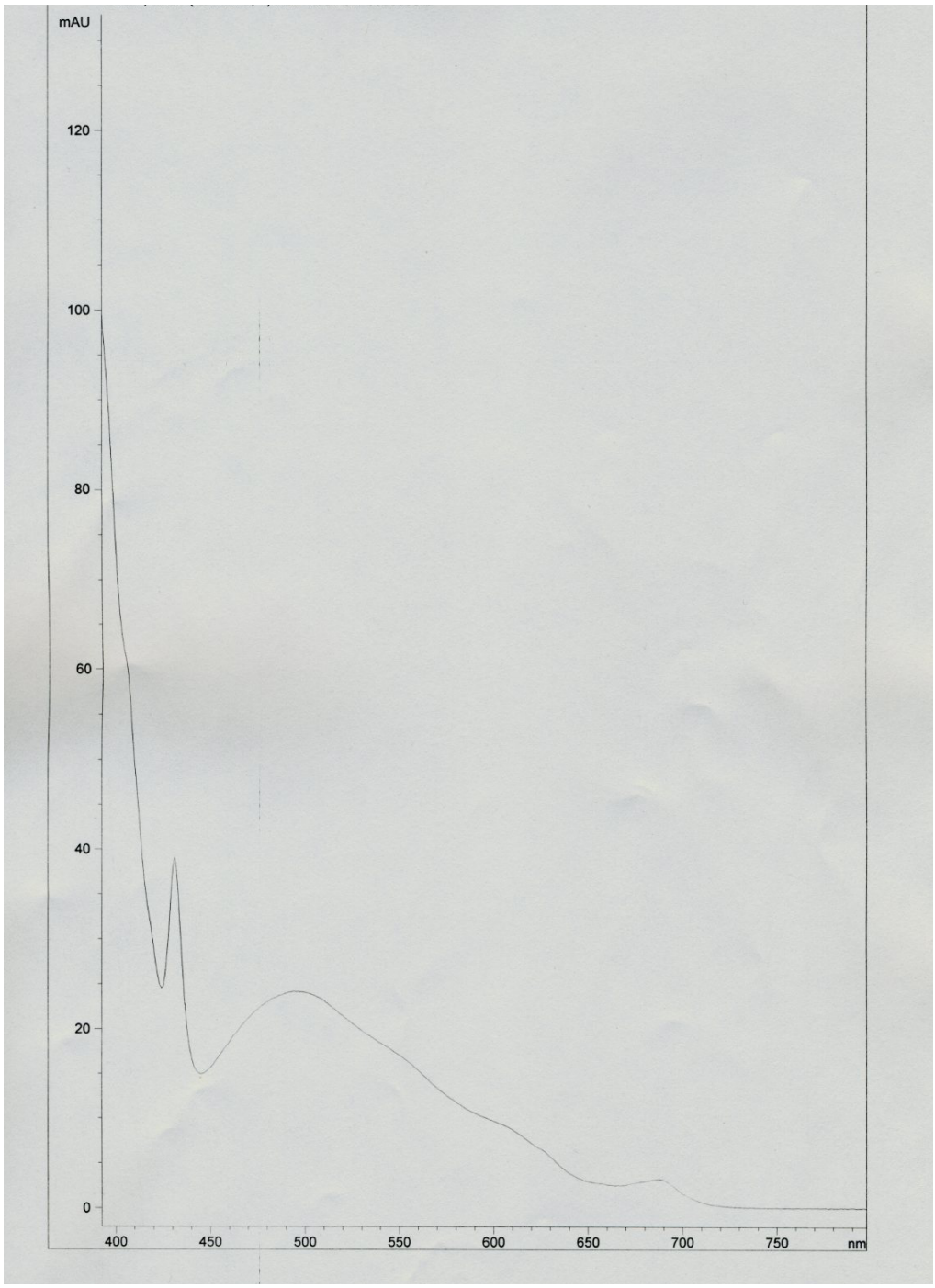

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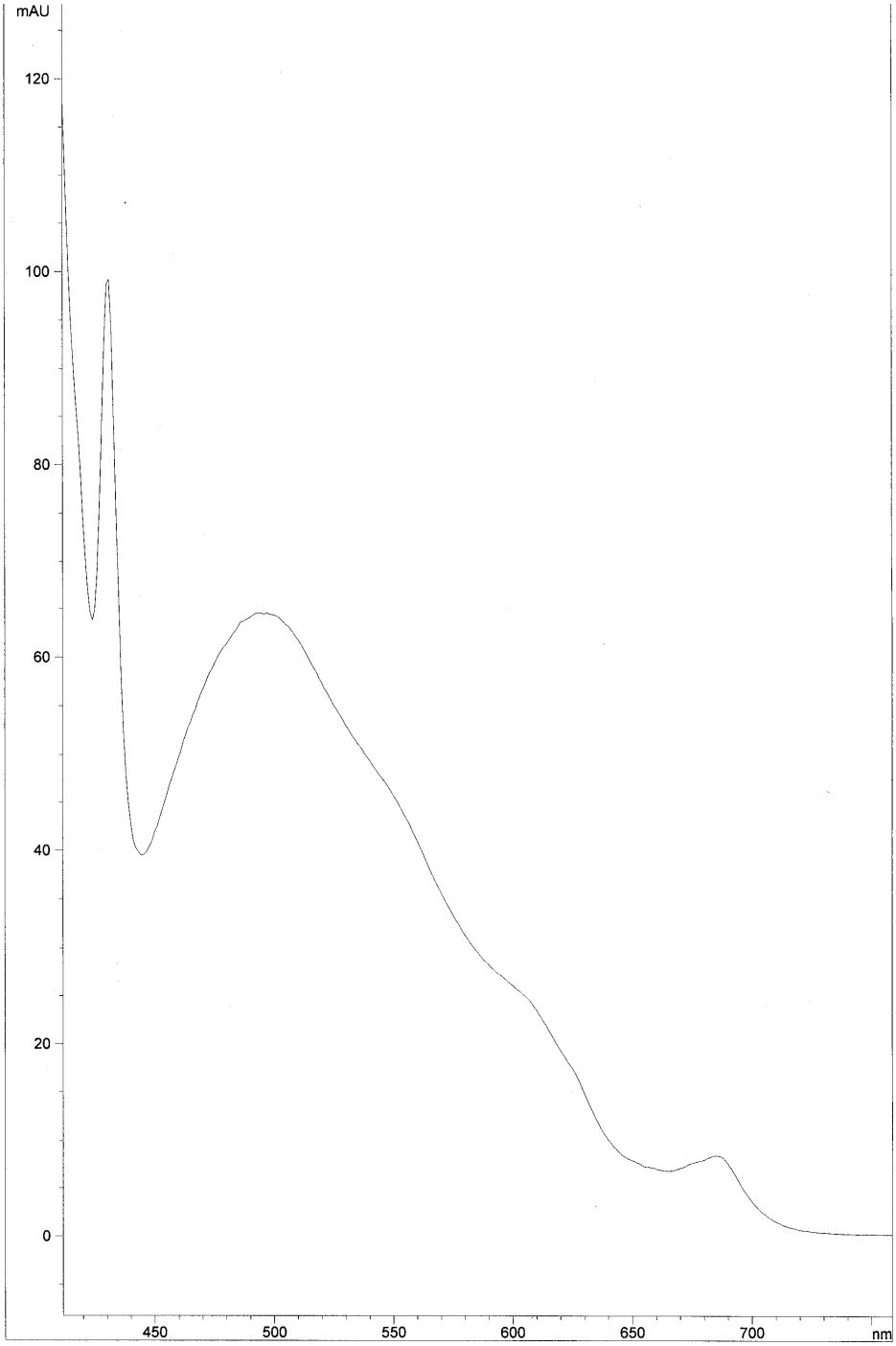

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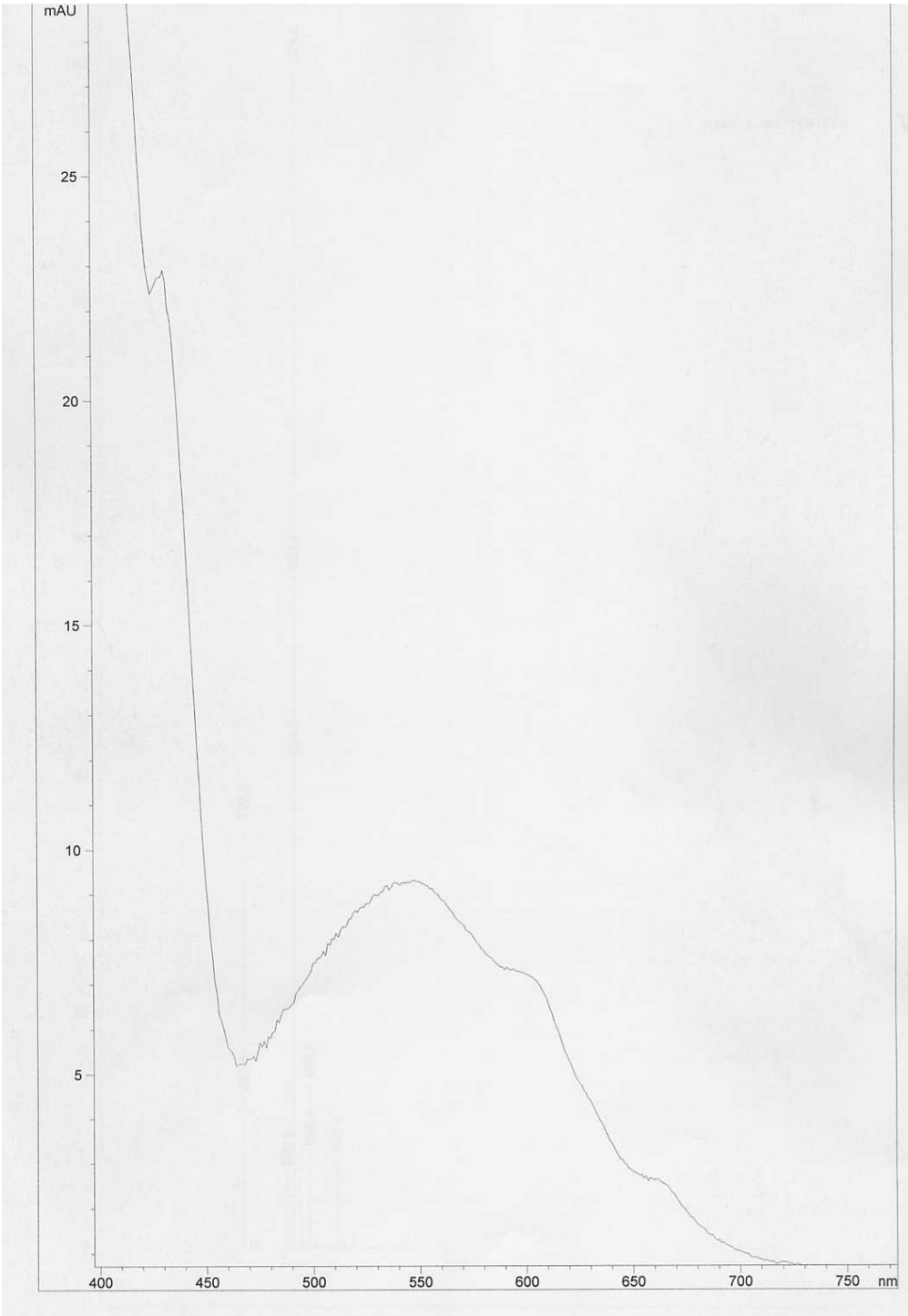

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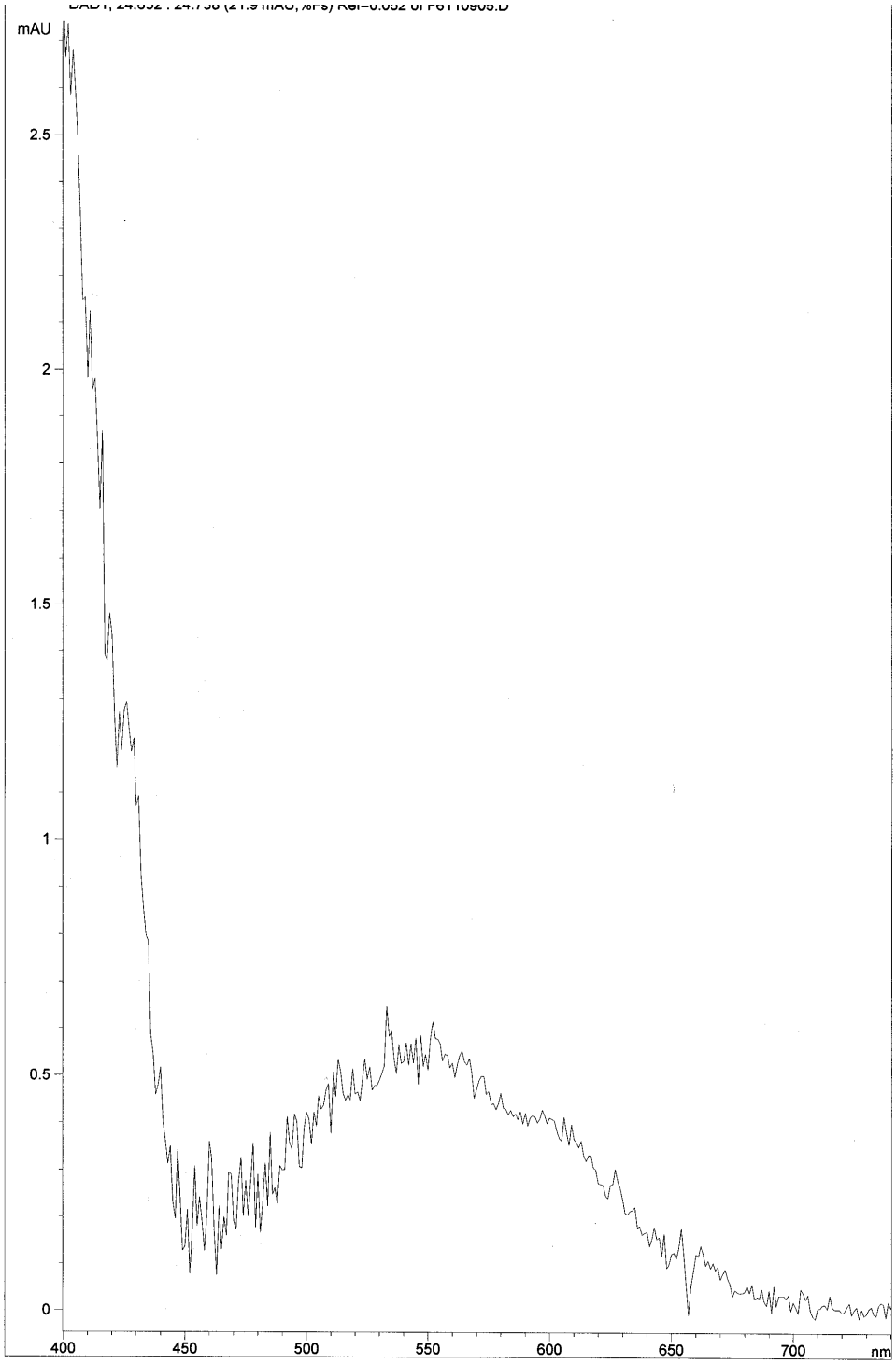

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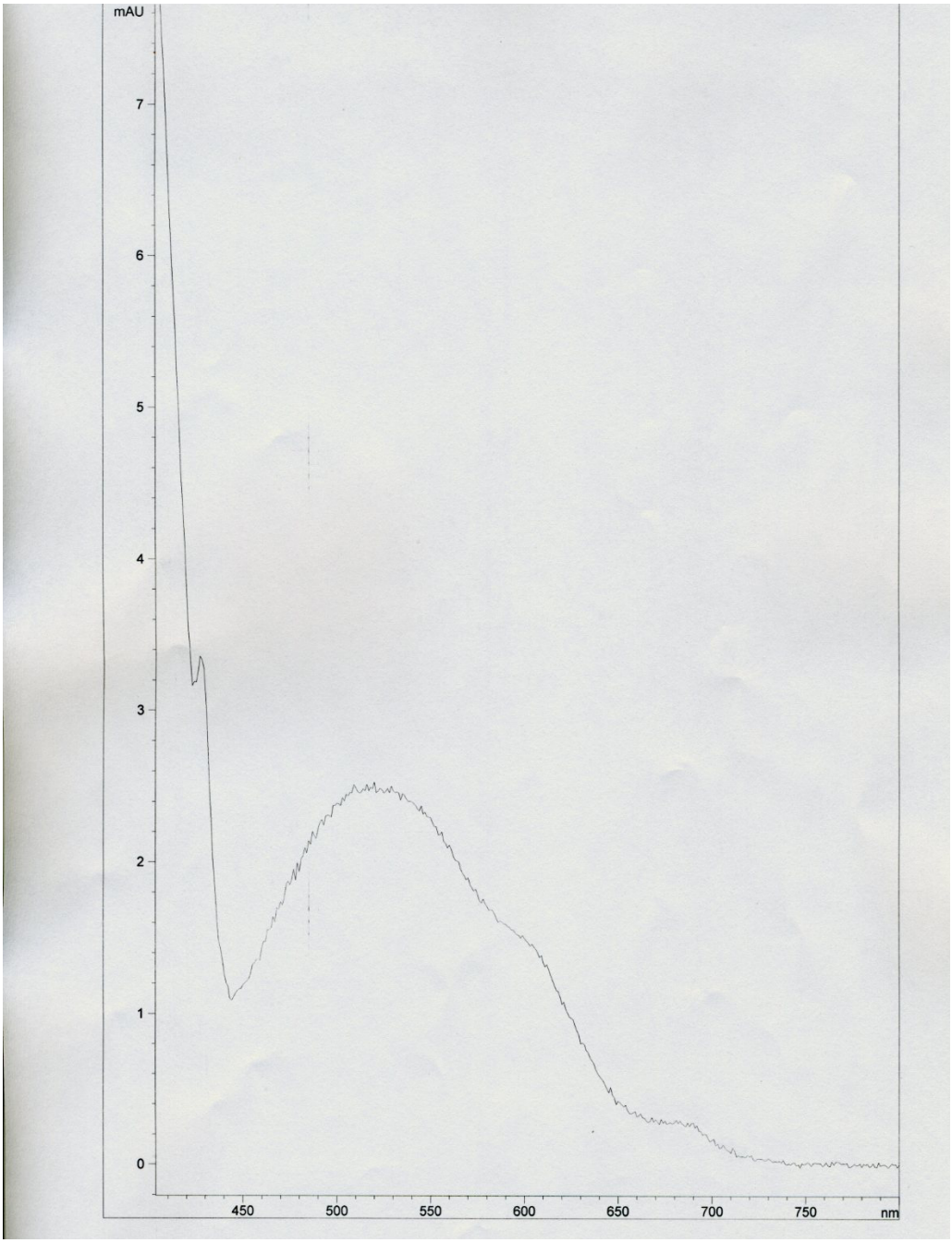

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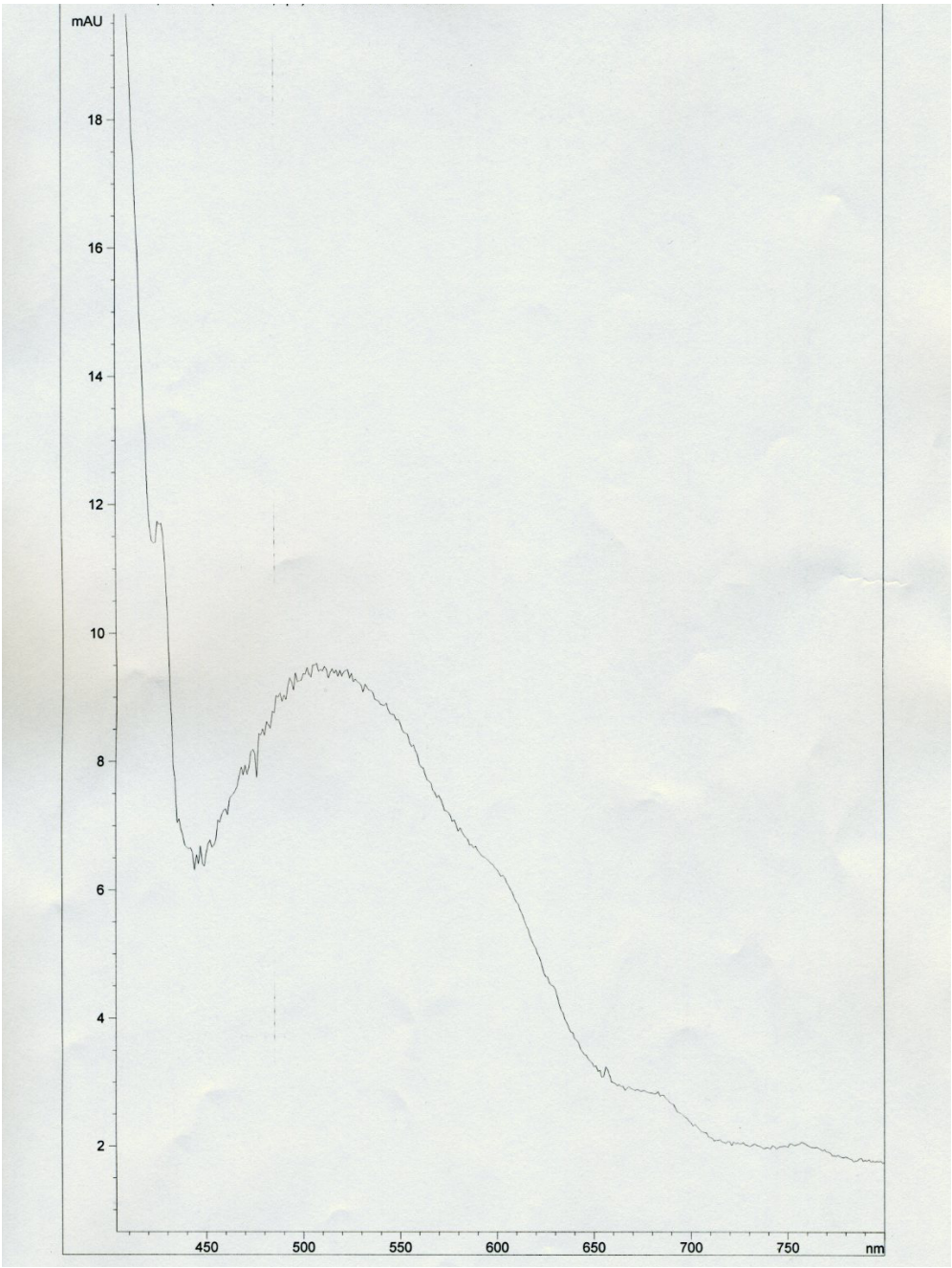

## $^1$H NMR Spectroscopy

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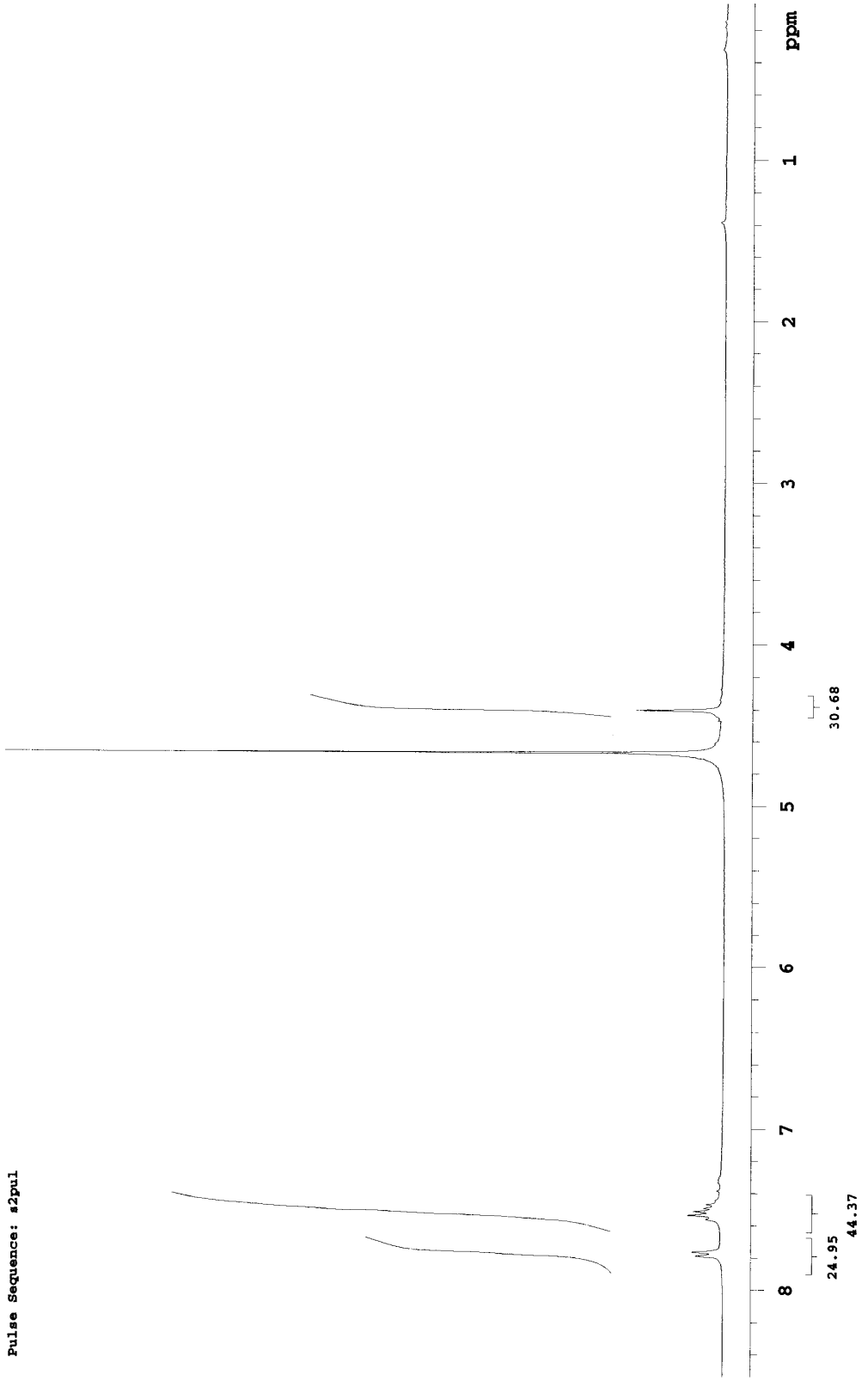

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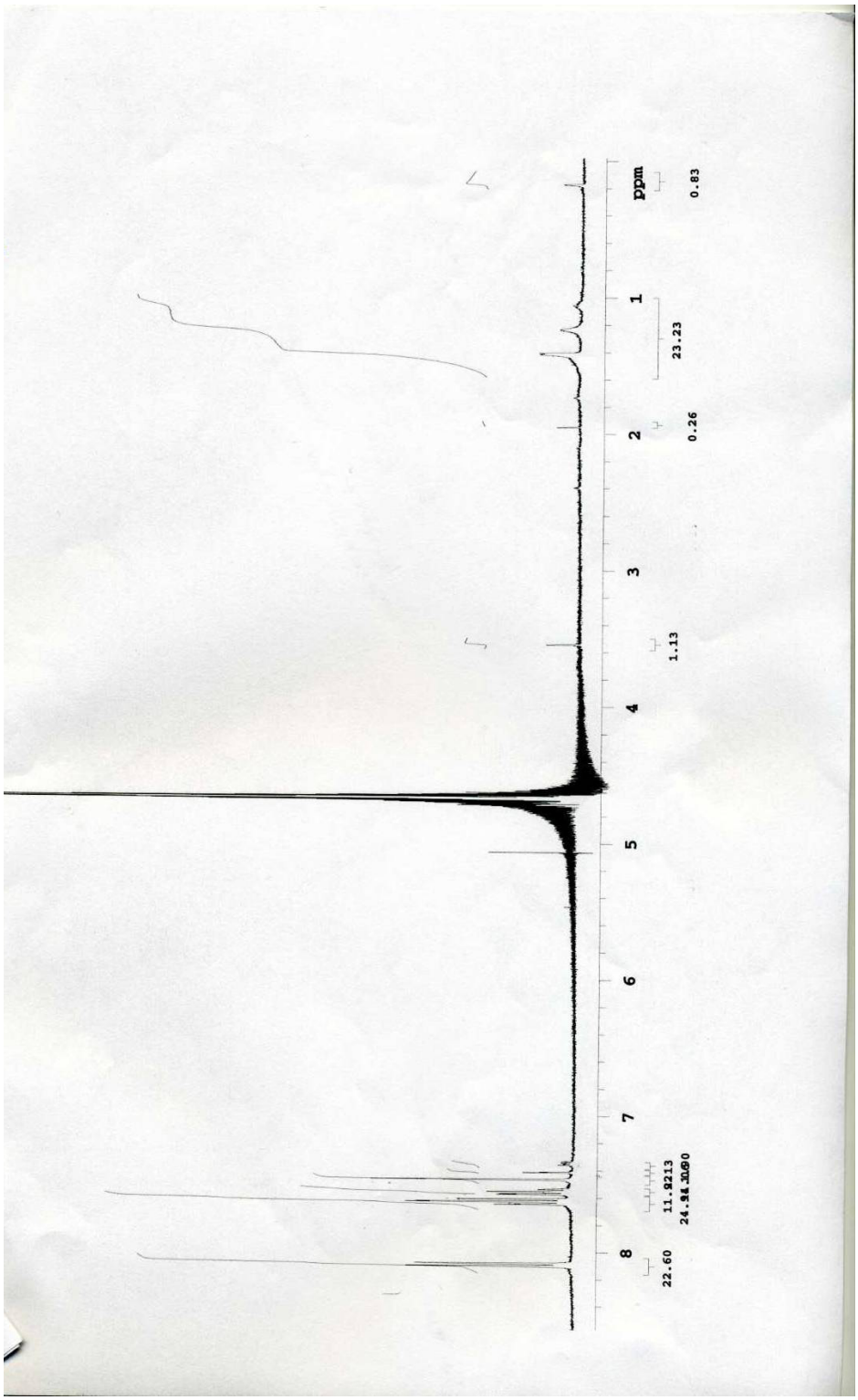

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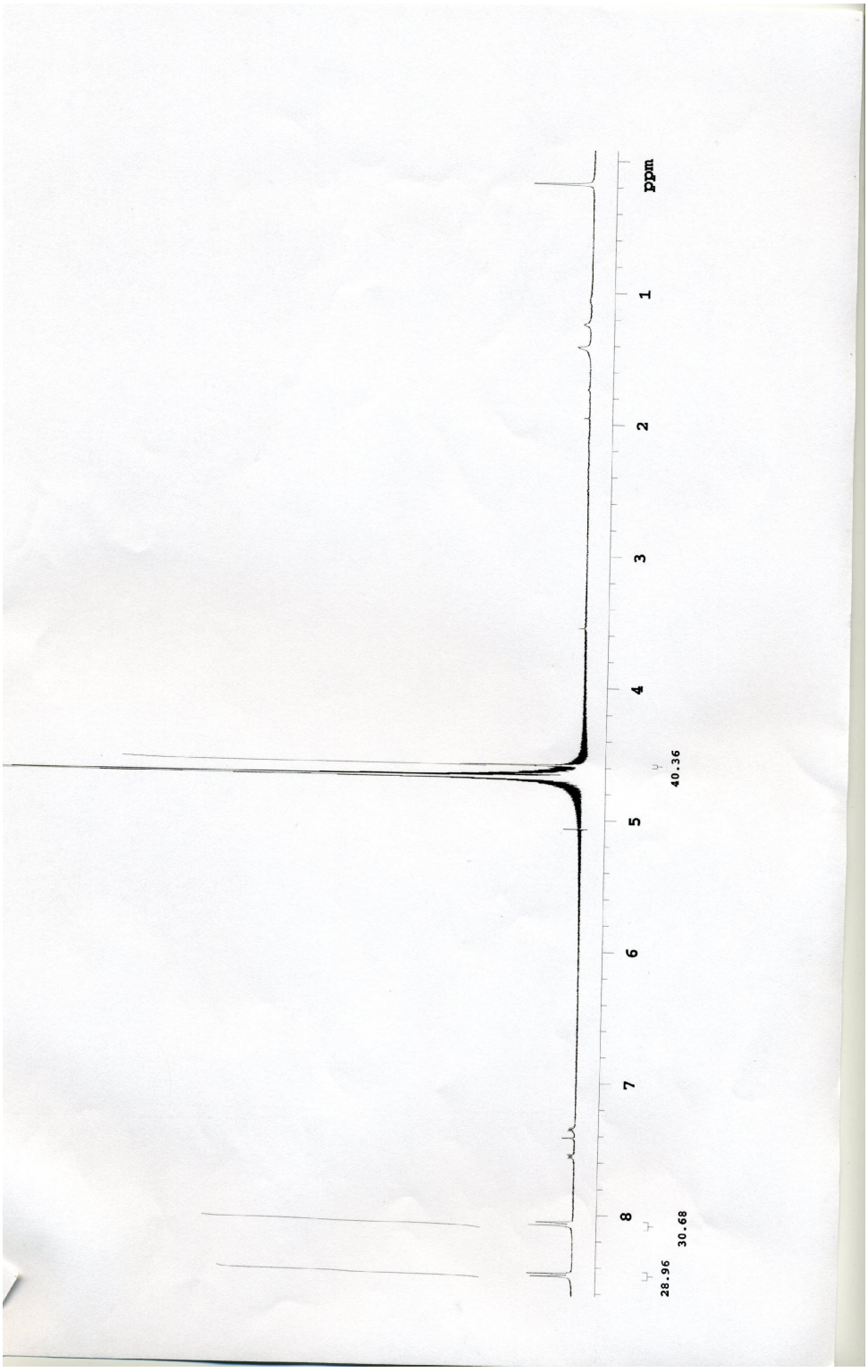

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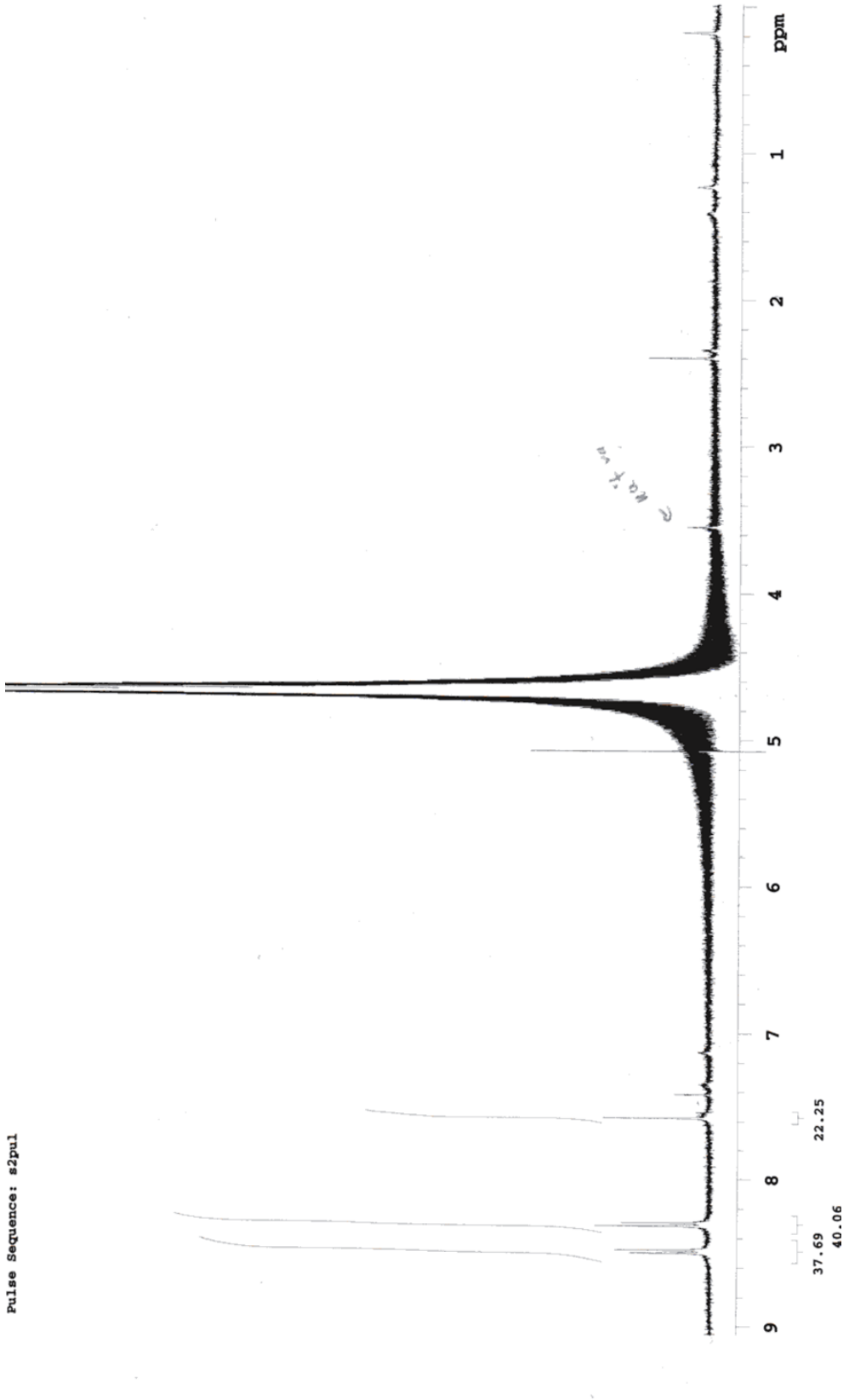

## 13C NMR spectroscopy

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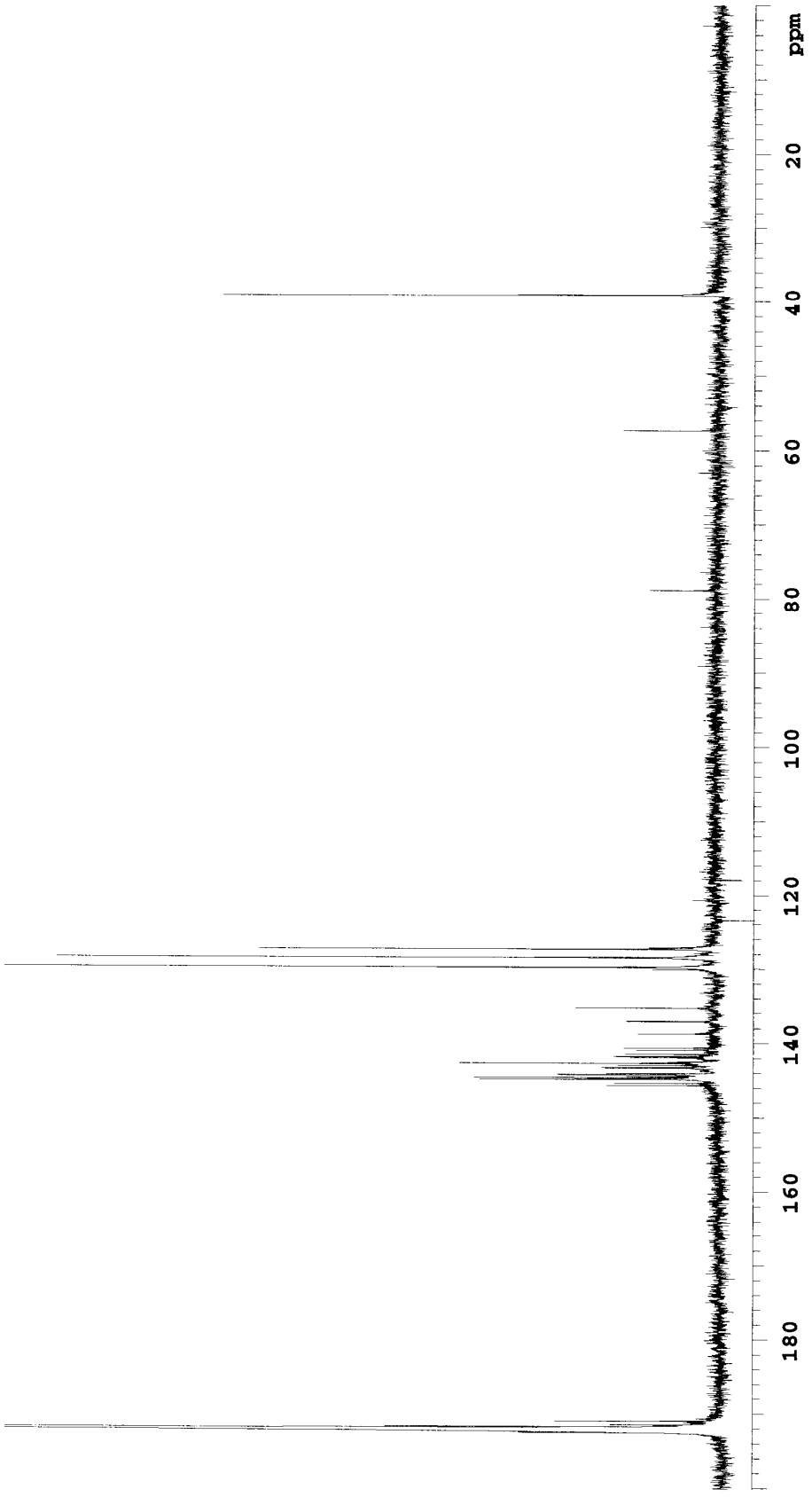

## Mass Spectrometry

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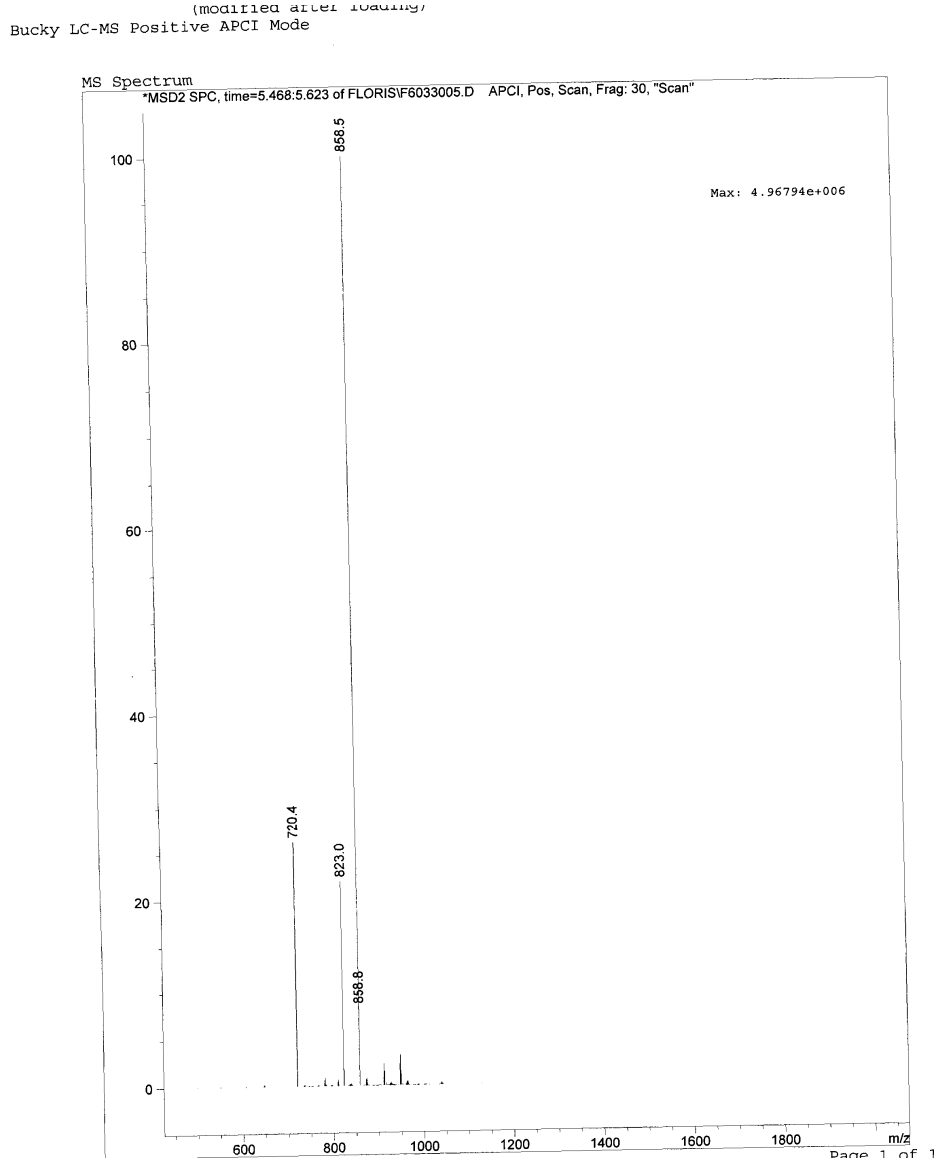

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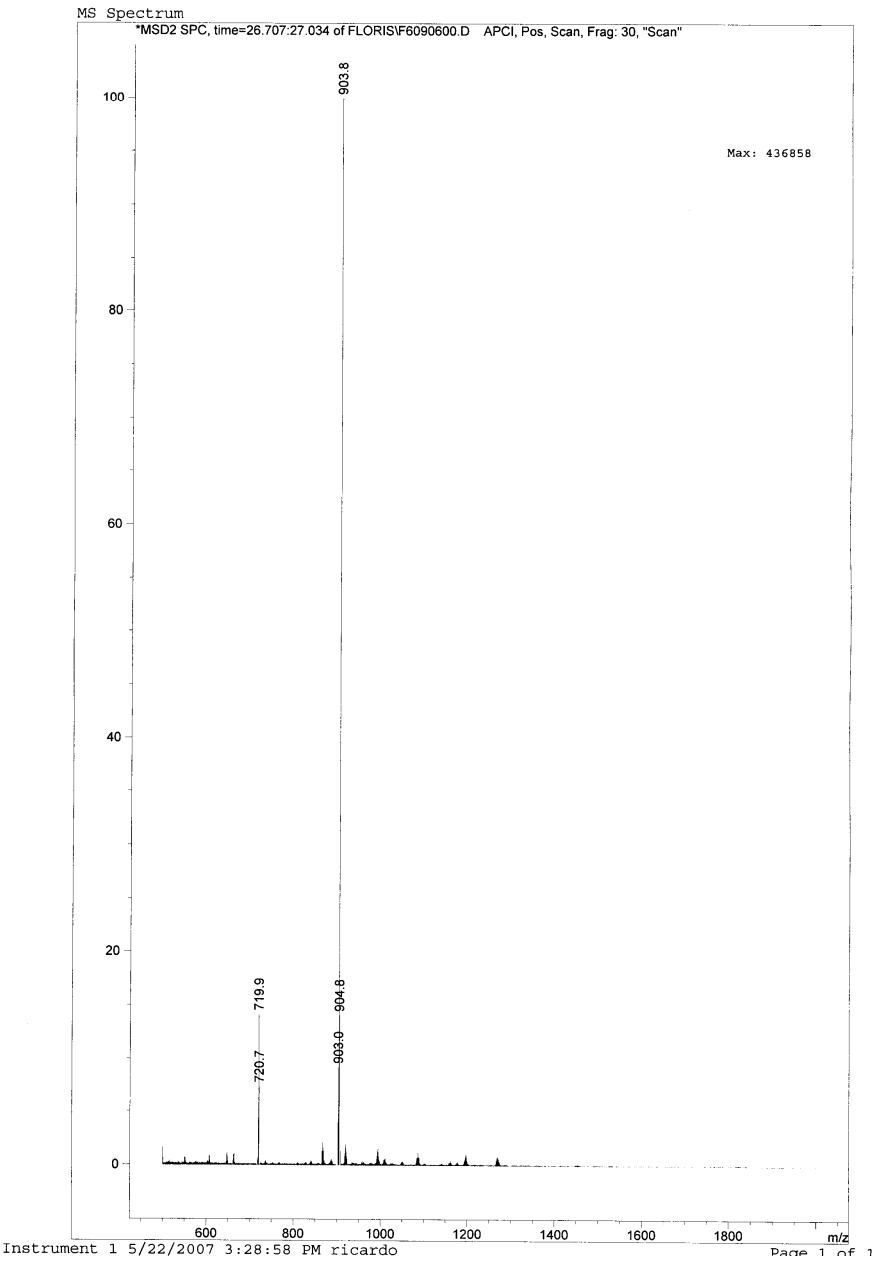
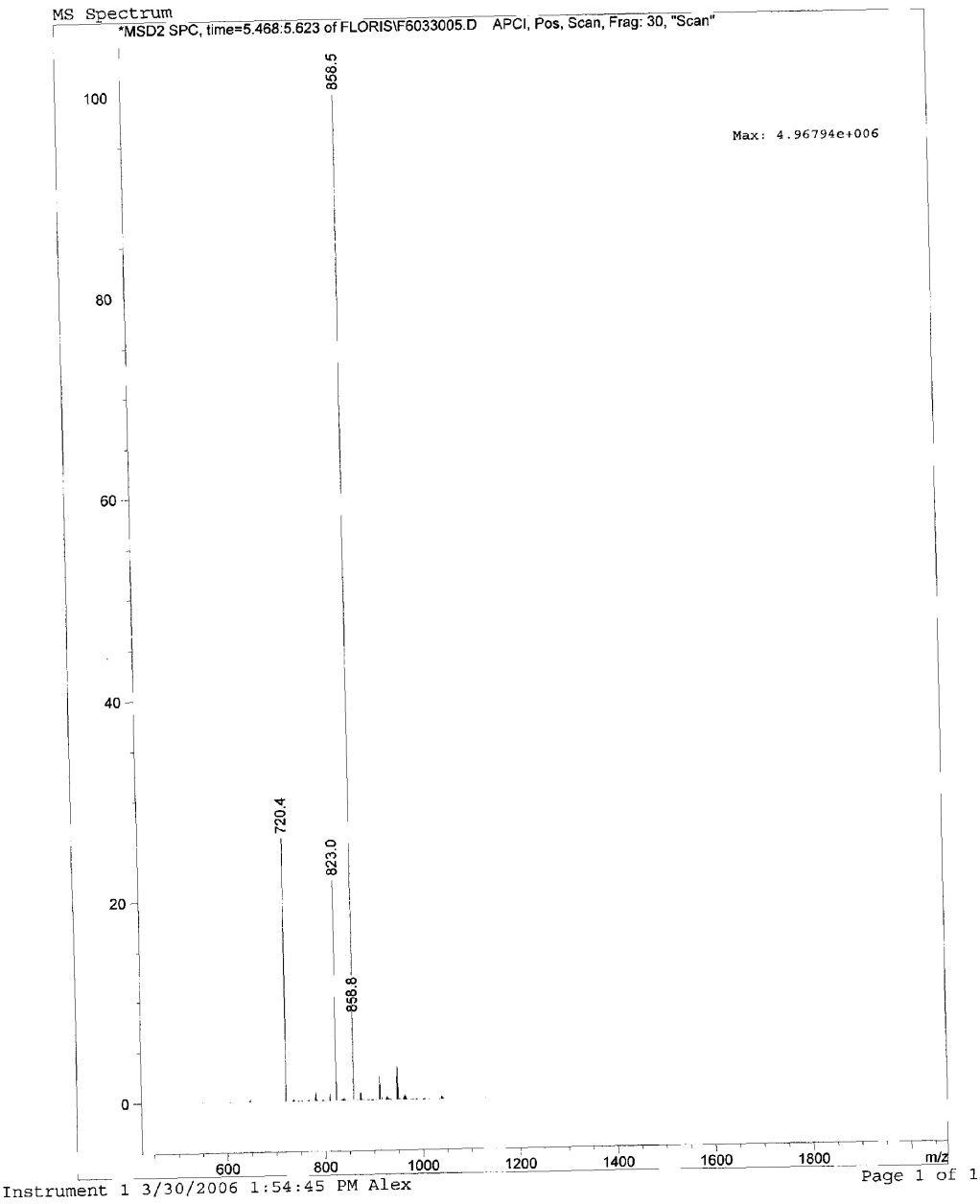


**Compound 6a**

Bucky LC-MS Positive APCI Mode



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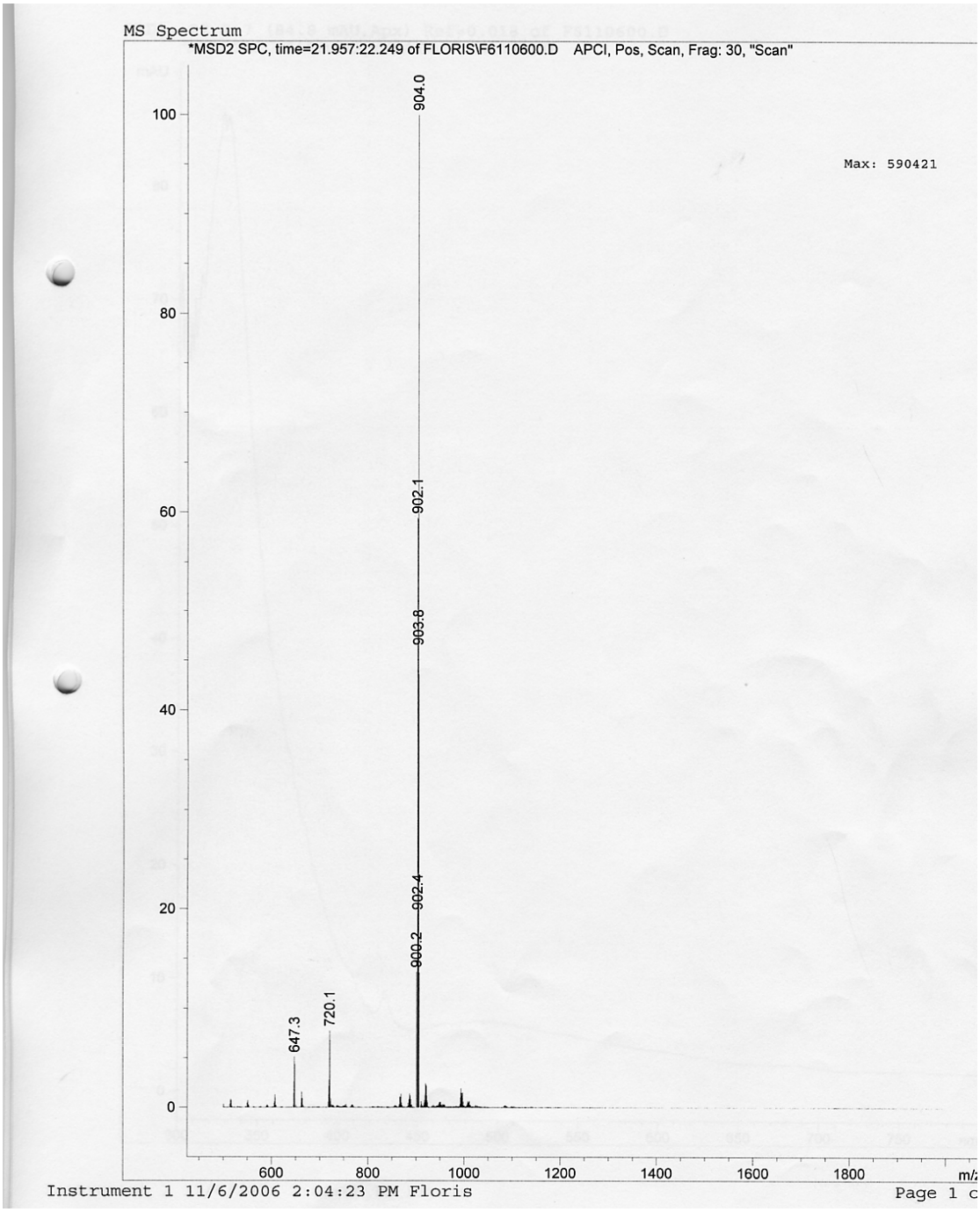
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902.4
900.2
720.1
647.3
100
80
60
40
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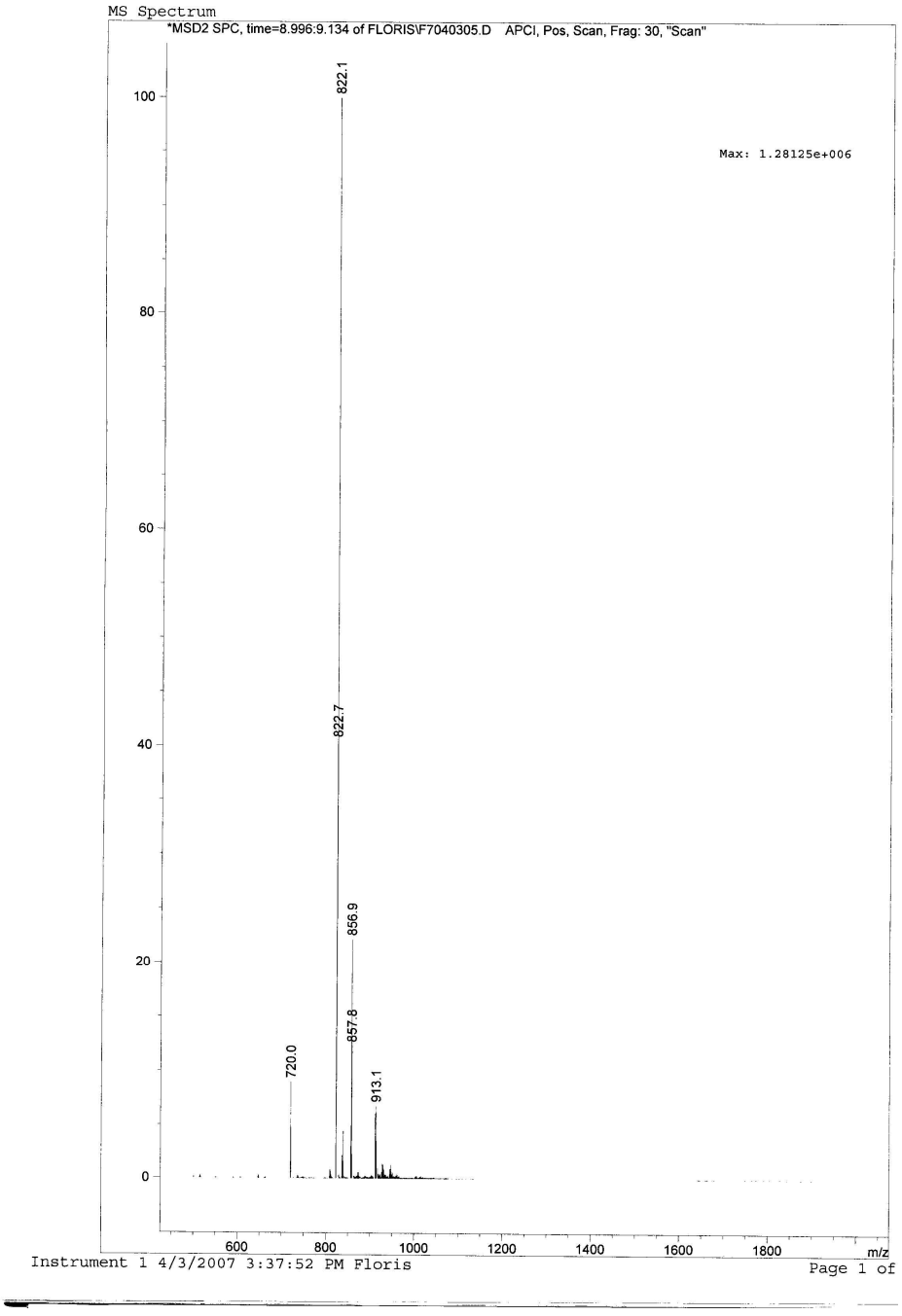
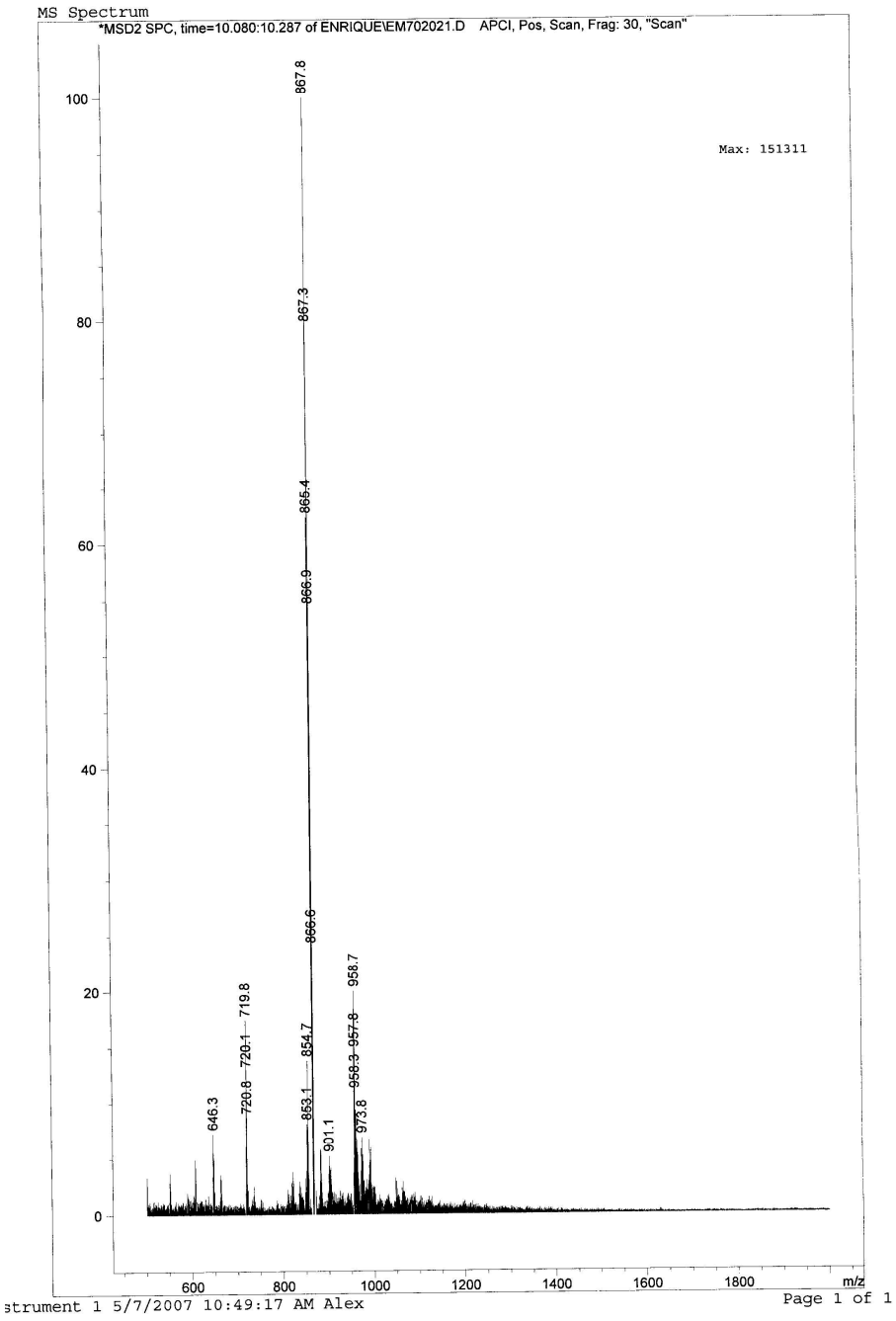
## Compound 7a

of window 80: MS Spectrum



## Compound 7b

of window 80: MS Spectrum



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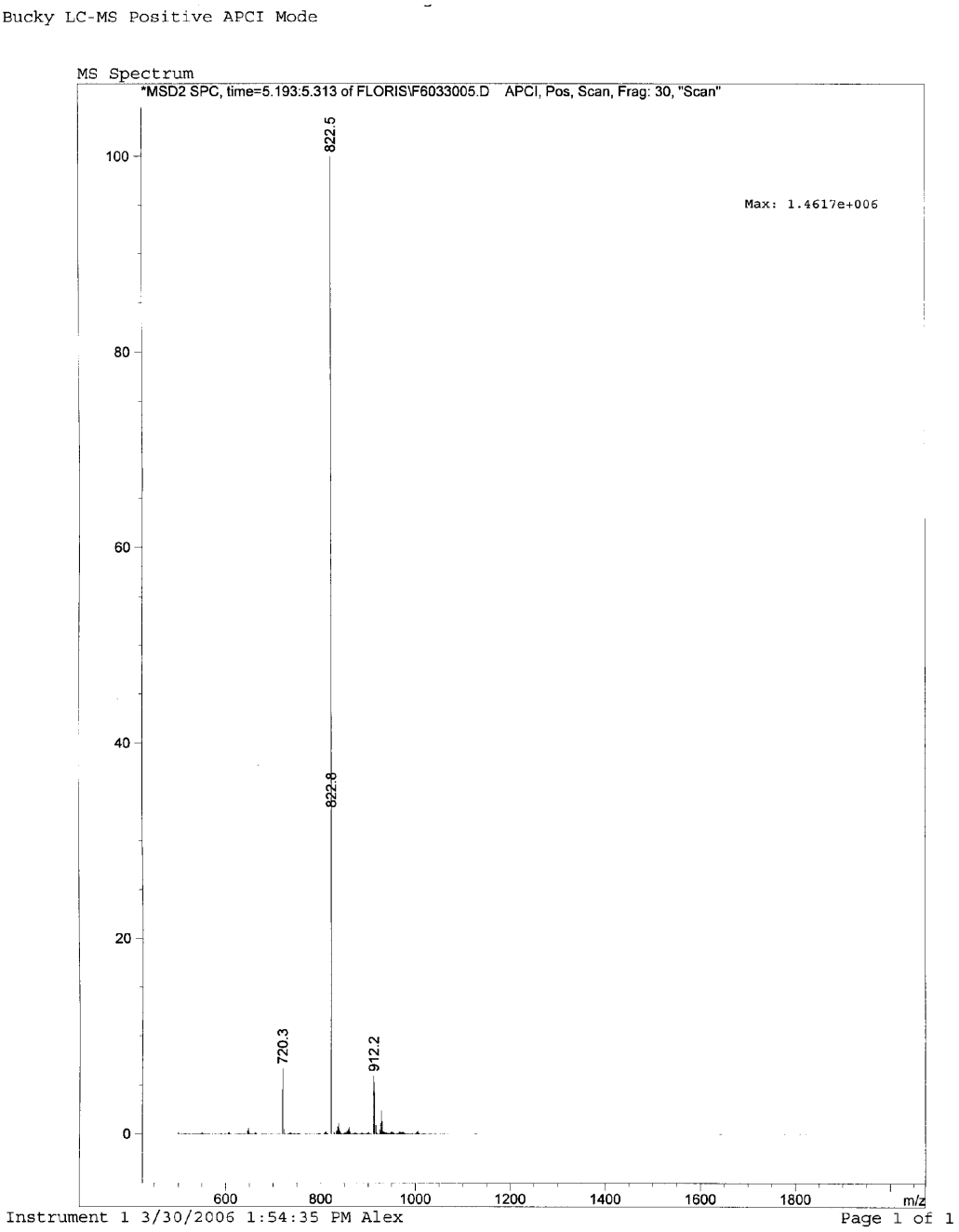
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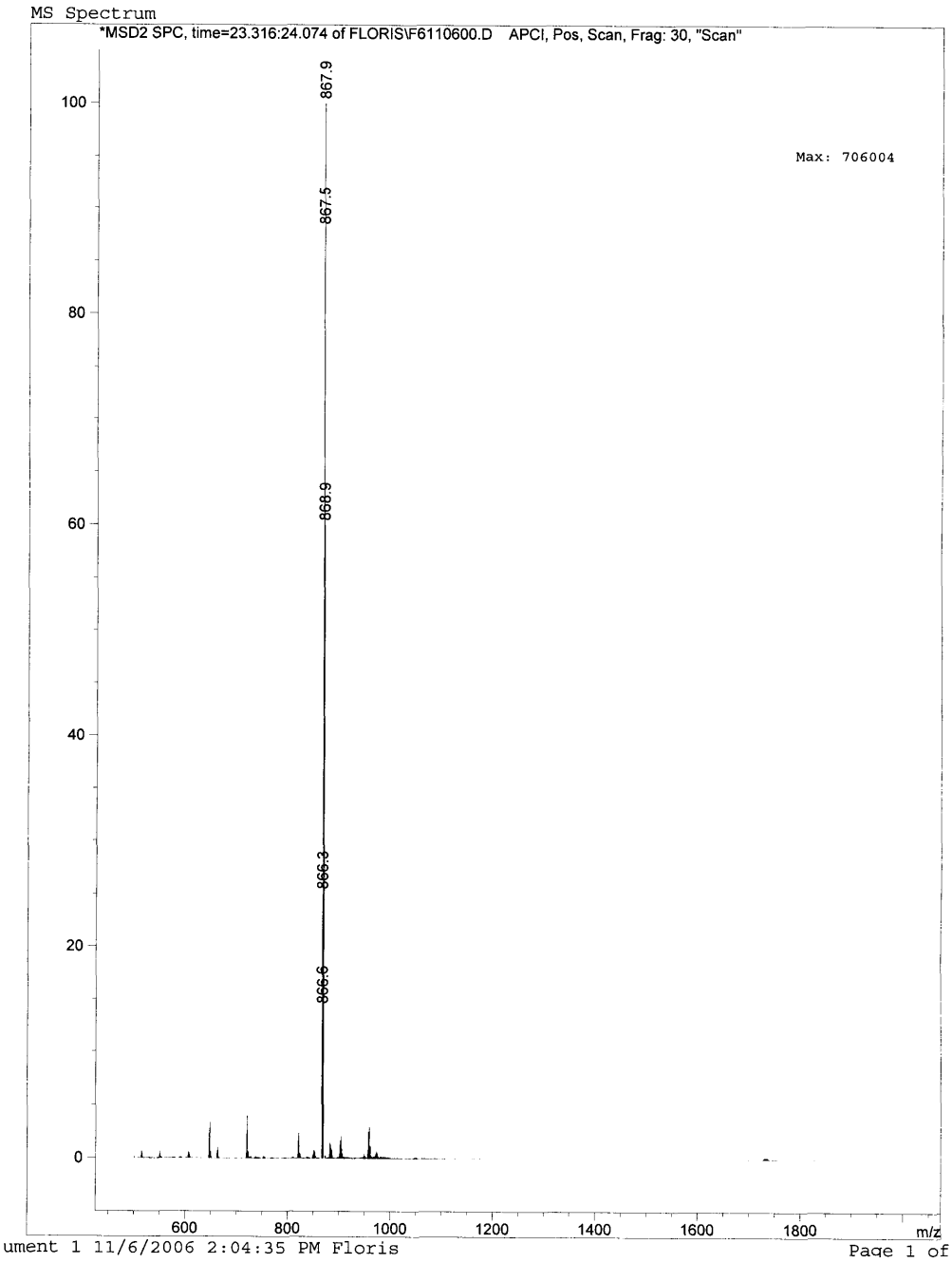
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