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Supplementary Information

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

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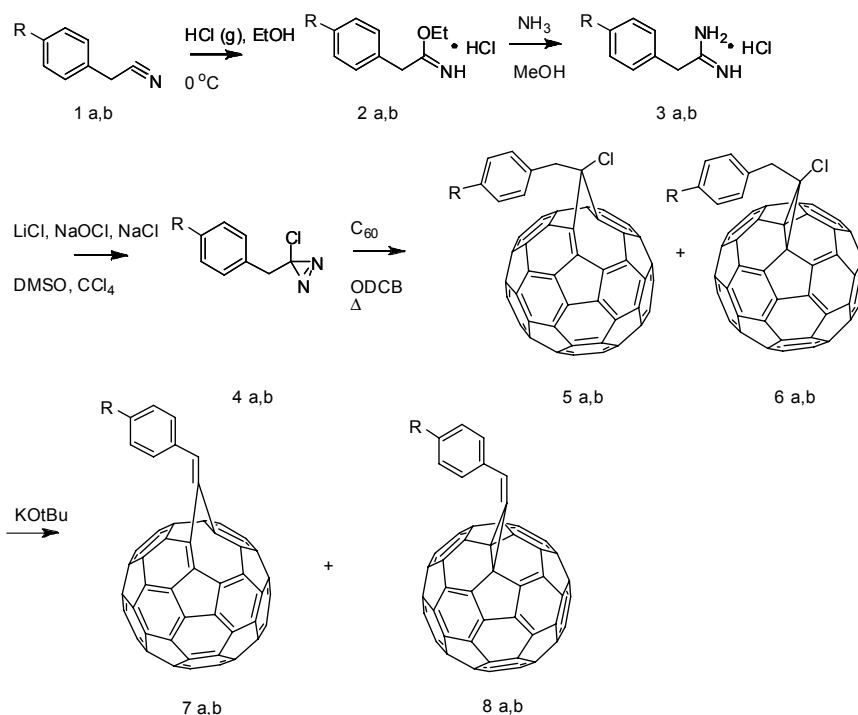


Figure 1: General Synthetic Scheme (a: R=H, b: R=NO₂)

General Procedure for Diazirine addition:

A flame-dried three-necked flask equipped with thermometer, condenser, 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 $60\text{ }^\circ\text{C}$. 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 C₆₈H₇Cl: 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 C₆₈H₆ClNO₂: 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). ¹H NMR (CS₂ with D₂O insert, 300 MHz); δ (ppm): 7.78 (d, *J* = 6.9 Hz, 2H), 7.47–7.7.56 (m, 3H), 4.67 (s, 2H). ¹³C NMR (D₂O/CS₂, 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 C₆₈H₇Cl: 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). ¹H NMR (CS₂ with D₂O 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 C₆₈H₆ClNO₂: 903.01. Found: 903.3.

Benzylidenehomofullerene 7a: UV/Vis (toluene/cyclohexane 1:1); λ (nm): 548, 603, 664. Mass m/z calcd. for C₆₈H₆: 822.04. Found: 822.7.

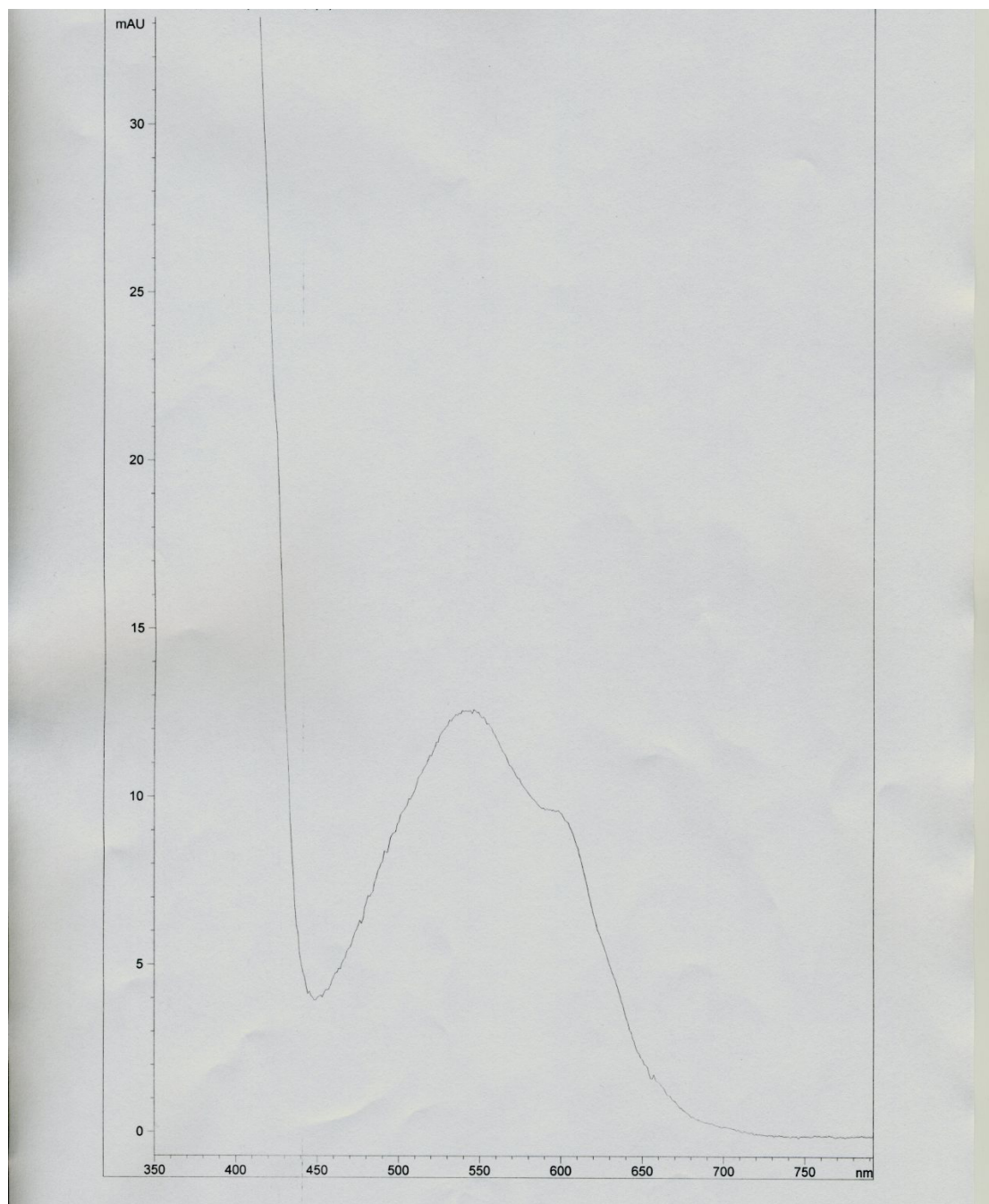
p-Nitrobenzylidenehomofullerene 7b: UV/Vis (toluene/cyclohexane 1:1); λ (nm): 547. Mass m/z calcd. for C₆₈H₅NO₂: 867.03. Found: 867.8.

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). ¹H NMR (CS₂ with D₂O 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 C₆₈H₆: 822.04. Found: 822.7.

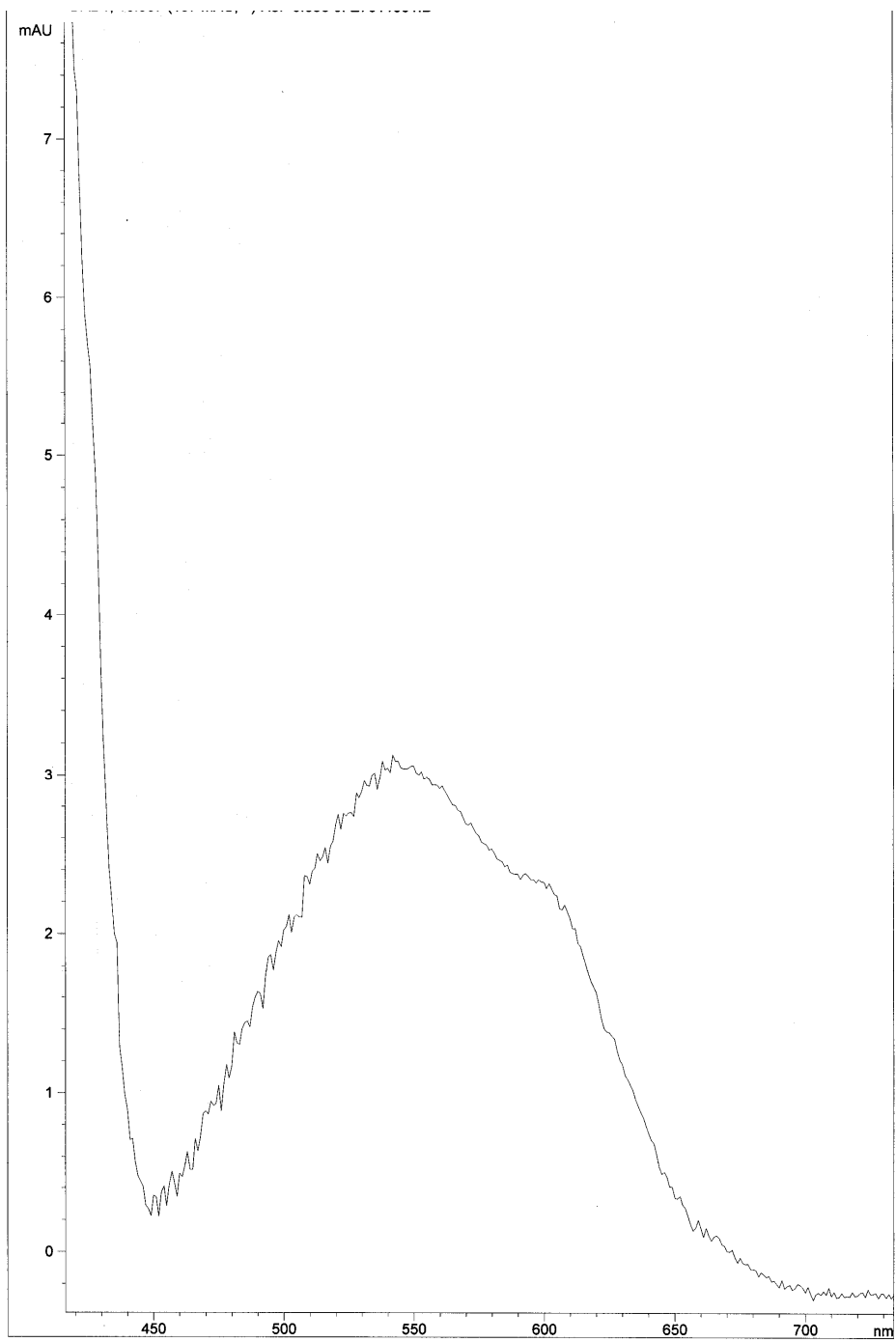
p-Nitrobenzylidenecyclopropafullerene 8b: IR (KBr) = ν (cm⁻¹): 3446 (s), 1597 (m), 1516 (s), 1429 (m), 1340 (s), 1109 (m), 526 (s). ¹H NMR (CS₂ with D₂O insert, 400 MHz); δ (ppm): 8.49 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 2H), 7.58 (s, 1H). UV/Vis (toluene/cyclohexane 1:1); λ (nm): 511. Mass m/z calcd. for C₆₈H₅NO₂: 867.03. Found: 867.7.

UV/VIS spectroscopy

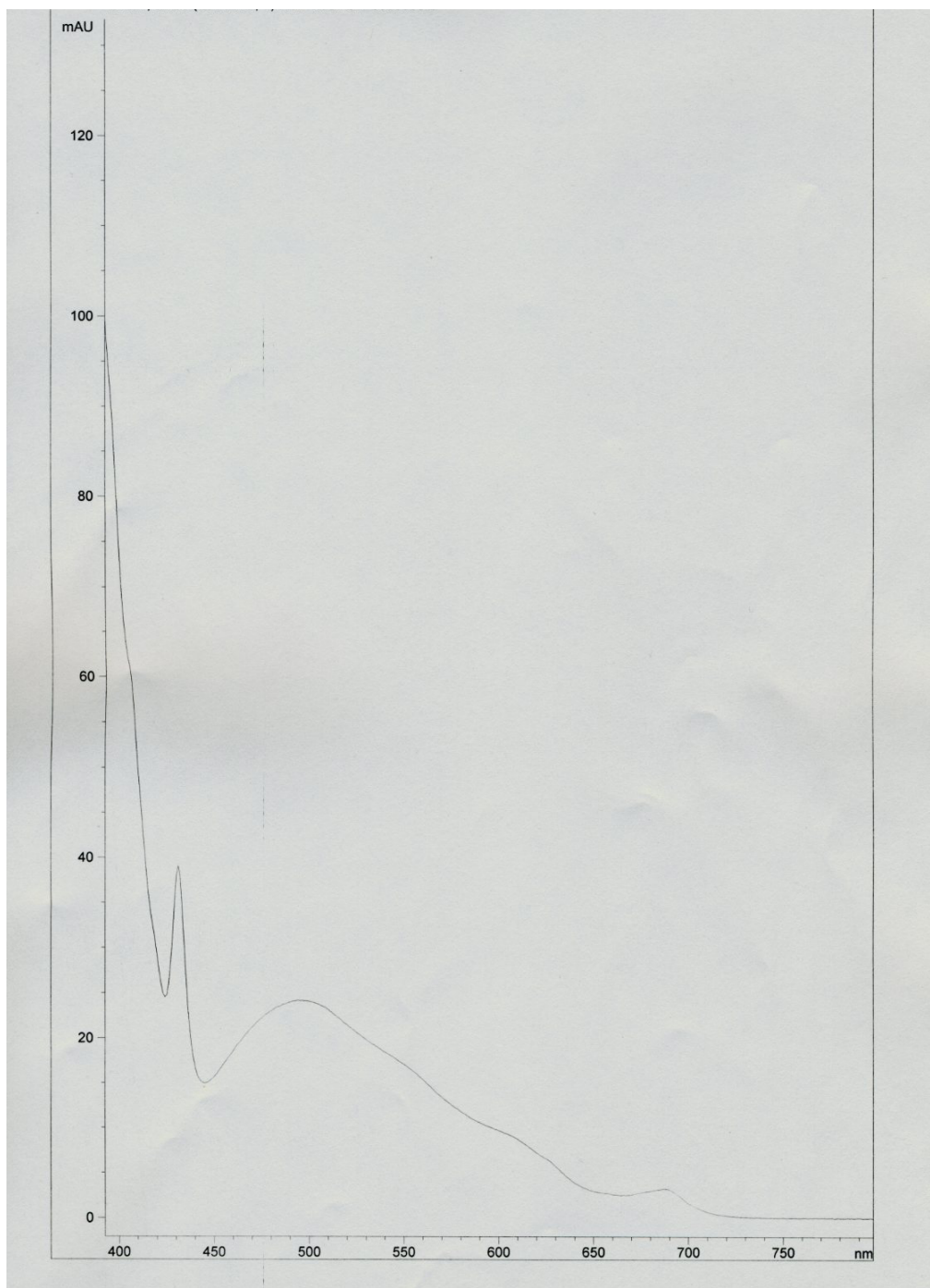
Compound 5a



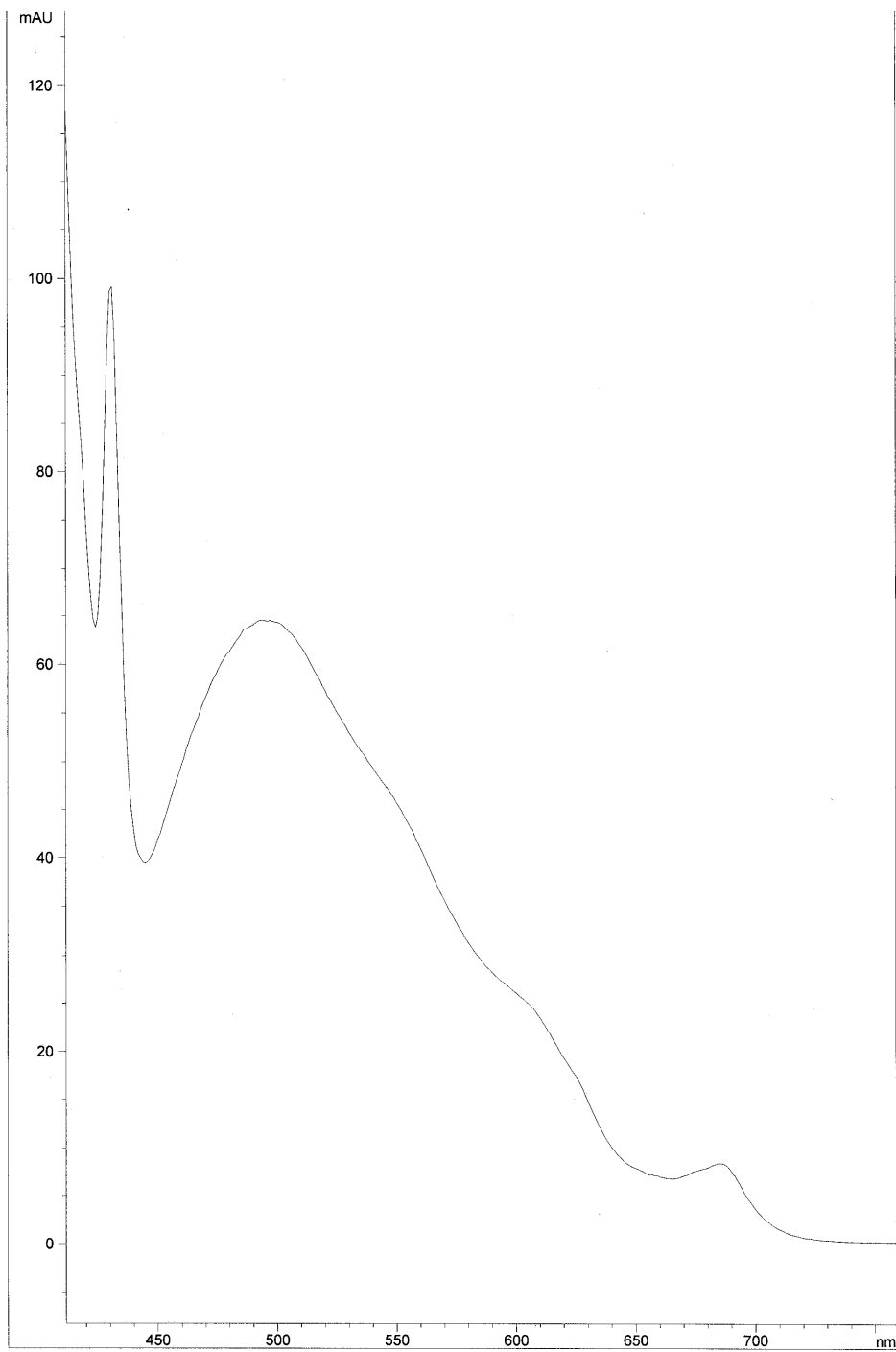
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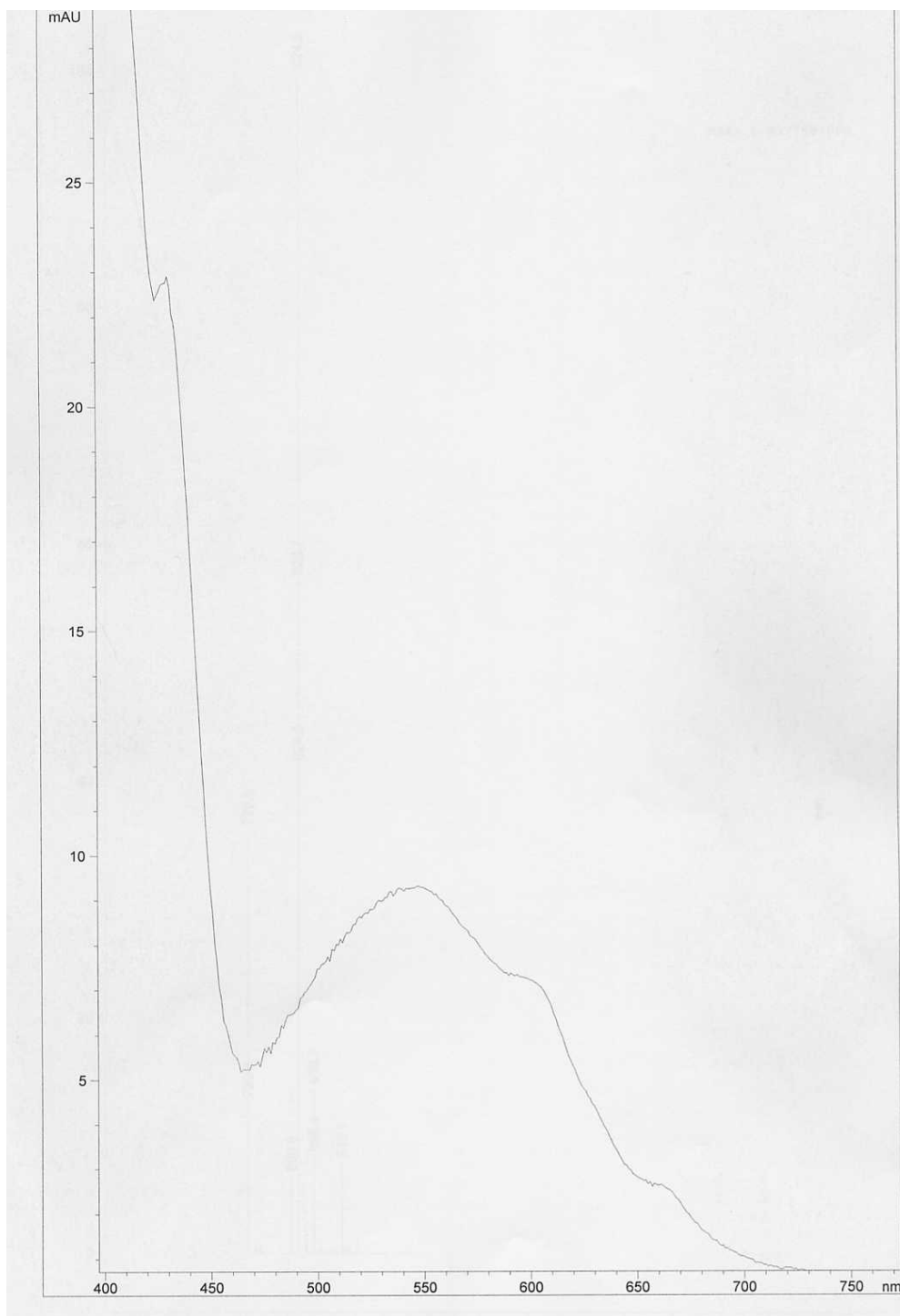
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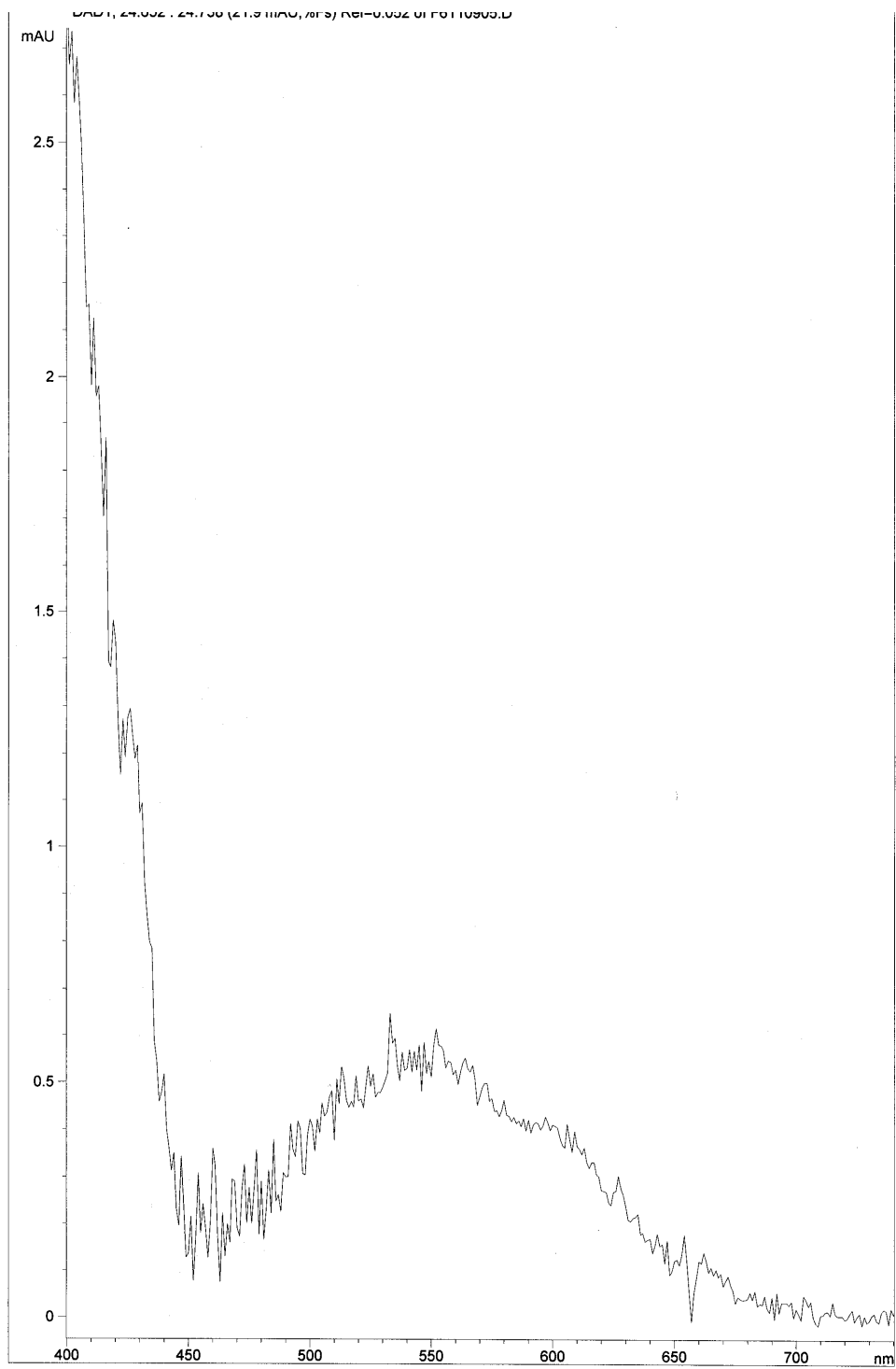
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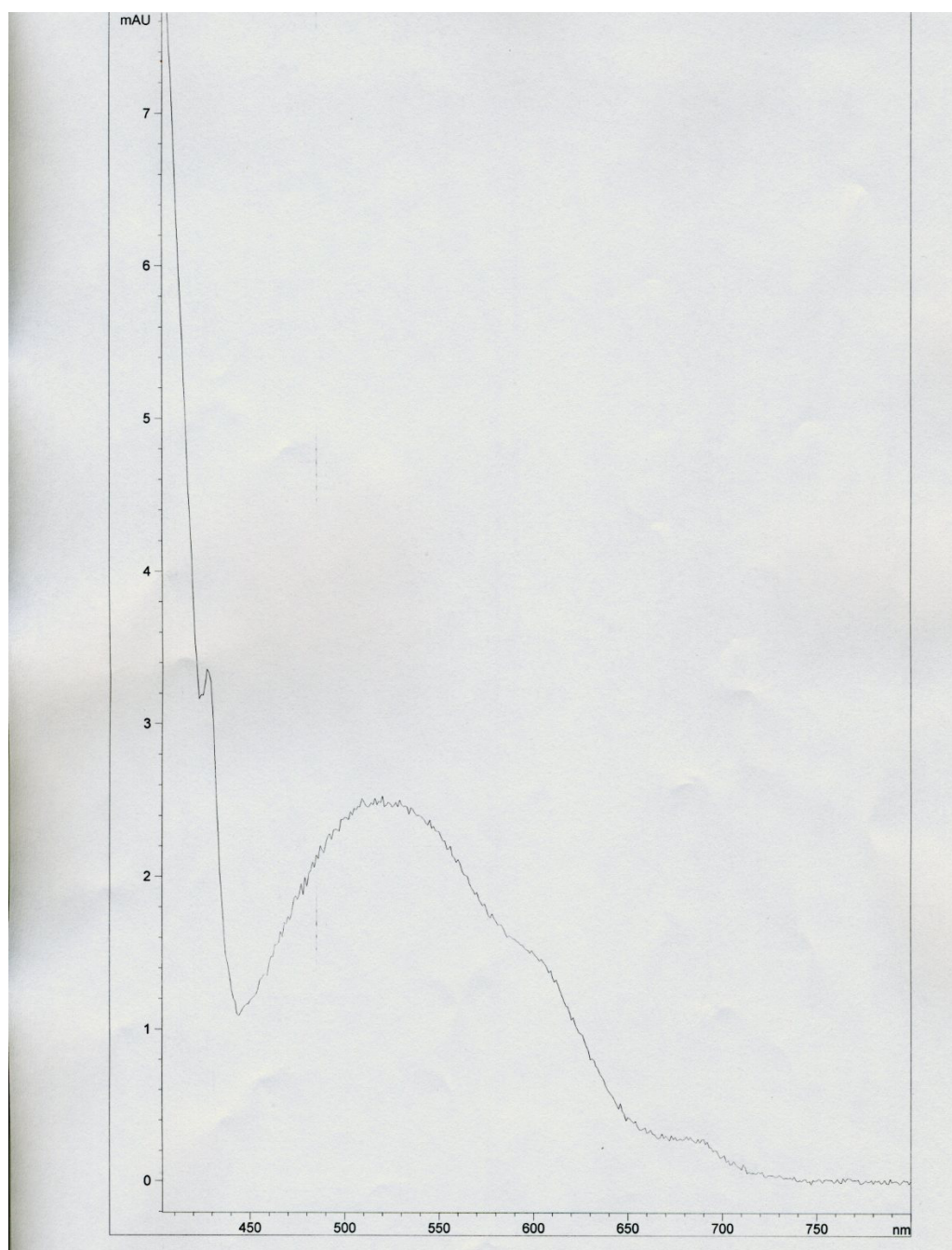
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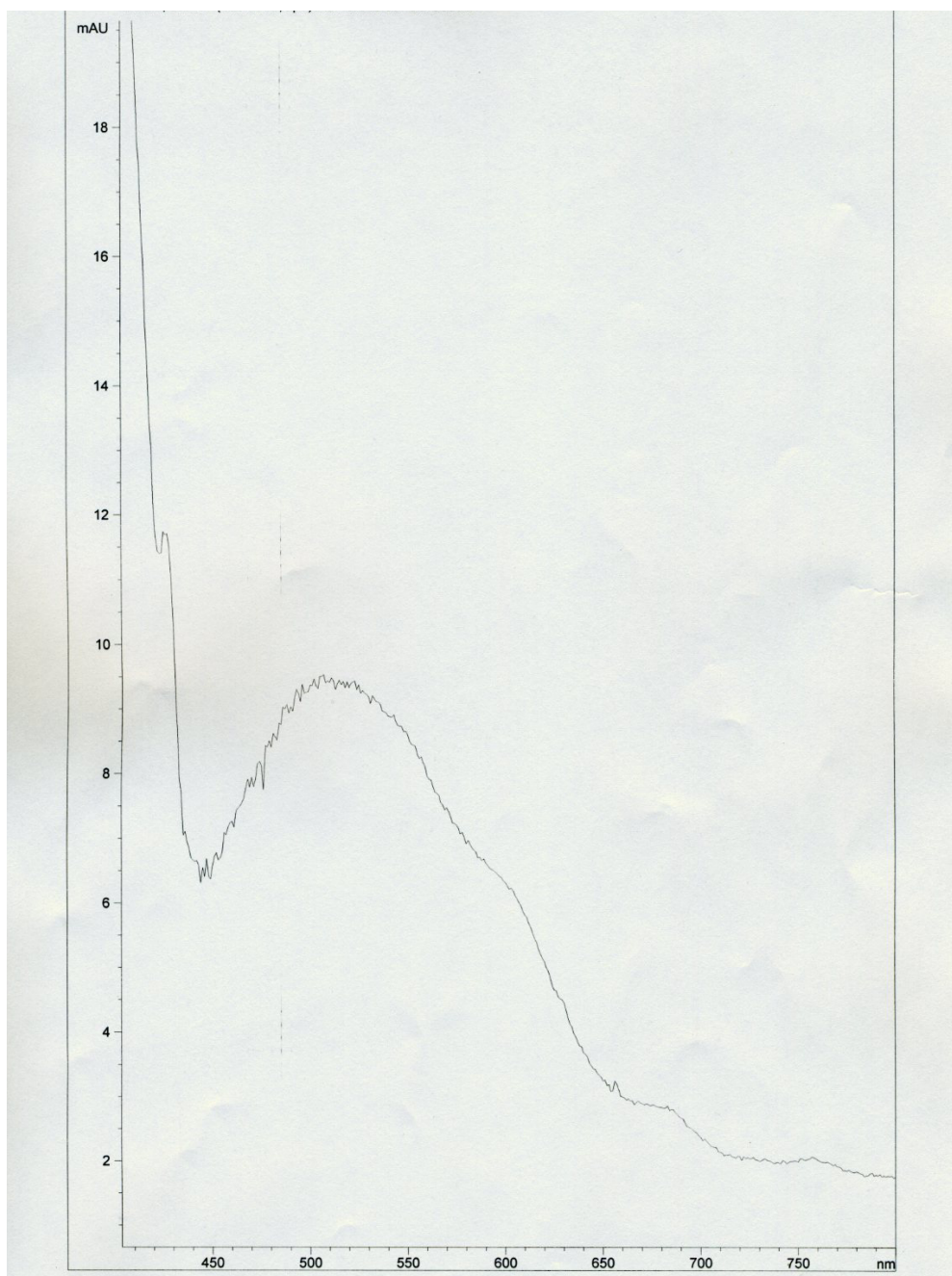
Compound 7b



Compound 8a

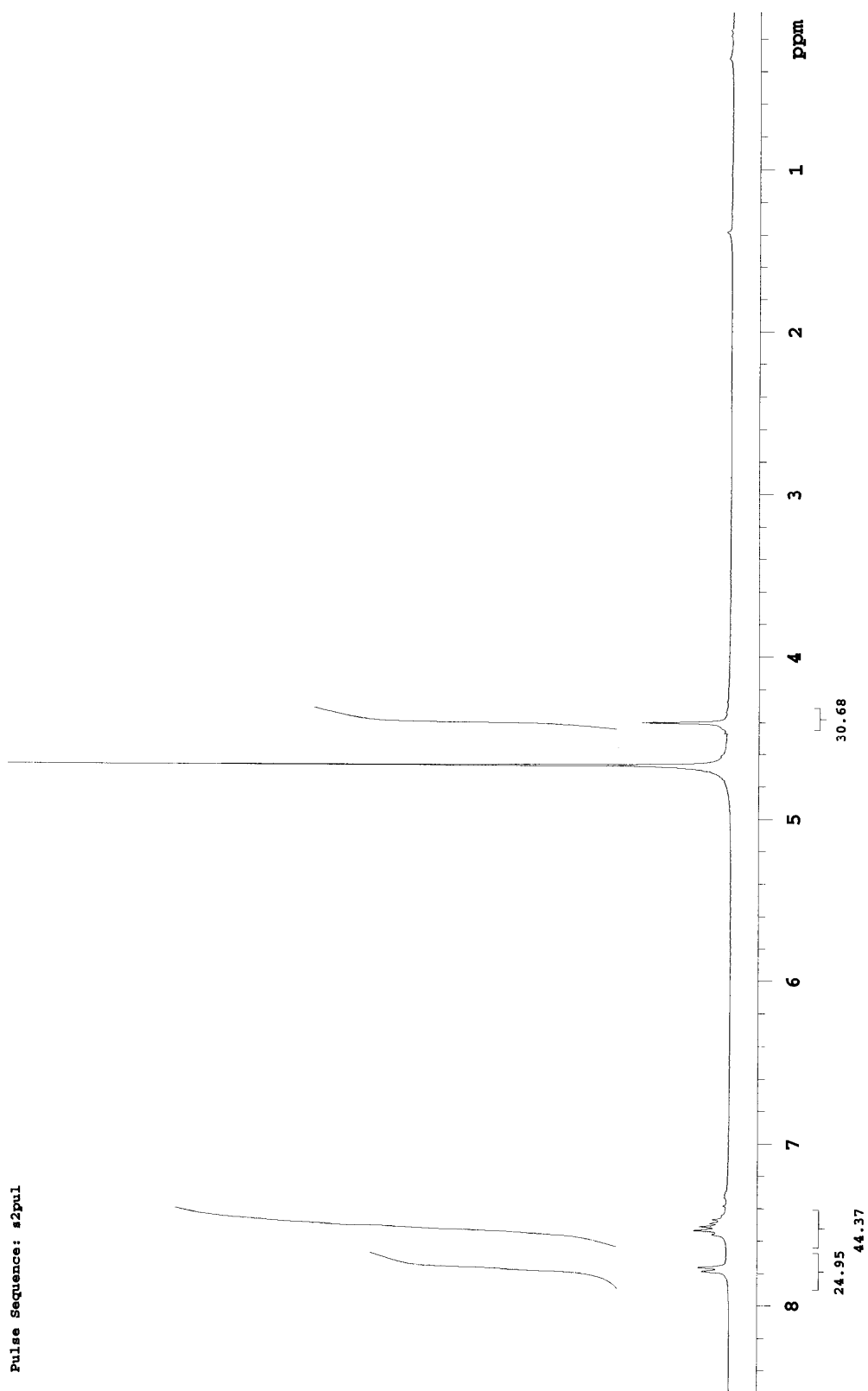


Compound 8b

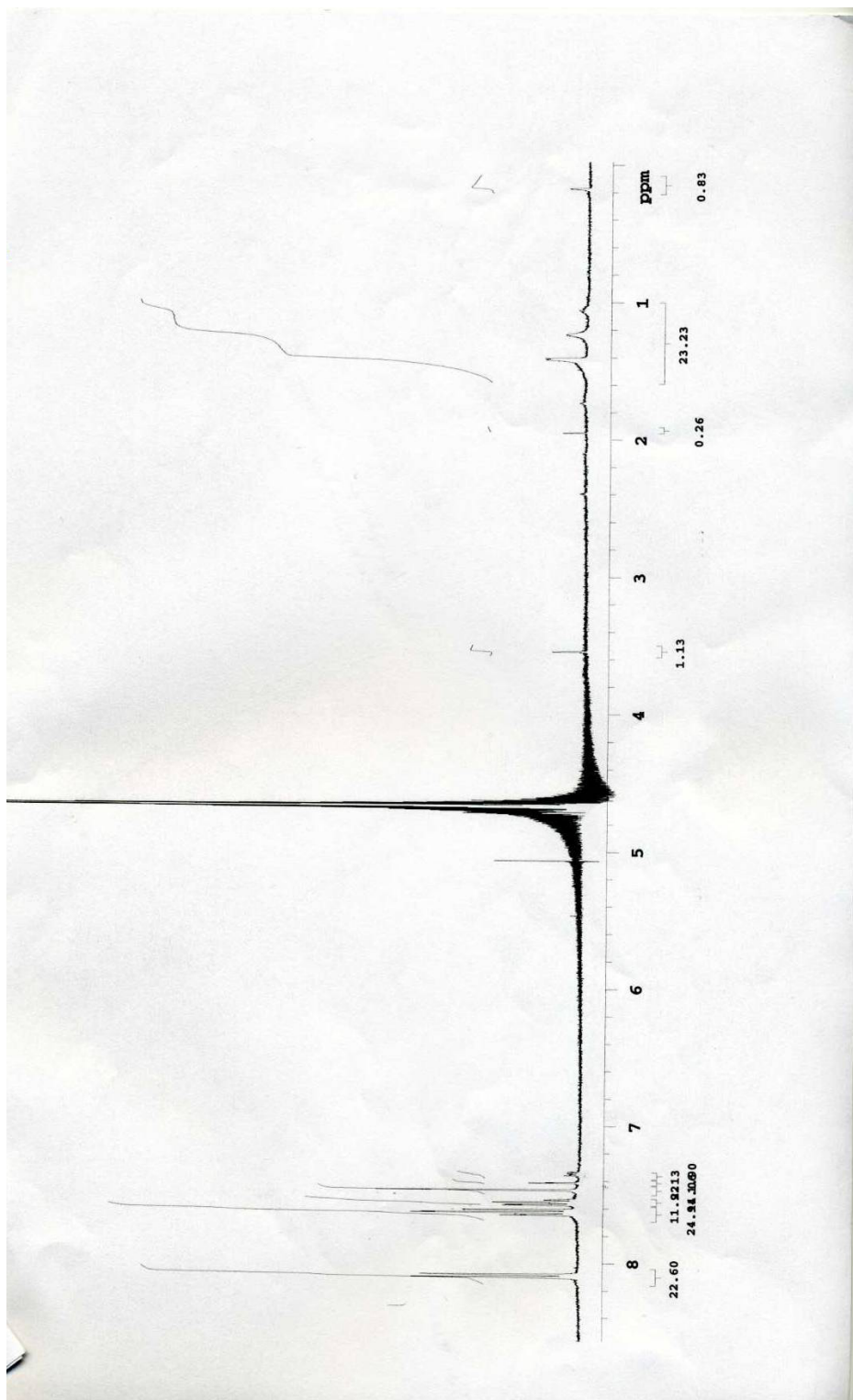


¹H NMR Spectroscopy

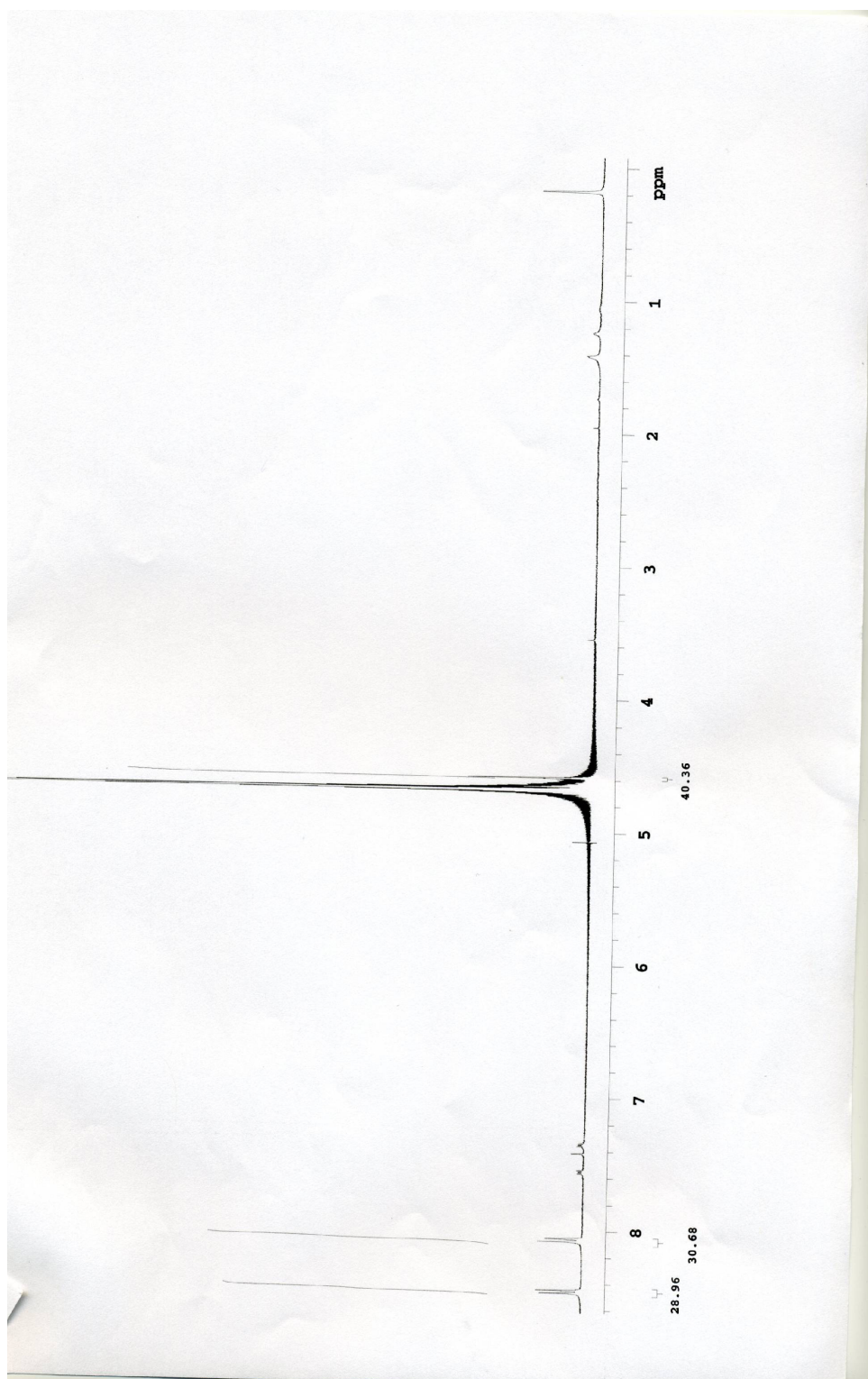
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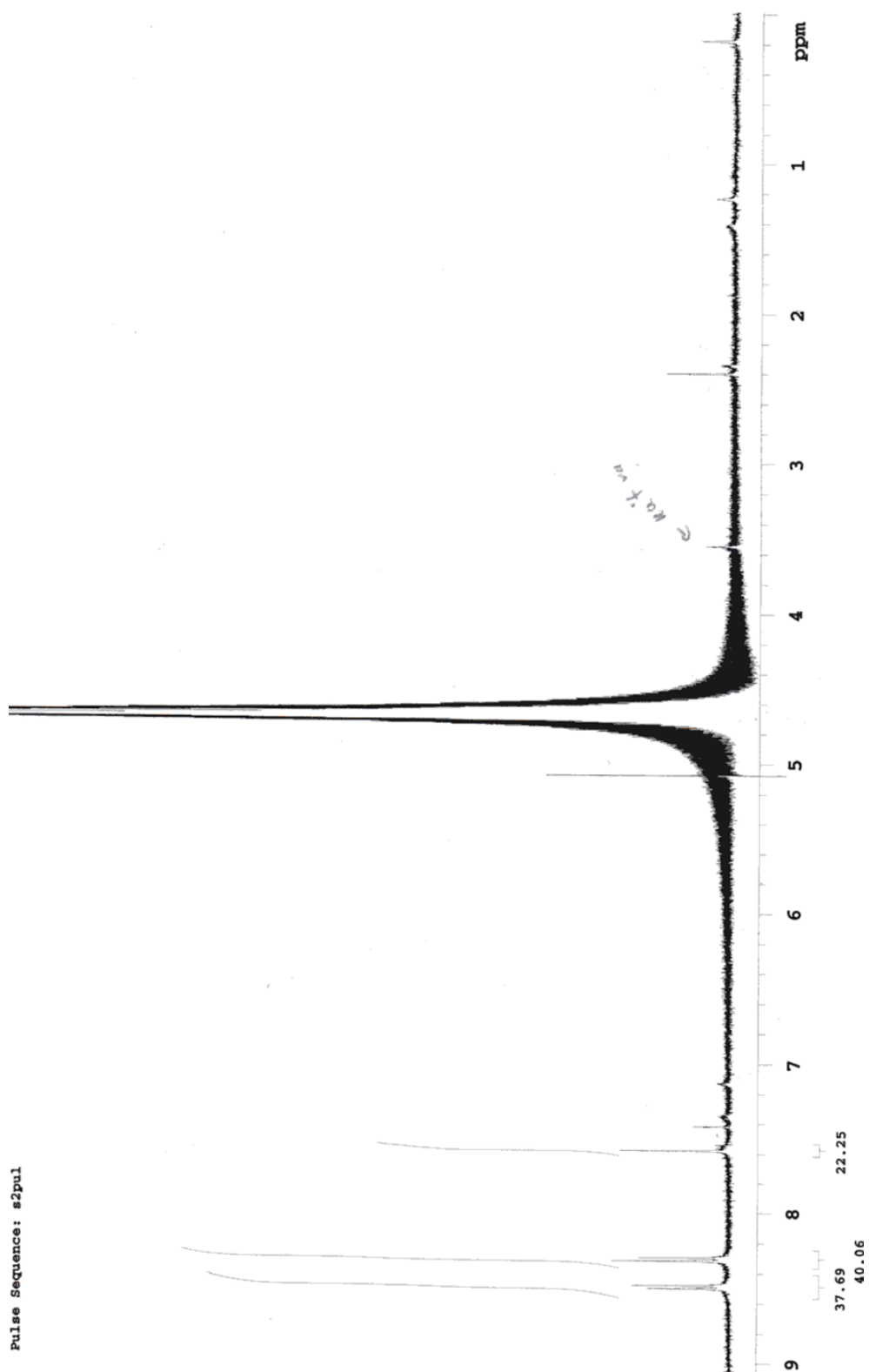
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Compound 6b

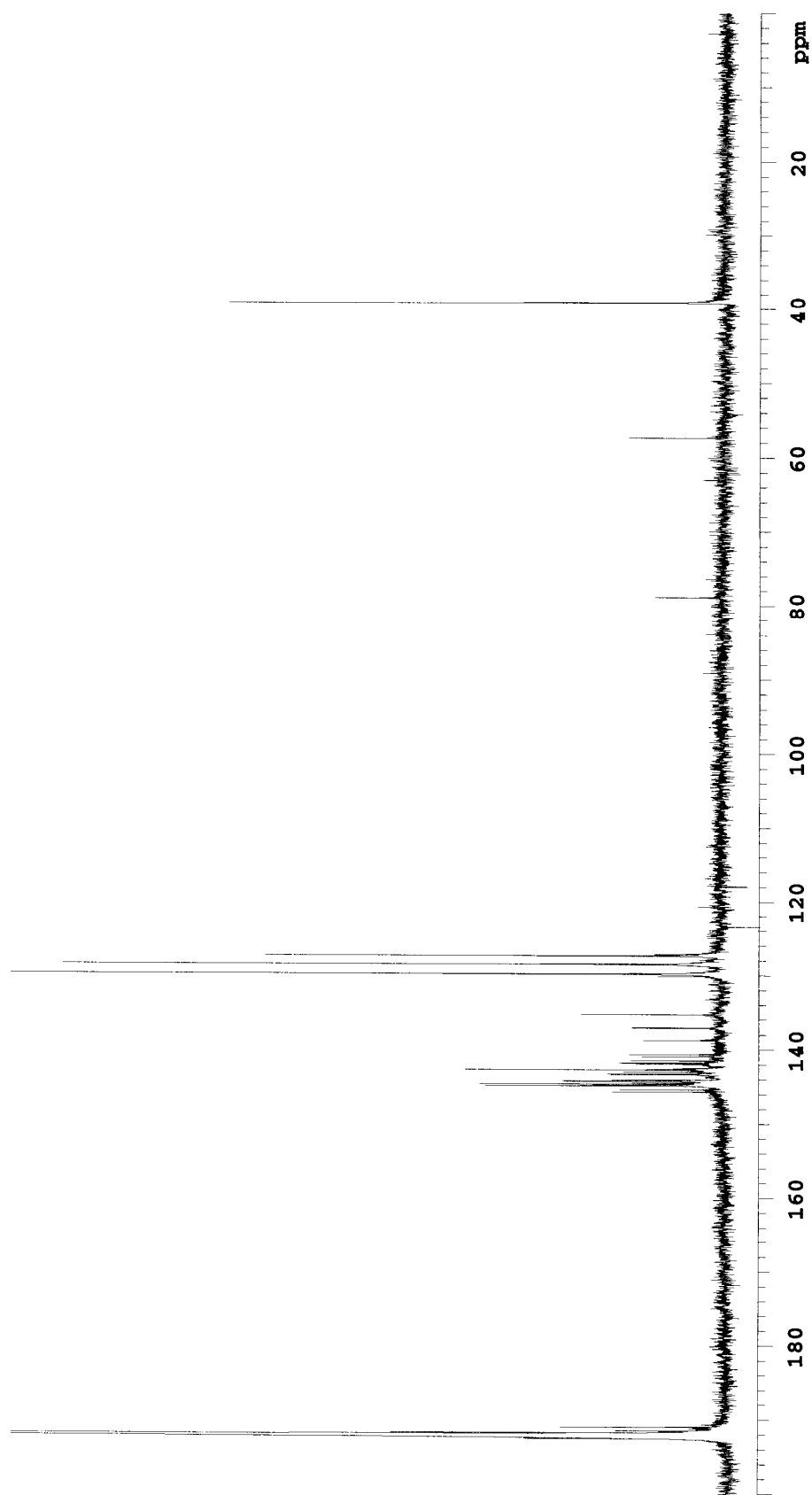


Compound 8b



¹³C NMR spectroscopy

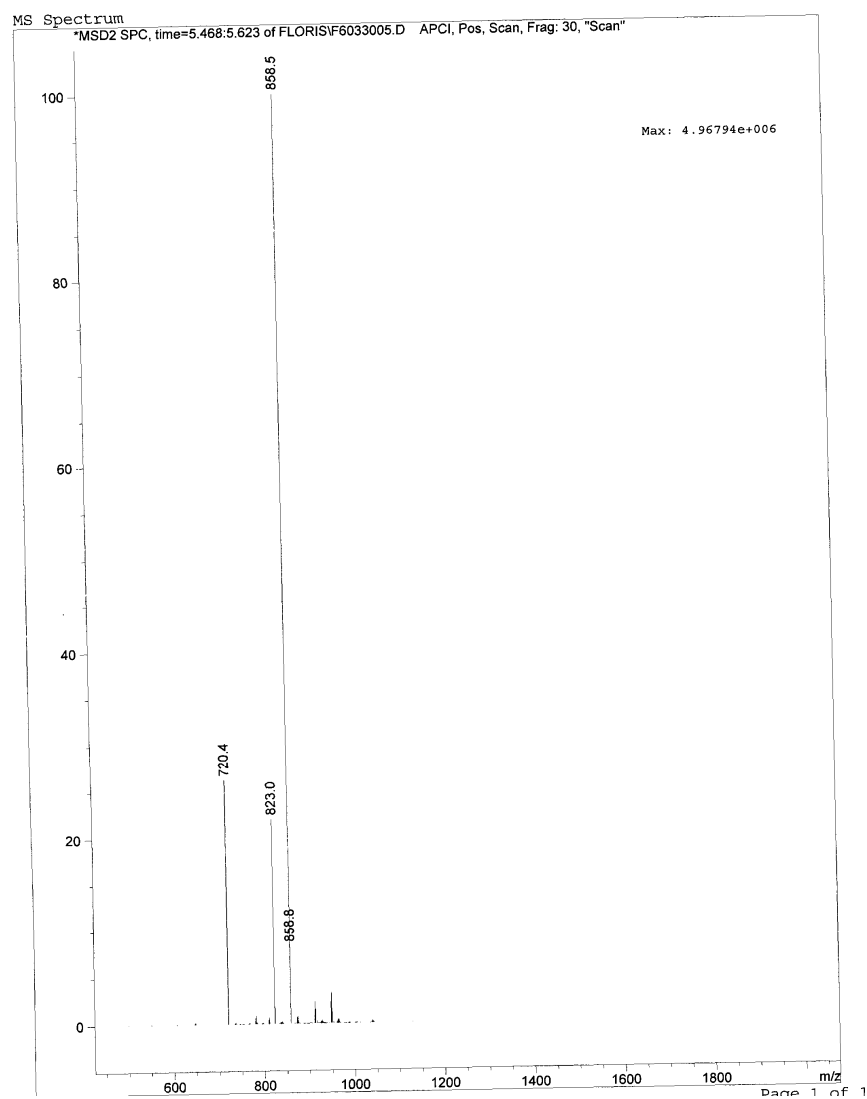
Compound 6a



Mass Spectrometry

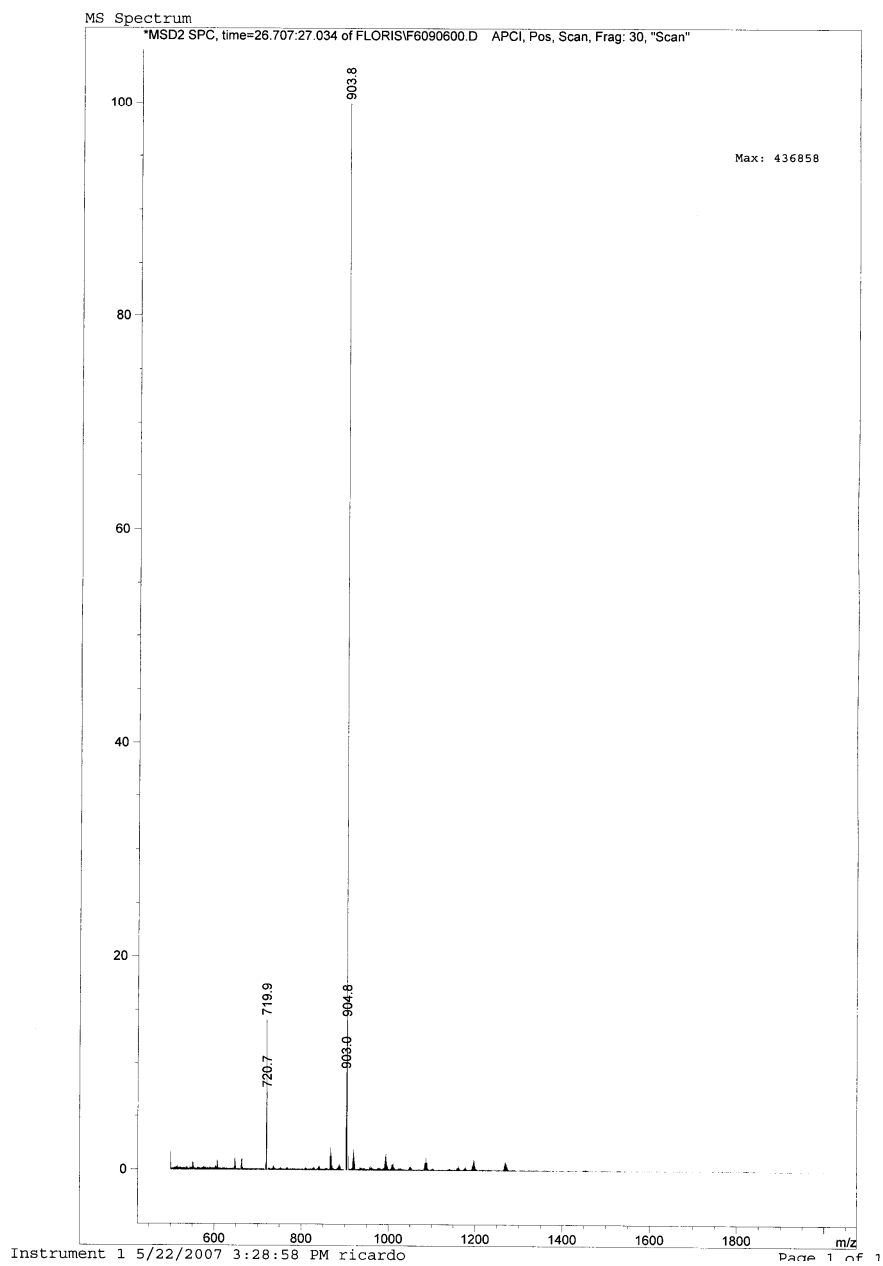
Compound 5a

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Bucky LC-MS Positive APCI Mode



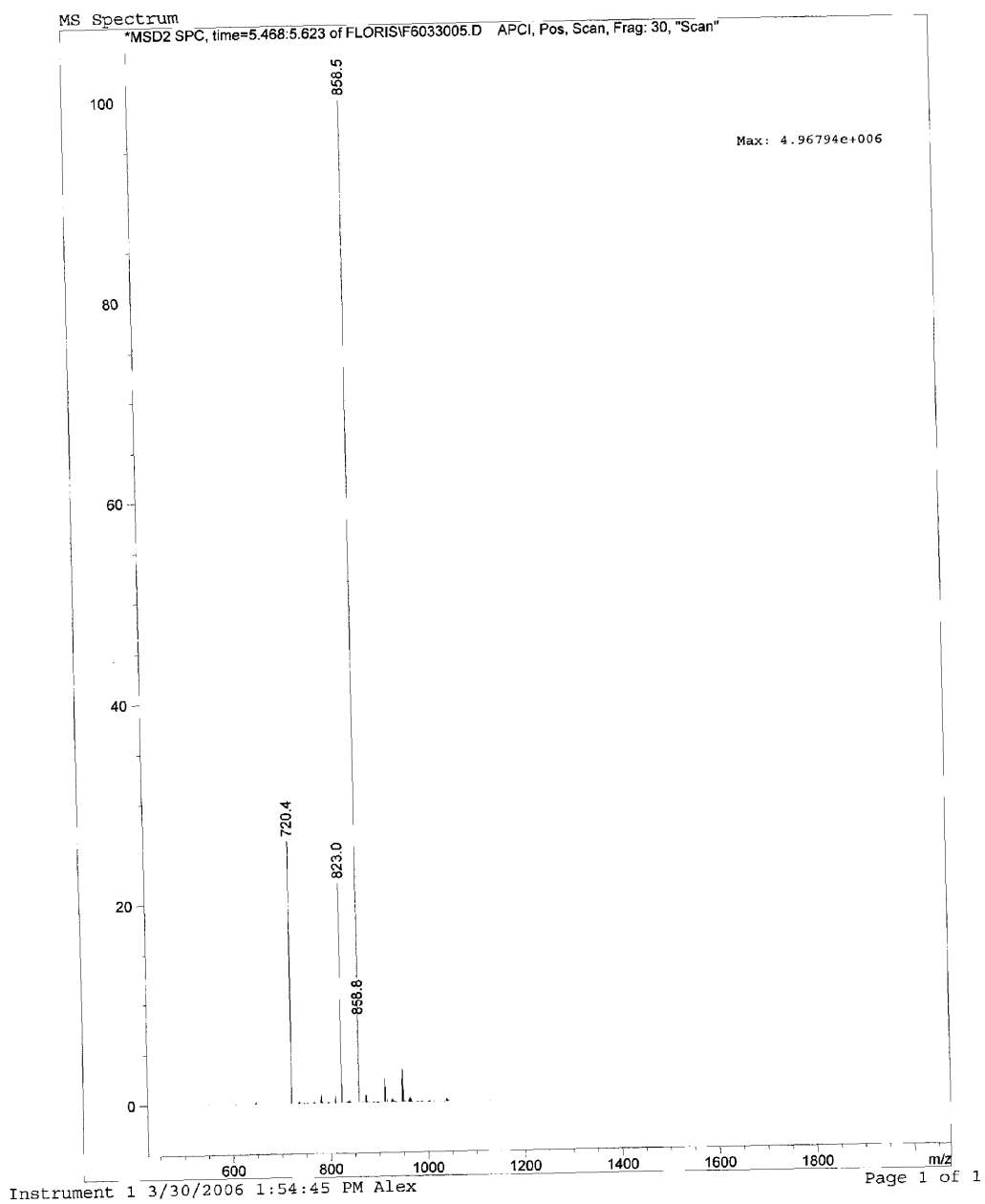
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Print of window 80: MS Spectrum

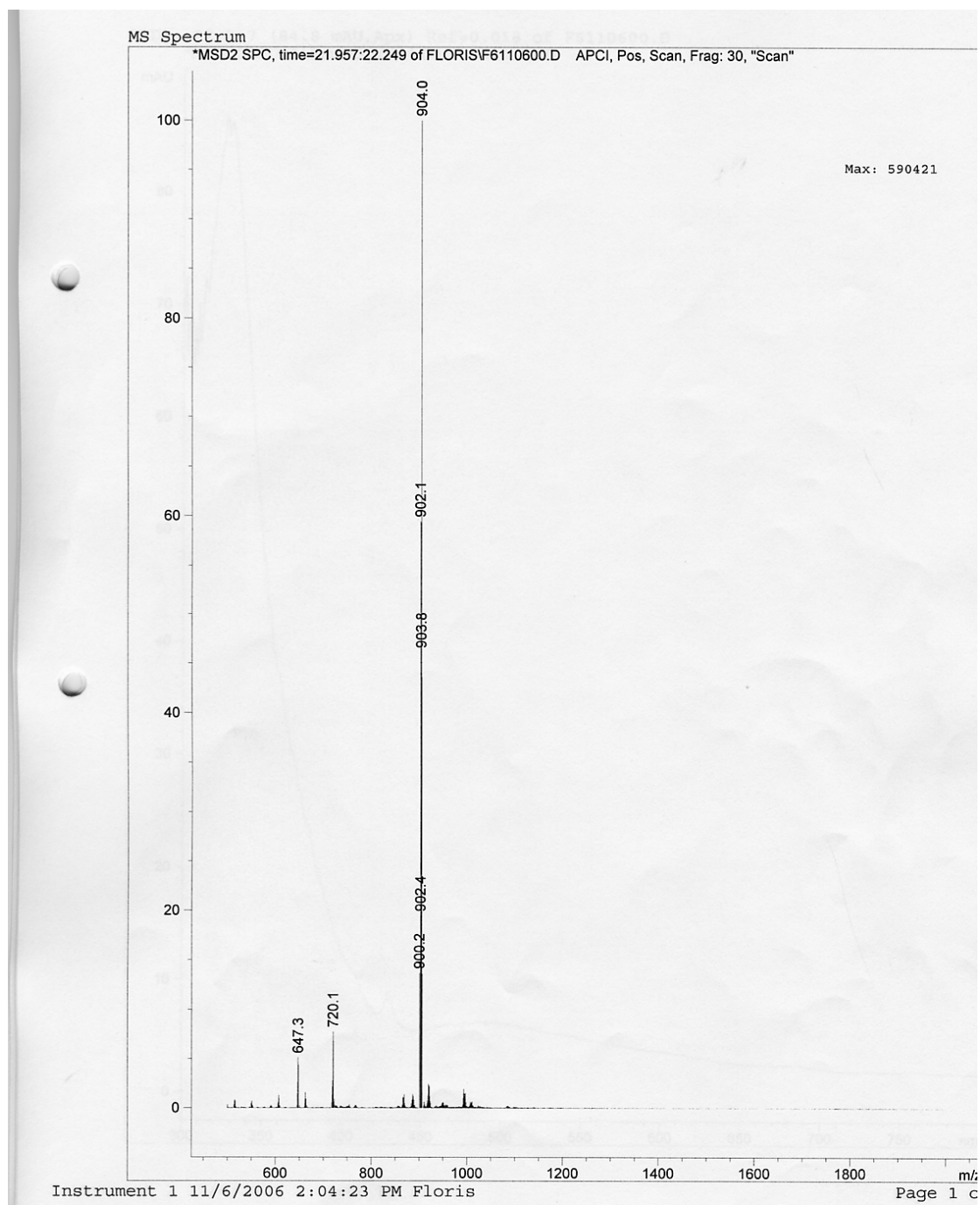


Compound 6a

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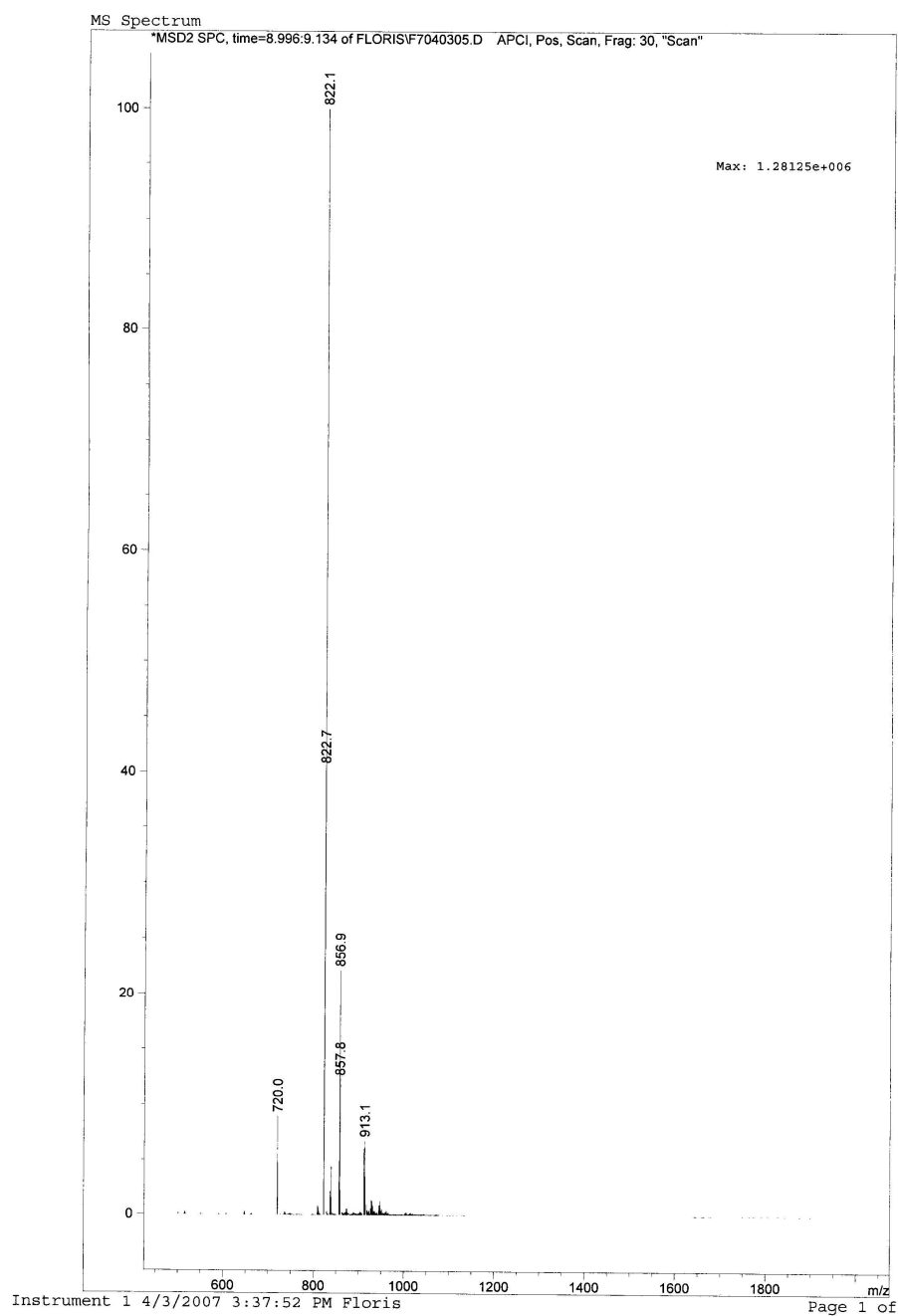


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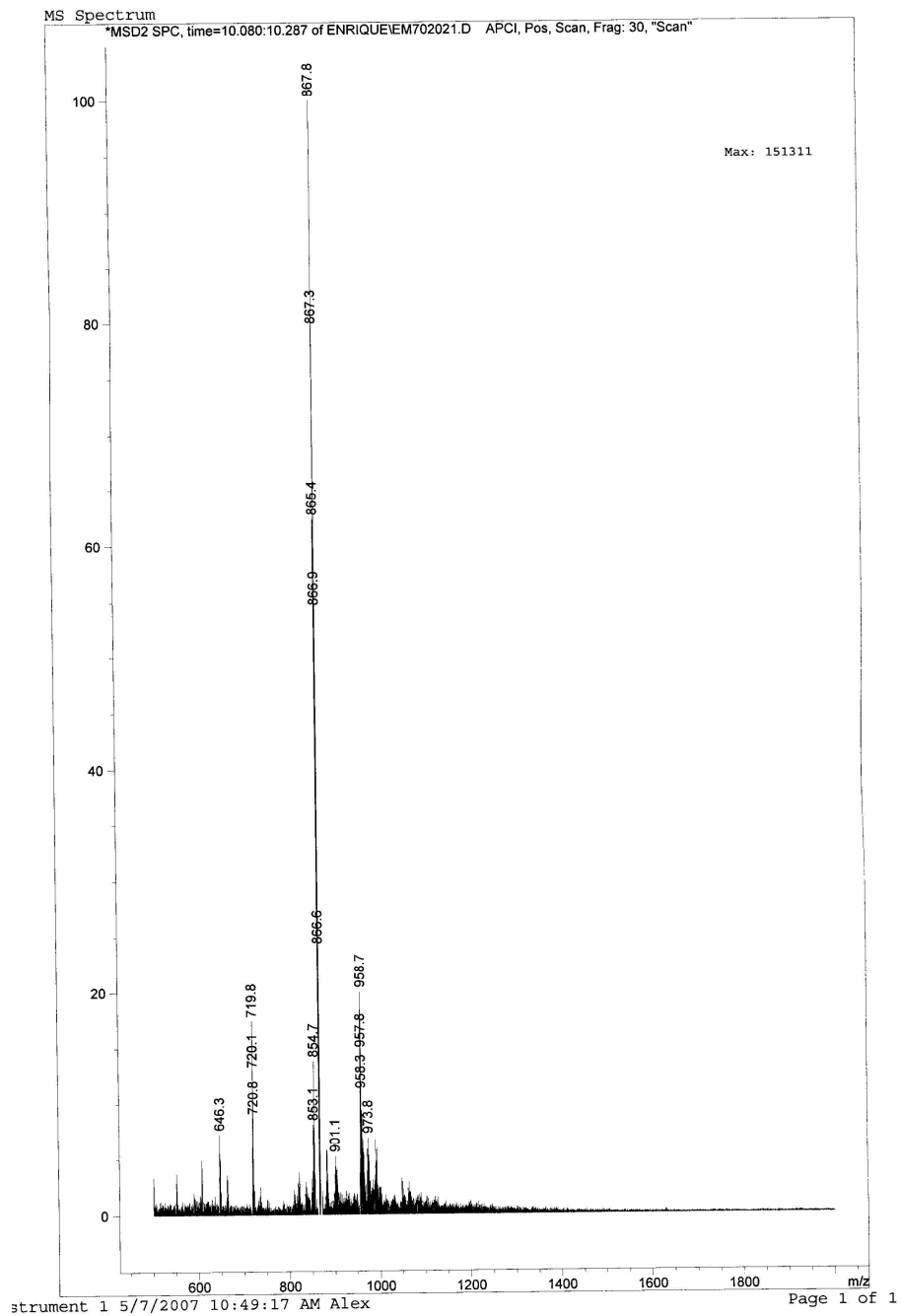
Compound 7a

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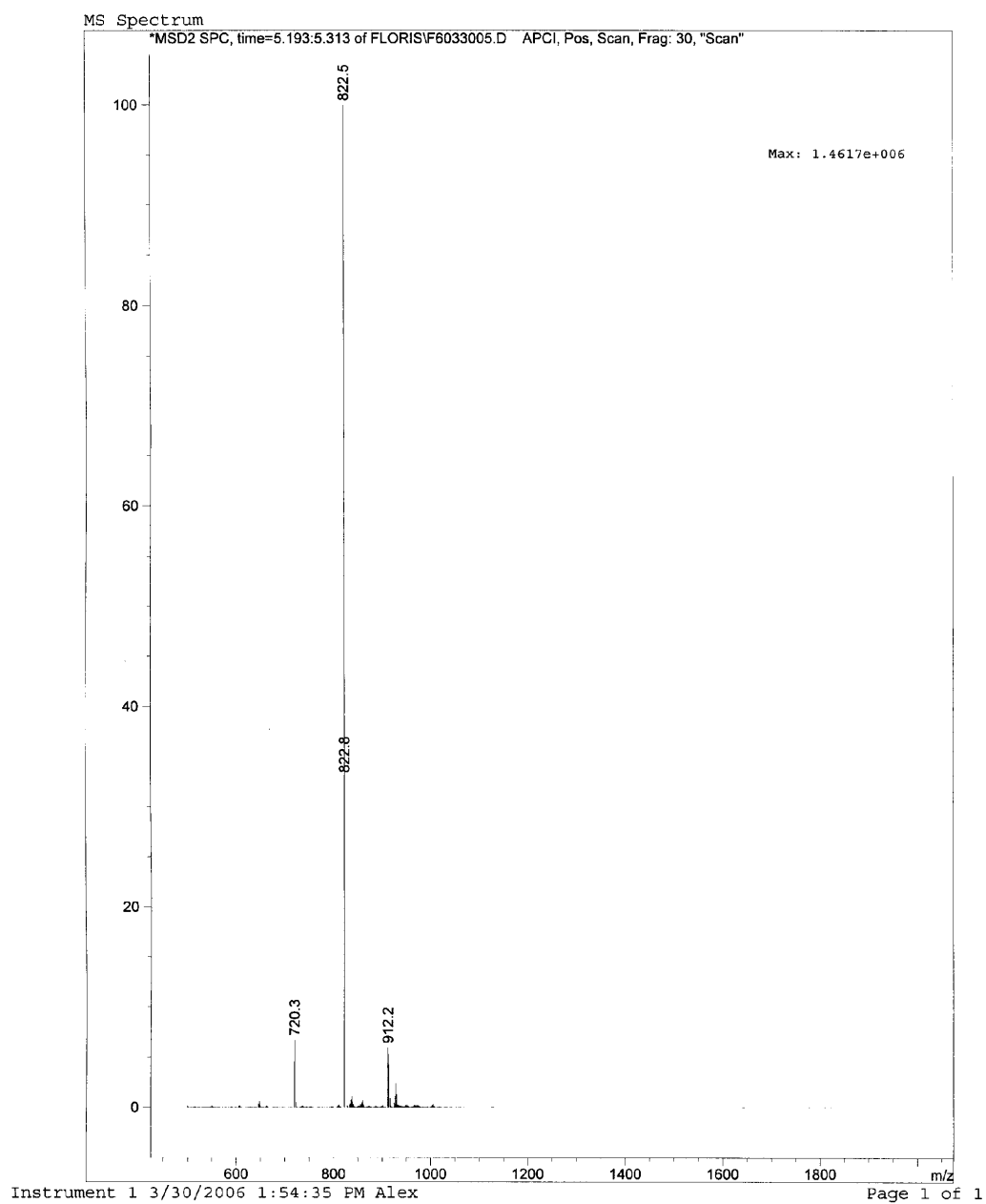
Compound 7b

of window 80: MS Spectrum



Compound 8a

Bucky LC-MS Positive APCI Mode



Compound 8b

