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Advances in Molecular Scale Electronics: Synthesis and Testing of Nanoscale Wires and Devices

by

Adam Madison Rawlett

A Thesis Submitted
In Partial Fulfillment of the
Requirements for the Degree

Doctor of Philosophy

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May, 1999

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For Kristen, Mom, and Dad

Abstract

Advances in Molecular Scale Electronics: Synthesis and Testing on Nanoscale Wires and Devices

by

Adam Madison Rawlett

Chapter 1 discusses advances in molecular scale electronics. With the miniaturization of transistors on silicon semiconductor chips comes faster processing speeds and more powerful computational power; however, certain size constraints on today's semiconductor industry will soon be realized. Therefore, a new method of computer architecture must be developed. The use of a discrete, highly conjugated organic molecule as a molecular scale wire to conduct an electric current has been demonstrated. We have developed molecular scale gates, from organic molecules, that can be altered "on" and "off" with the use of an electric field. Additionally, we have synthesized and tested nanoscale devices that exhibit negative differential resistance with a valley to peak ratio of over 1000:1 that is 10 times that of current solid-state devices and shown long lasting random access memory. The use of these molecular scale wires and devices should allow us to overcome the miniaturization barrier.

Chapter 2 describes a simple bench-top gravity column chromatography method for the purification of C_{60}, C_{70}, and the higher fullerenes $<C_{100}$. The stationary phase is based on poly(dibromostyrene)/divinylbenzene and the eluent is chlorobenzene. This new stationary phase (1) uses an inexpensive monomer that can be easily polymerized by standard suspension techniques, (2) permits the use of potent fullerene solvents, and (3) can be reused without additional preparation.

Chapter 3 discusses the use of phenylene ethynylene oligomers as self assembled monolayer negative tone resist for the manufacture of even smaller semiconductor chips. With current methods of silicon etching with polymer resists, devices with sub-25 nm feature size are not obtainable. We have prepared the first self-assembled monolayer that upon irradiation acts as a negative tone resist. In addition, we have synthesized a phenylene-ethynylene substituted trichlorosilane that should crosslink with exposure to irradiation to be a superior resist material. We are currently in the process of evaluating what functionalities are necessary to form negative tone resists at lower doses of energy. This will allow the fabrication of device feature sizes below 8 nm.

Chapters 4, 5, and 6 discuss the great utility of substituted phenylene ethynylenes in the areas of cluster and surface binding study, STM patterning, and organic LEDs.

Major Professor
James M. Tour

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First and foremost, I would like to thank God for all the blessings that he has bestowed on me over the last 26 years. Without his guidance and love, I would not be able to achieve what I have today.

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List of Symbols and Abbreviations

Å	Angstrom
Ac	Acetyl
AIBN	Azoisobutylnitrile
AFM	Atomic force microscopy
Ar	Aryl
bp	Boiling Point
br	Broad (spectral)
Bu	Butyl
t-Bu	tert-Butyl
Bz	Benzyl
°C	Degrees Celsius
calcd	Calculated
CH_2Cl_2	Methylene Chloride
CuI	Copper Iodide
cm	Centimeter(s)
cm^{-1}	Inverse Centimeter(s)
concd	Concentrated
δ	Chemical Shift in Parts per Million Downfield from Tetramethylsilane
d	Day(s); Doublet (spectral)
DFT	Density Functional Theory
DMF	*N,N*-dimethylformamide
DMSO	Dimethylsulfoxide
ε	Extinction Coefficient
E_a	Activation Energy
EIMS	Electron Impact Mass Spectroscopy
Et	Ethyl
Et_2O	Diethyl ether

eV	Electronvolt
FT	Fourier Transform
g	Gram(s)
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
h	Hour(s)
HCl	Hydrochloric Acid
HF	Hydrofluoric Acid
HOMO	Highest Occupied Molecular Orbital
HPLC	High Pressure Liquid Chromatography
HRMS	High-Resolution Mass Spectrum
Hz	Hertz
IR	Infrared
I(V)	Function of Current versus Voltage
J	Coupling Constant (in NNIR)
K	Degrees Kelvin
KBr	Potassium Bromide
K_2CO_3	Potassium Carbonate
KOH	Potassium Hydroxide
λ	Wavelength
L	Liter(s)
LED	Light Emitting Diode
LRMS	Low-Resolution Mass Spectrum
LUMO	Lowest Unoccupied Molecular Orbital
μ	Micro
m	Multiplet (spectral), Meter(s), Milli
M	Moles per Liter
Me	Methyl
MeOH	Methanol
$MgSO_4$	Magnesium Chloride
MHz	Megahertz

min	Minute(s)
mol	Mole(s)
MP	Melting Point
mRAM	Single Molecular Random Access Memory
MS	Mass Spectrometry
MW	Molecular Weight
N	Equivalents per Liter
NDR	Negative Differential Resistance
NH_4Cl	Ammonium Chloride
nm	Nanometer
NMR	Nuclear Magnetic Resonance
Ω	Ohm
p	Pico, pentet (in NMR)
PDBS/DVB	Poly(dibromostyrene)/divinylbenzene
Ph	Phenyl
PPh_3	Triphenylphosphine
ppm	Parts per Million (in NMR)
PVR	Peak to Valley Ratio
q	Quartet (spectral)
Q	Charge
RAM	Random Access Memory
RIE	Reactive Ion Etching
Rf	Retention Factor (in chromatography)
rt	Room Temperature
σ	Conductive State
s	Singlet (NMR); Second(s)
SAM	Self-Assembled Monolayer
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SET	Single Electron Transistor
$SiCl_3$	Trichlorosilane

SRAM	Static Random Access Memory
STM	Scanning Tunneling Microscopy
τ	Time Constant
t	Triplet (spectra)
TBAF	Tetrabutylammonium Floride
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsilyl, Tetramethylsilane
UV	Ultraviolet
V	Volt
Vis	Visible
w	Weight

Chapter 1

Advances in Molecular Scale Electronics:

Synthesis and Testing of Nanoscale Wires and Devices

Introduction

With the miniaturization of transistors on silicon semiconductor chips comes faster processing speeds and more powerful computational power; however, certain size and cost constraints on today's semiconductor industry will soon be realized.[1-7] Gordon Moore, one of the founders of Intel, predicted in 1968 that the minimum device feature size on a semiconductor chip would decrease by a factor of 2 every 18 months. Moore's predict has held true over the last 32 years. What does that mean for the computer industry? The routine feature size of microchips has dramatically declined to ~0.1 μm. Although a further decrease is likely, once the line size on integrated circuits becomes < 0.01 μm, several quantum limitations will likely limit the proper performance of solid state devices. Moreover, the simple cost of the more complex semiconductor fabrication centers, in addition to the inability to create ever-smaller semiconductor devices, could severely handicap this industry in the next few decades.

Therefore, a new paradigm of computer architecture must be developed. Molecular scale electronics is a field of study that proposes the use of single molecules to function as the key components in future computational devices.[8] The use of a single organic molecule, of the approximate size 5 Å × 20 Å, has the advantage of being 10^6 times smaller in area than current silicon devices.[1] Molecular-based systems can offer distinct advantages in uniformity and potential fabrication costs.[9] Additionally, these organic wires offer the advantage of ease of synthesis and the ability to create large varieties of wires by the use of facile organic transformations. If devices were to be based upon single molecules, using routine chemical syntheses, one could prepare 6 ×

10^{23} (Avogadro's number) devices in a single reaction flask; hence, more devices than are presently in use by all the computational systems combined, world-wide.[5,6]

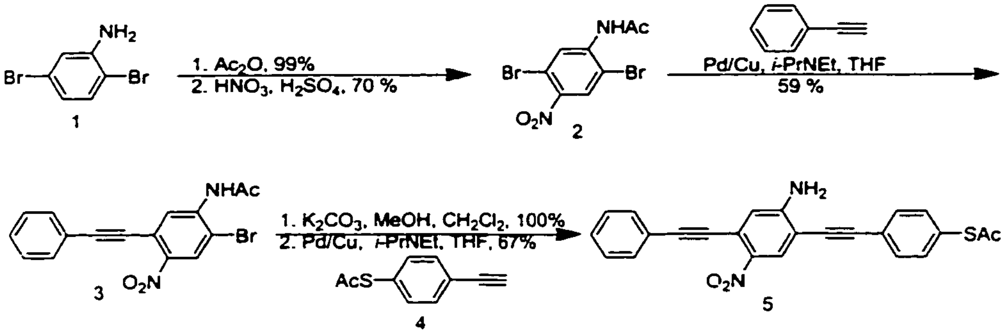
The use of discrete, highly conjugated oligo(phenylene ethynylene)s as molecular scale wires that conduct an electric current has been demonstrated.[10,11] Electronic measurements of these molecular scale wires were performed in a nanostructure that have a metal top contact, a self-assembled monolayer (SAM) active region, and a metal bottom contact. This nanostructure is similar to that reported previously.[12,13] The essential feature of the fabrication process is the use of nanoscale device area that gives rise to a small number of self-assembled molecules (≈ 1000) and also eliminates pinhole and other defect mechanisms that hamper through-monolayer electronic transport measurements.

Using this device structure, we showed that a functionalized molecular scale wire can exhibit non-linear current versus voltage (I(V)) plots, and it functions as a reversible, reproducible switching device.[13] Moreover, related systems have shown room temperature, long lasting static random access memory (SRAM) properities.[14] The use of these molecular scale electronic devices should allow for a plethora of new and exciting computing architectures. Although numerous obstacles remain, molecular electronics offers an exciting incentive to consider molecular scale electronic architectures for future computing.

Synthesis of Functionalized Molecular Scale Devices

Described here are the syntheses of functionalized molecular scale devices that have shown remarkable electronic properties, i.e. negative differential resistance and

SRAM, and other potential electronic devices. The majority of these molecules are based on functionalized oligo(phenylene ethynylene)s, which are substituted with electron withdrawing and donating groups and are terminated with thioacetyl groups. The thioacetyl groups, after hydrolysis to the free thiols, are to serve as the molecular "alligator clips" for adhesion to gold probes.[15,16] The synthesis of potential molecular scale devices whose current vs. voltage, I(V), curves exhibit non-linear behavior, are described below.



(1)

The synthesis of molecular scale devices with amino and nitro moieties are described in eq 1. The formation of 2,5-dibromo-4-nitroacetanilide **2** went well according to literature procedure.[17] Caution must be used during the synthesis of **2** due to the possibility of multiple nitrations on the phenyl ring which may generate polynitrated compounds that could be explosive. The Pd/Cu-catalyzed coupling of phenylacetylene to the substituted dibromobenzene gave a moderate yield of 59% due to the expected statistical mixture of the mono and dicoupled products. The regiochemistry of **3** is determined by the coupling preceeding faster at the bromide ortho to the nitro moiety. This occurs due to its lability of the carbon-bromide bond alpha to the nitro group since it is weakened by the electron withdrawing properties and resonance with the nitro moiety, toward oxidative addition by the Pd compared to the meta bromide. A sample was submitted for X-ray analysis to definitively assign the regiochemistry. The ORTEP of the crystal structure is seen in Figure 1.

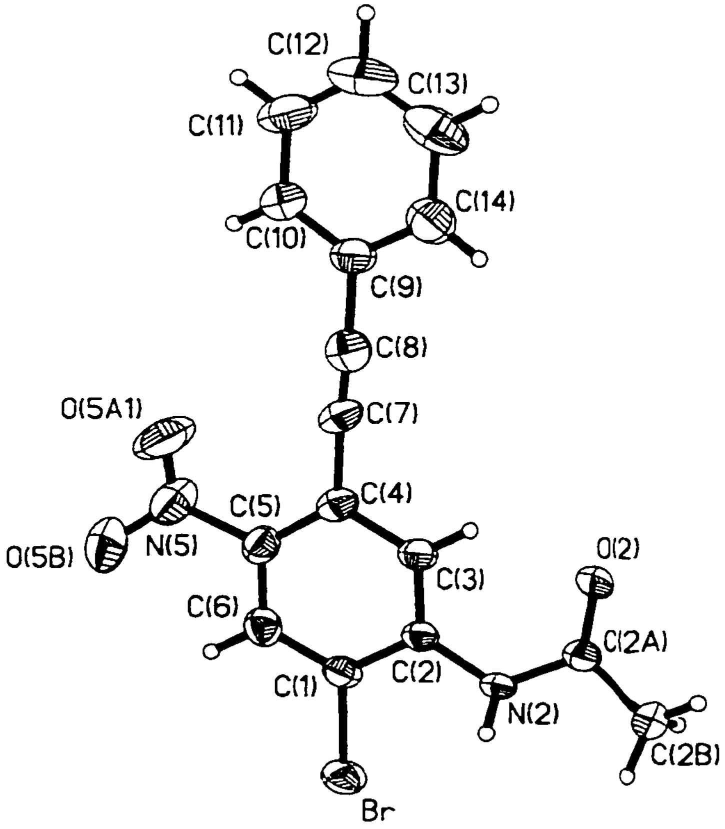
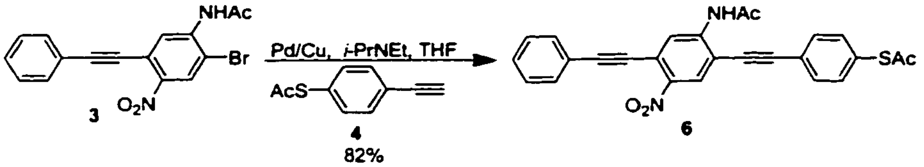


Figure 1: Crystal Structure of Compound **3**

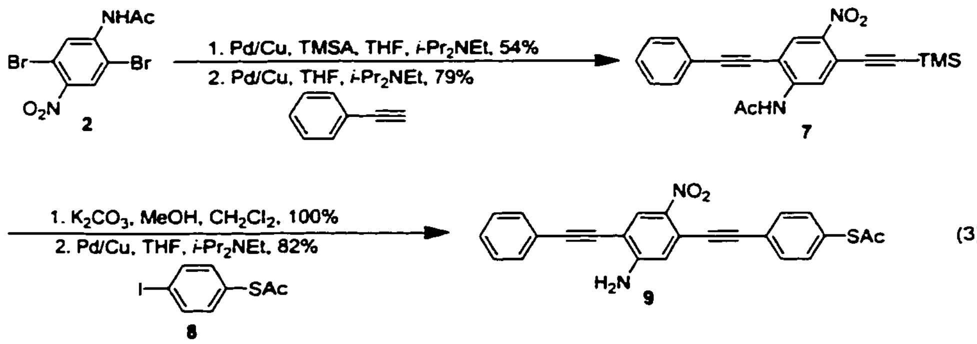
The acetamide-protecting group is removed during the deprotection of the terminal alkynes in the presence of potassium carbonate and methanol. It is believed that the electron withdrawing ability of the nitro moiety allows for the removal of the acetamide-protecting group under such mild conditions. Finally, intermediate **3** is coupled by Pd/Cu-catalysis to alligator clip **4**[15] to afford molecular scale device **5**. An additional method for the synthesis of **5** has been developed. Intermediate **3** is coupled with trimethylsilylacetylene, then deprotection of the terminal acetylene and the amine with potassium carbonate, and finally subsequent coupling with 1-iodo-4-thioacetylbenzene that afforded **5** in slightly lower yields than described in eq 1. The dipole moment of the interior phenyl ring, which is directed away from the thioacetate protecting group, of molecule **5**, is calculated to be 5.77 Debye.[18] Conductivity measurements on compound **5** will be discussed in the next section.



(2)

Compound **6** differs from molecule **5** in that it possesses an acetamide rather than an amine moiety. The Pd/Cu-catalyzed coupling reaction to form molecule **6** proceeded at a faster rate than the coupling to the amine/nitro compound due to the lesser electron donating potential of the acetamide allowing for faster palladium oxidative addition across the aryl bromide bond. The overall net dipole moment of this compound has been calculated to be 2.74 Debye.[18]

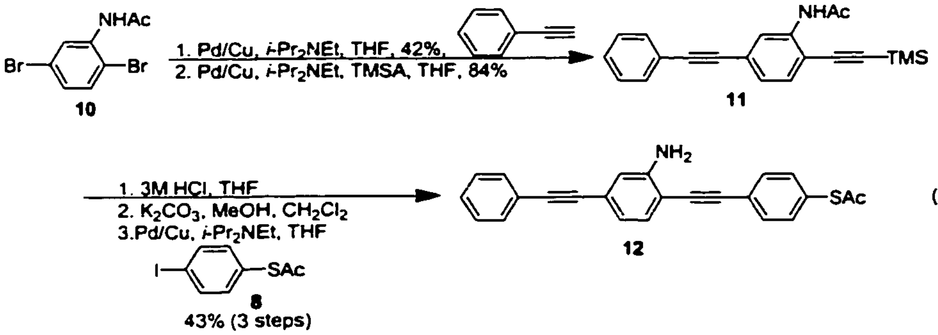
To determine the effect of the direction of the dipole moment on conductivity, compound **9** was synthesized, according to eq 3. It possesses a dipole that is directed toward the thioacetyl terminus, a direction opposite that of the dipole in **7**.


NHAc
Br
Br
O₂N
2
1. Pd/Cu, TMSA, THF, i-Pr₂NEt, 54%
2. Pd/Cu, THF, i-Pr₂NEt, 79%
NO₂
TMS
AcHN
7
1. K₂CO₃, MeOH, CH₂Cl₂, 100%
2. Pd/Cu, THF, i-Pr₂NEt, 82%
I
SAc
8
NO₂
SAc
H₂N
9

(3)

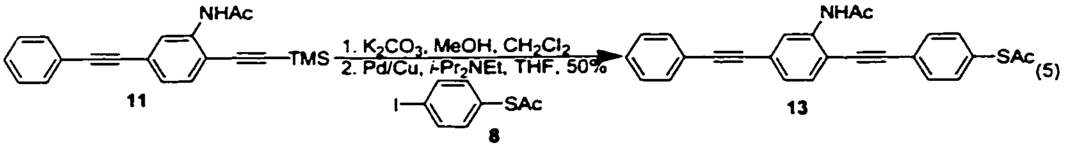
The regiochemistry **9** is assumed. With a deficient amount of trimethylsilylacetylene, the coupling with intermediate **2** should proceed at the more labile bromide. Subsequent coupling to phenylacetylene should provide the regiochemistry shown in intermediate **7**. Deprotection of the amine and the terminal acetylene, followed by coupling to 1-iodo-4-thioaceteylbenzene afforded molecular scale device **9**.

To determine the effects of an electron withdrawing or donating moiety on electrical properties of these compounds, materials with solely an amine, nitro, or acetamide moiety have been synthesized.

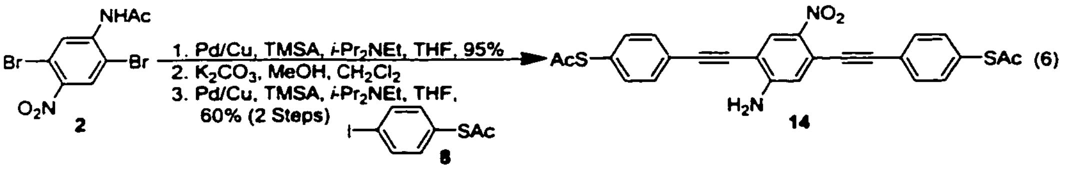

NHAc
Br
Br
10
1. Pd/Cu, i-Pr₂NEt, THF, 42%,
2. Pd/Cu, i-Pr₂NEt, TMSA, THF, 84%
NHAc
TMS
11
1. 3M HCl, THF
2. K₂CO₃, MeOH, CH₂Cl₂
3. Pd/Cu, i-Pr₂NEt, THF
I
SAc
8
43% (3 steps)
NH₂
SAc
12

(4)

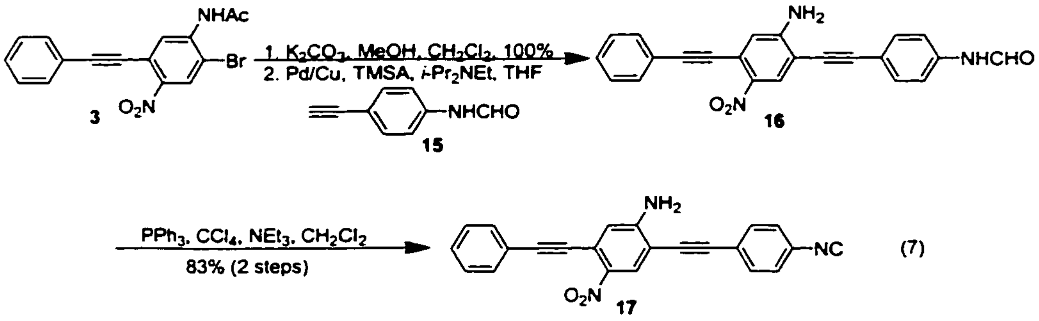
The molecular scale device, which possesses an amino moiety, was synthesized according to eq 4. Following the couplings of trimethylsilylacetylene and phenylacetylene to **10**, the deprotection of compound **11** with 3 M HCl, two compounds were obtained. The desired amine product and the amine cyclized bicyclic indole product, also seen in literature with similar compounds,[19] were synthesized. The separation of these compounds was not attempted due to similar retention factors on silica gel in most eluents. The terminal acetylene was revealed using potassium carbonate and methanol followed by Pd/Cu-catalyzed coupling to 1-iodo-4-thioacetylbenzene to form molecular scale wire **12**.


NHAc
TMS
11
1. K2CO3, MeOH, CH2Cl2
2. Pd/Cu, i-Pr2NEt, THF, 50%
I
SAc
8
NHAc
SAc
13
(5)

Similar to molecular scale device **12**, the acetamide adduct was synthesized according to eq 5. In this case, the deprotection of the terminal alkyne with potassium carbonate and methanol did not remove the acetamide-protecting group. A two terminal molecular scale device that is similar to compound **5** has been synthesized according to eq 6.


NHAc
Br
Br
O2N
2
1. Pd/Cu, TMSA, i-Pr2NEt, THF, 95%
2. K2CO3, MeOH, CH2Cl2
3. Pd/Cu, TMSA, i-Pr2NEt, THF,
60% (2 Steps)
I
SAc
8
AcS
NO2
H2N
14
SAc
(6)

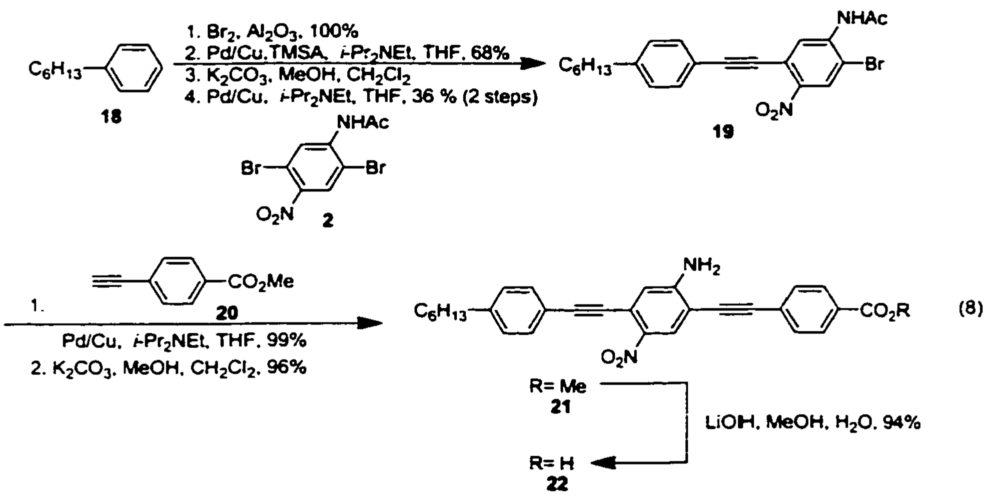
To study the effects of other alligator clips, for the attachment of the molecular scale devices to metal contacts, compounds with isonitrile endgroups were synthesized. Molecular scale device **17** with an isonitrile attachment moiety was synthesized according to eq 7. The amine moiety in intermediate **3** was unmasked with potassium carbonate and methanol followed by Pd/Cu-catalyzed cross coupling with the formamide bearing alligator clip **15** to afford compound **16**. Intermediate **16** was found to be insoluble in most solvent systems and therefore taken on impure into the next reaction.


NHAc
Br
3
O2N
1. K2CO3, MeOH, CH2Cl2, 100%
2. Pd/Cu, TMSA, i-Pr2NEt, THF
NHCHO
15
NH2
NHCHO
O2N
16
PPh3, CCl4, NEt3, CH2Cl2
83% (2 steps)
NH2
NC
O2N
17

(7)

The formamide was dehydrated in the presence of carbon tetrachloride, triphenylphosphine, triethylamine, and methylene chloride to afford molecular scale device **17**.[20]

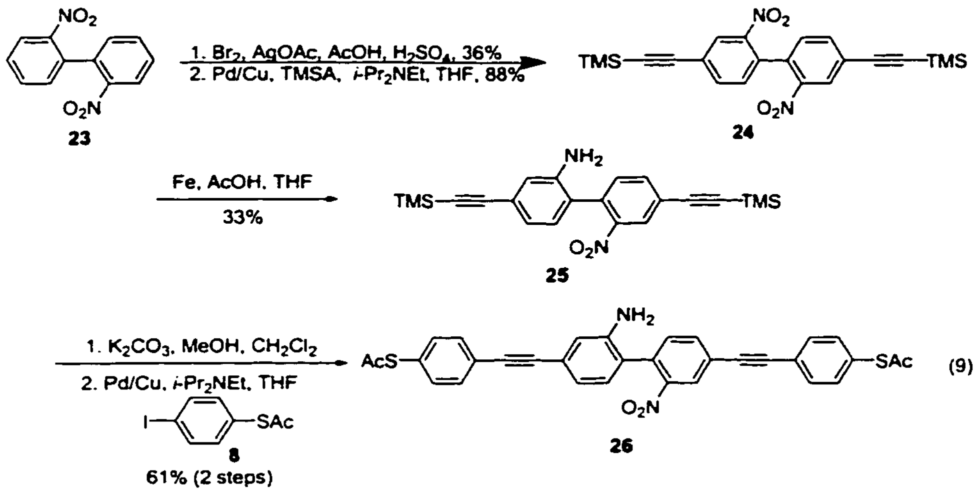
Currently, the formation of a SAM is the method of attachment of these molecular scale wires to the metal probe. An additional method of preparing ordered monolayers of molecular devices is the use of Langmuir-Blodgett films.[21] Therefore, a compound with hydrophilic and hydrophobic subunits with the central amino/nitro core of molecule **5** was synthesized as in eq 8.



1. Br$_2$, Al$_2$O$_3$, 100%
2. Pd/Cu,TMSA, i-Pr$_2$NEt, THF, 68%
3. K$_2$CO$_3$, MeOH, CH$_2$Cl$_2$
4. Pd/Cu, i-Pr$_2$NEt, THF, 36 % (2 steps)
18
2
19
1.
20
Pd/Cu, i-Pr$_2$NEt, THF, 99%
2. K$_2$CO$_3$, MeOH, CH$_2$Cl$_2$, 96%
R= Me
21
R= H
22
LiOH, MeOH, H$_2$O, 94%
(8)

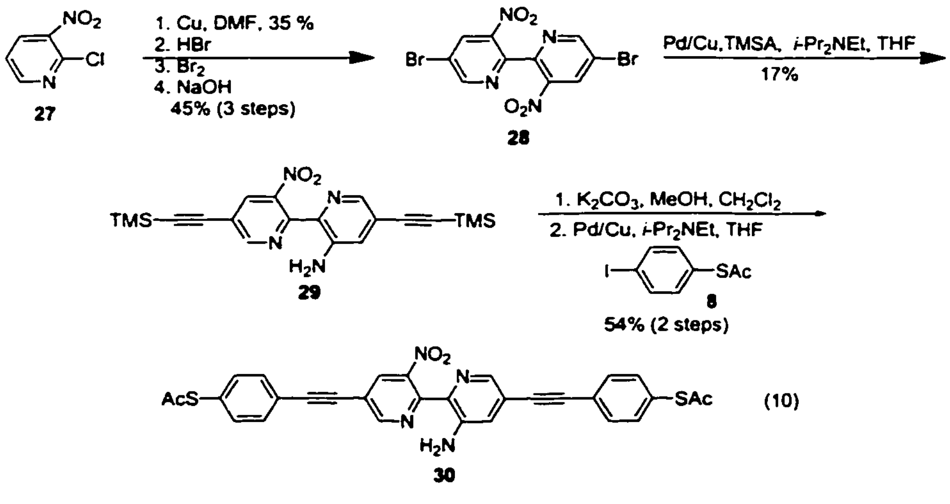
n-Hexylbenzene was easily brominated on neutral alumina in high yields[22] and coupled to trimethylsilylacetylene followed by deprotection of the terminal acetylene and coupling to the amino/nitro core intermediate **2** to afford intermediate **19**. The methyl ester, intermediate **21**, was synthesized by the coupling of 4-ethynyl-1-methylbenzoate to **20**. The amine was unmasked and the methyl ester was saponified with lithium hydroxide to afford molecular scale device **22**.[23] Compound **22** is suitable for the formation of a Langmuir-Blodgett film due to its hydrophilic carboxylic acid endgroup and the hydrophobic *n*-hexyl endgroup.

Similar compounds with substituted biphenyl and bipyrindyl core units have been synthesized according to eqs 9 and 10.


NO2
O2N
23
1. Br2, AgOAc, AcOH, H2SO4, 36%
2. Pd/Cu, TMSA, i-Pr2NEt, THF, 88%
TMS
NO2
O2N
TMS
24
Fe, AcOH, THF
33%
TMS
NH2
O2N
TMS
25
1. K2CO3, MeOH, CH2Cl2
2. Pd/Cu, i-Pr2NEt, THF
I
SAc
8
61% (2 steps)
AcS
NH2
O2N
SAc
26

(9)

2,2′-Dinitrobiphenyl was brominated at the 4 and 4′ positions on the biphenyl core using bromine, silver acetate, and sulfuric acid.[24] The brominated biphenyl was coupled to trimethylsilylacetylene to afford **24** in high yield which was then mono reduced to the amino/nitro compound in the presence of iron and acetic acid.[25] Finally, the terminal acetylenes were revealed and coupled using Pd/Cu catalysis, to two equivalents of alligator clip **8** to afford compound **26**.


NO2
Cl
N
27
1. Cu, DMF, 35 %
2. HBr
3. Br2
4. NaOH
45% (3 steps)
Br
NO2
N
N
O2N
Br
28
Pd/Cu,TMSA, i-Pr2NEt, THF
17%
TMS
NO2
N
N
H2N
TMS
29
1. K2CO3, MeOH, CH2Cl2
2. Pd/Cu, i-Pr2NEt, THF
I
SAc
8
54% (2 steps)
AcS
NO2
N
N
H2N
SAc
30

(10)

A similar compound with a bipyrindyl central core has been synthesized according to eq 10. 2-Chloro-3-nitropyridine was homocoupled in the presence of copper bronze and dimethylforamide.[26] The bipyridine ring system was brominated at the 5-and 5′-position under harsh conditions[27] to afford intermediate **28** that was then coupled with two equivalents of trimethylsilylacetylene. This reaction fortuitously gave the dinitro coupled product as well as the monoreduced amino/nitro coupled product that may arise from hydropalladation of one of the labile nitro groups in the Pd/Cu-catalyzed reaction conditions. X-ray analysis will definitively confirm product formation. Intermediate **29** was then deprotected in the presence of potassium carbonate and then coupled to 1-iodo-4-thioacetylbenzene using typical Pd/Cu cross coupling conditions to afford potential molecular scale switch **30**.

Testing of Molecular Scale Devices and Testing

As mentioned before, electronic measurements on molecular scale wires and devices were performed in the nanopore summarized in Figure 2. Fabrication of nanopore devices and conductivity measurements for all of the compounds have been performed in the laboratories of Dr. Mark Reed in the Electrical Engineering Department at Yale University.

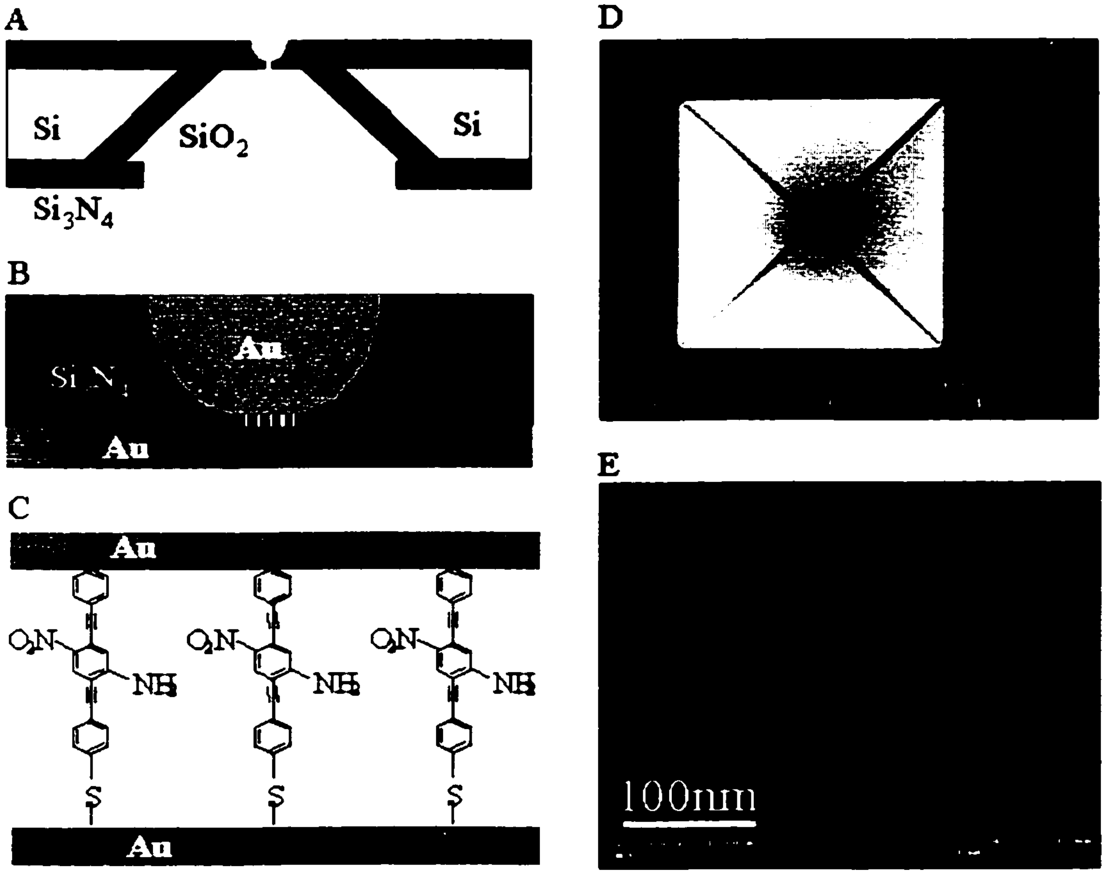
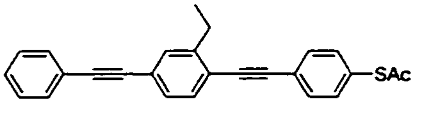


Figure 2: Schematics of device fabrication: (A) cross section of a silicon wafer with a nanopore etched through a suspended silicon nitride membrane; (B) Au-SAM-Au junction in the pore area; (C) blowup of (B) illustrated with **5** sandwiched in the junction although we have sandwiched many compounds in this device; (D) scanning electron micrograph (SEM) of pyramid Si structure after unisotropic Si etching (that is, the bottom view of (A)); (E) SEM of an etched nanopore through the silicon nitride membrane.

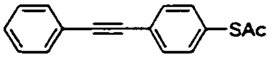
The starting substrate for the device fabrication is a 250 μm-thick double side polished silicon (100) wafer, upon which 50 nm of low stress Si_3N_4 was deposited by low-pressure chemical vapor deposition (LPCVD). On the back surface, the nitride was removed in a (400 μm by 400 μm) square by optical lithography and reactive ion etching (RIE). The exposed silicon was etched in an orientation-dependent anisotropic etchant

(85°C, 35% KOH solution) through to the top surface to leave a suspended (40 μm by 40 μm) silicon nitride membrane. We then grew 1000 Å of SiO_2 thermally on the Si sidewalls to improve electrical insulation. A single hole 30 to 50 nm in diameter was made through the membrane by electron beam lithography and RIE. Because of the constrained geometry, the RIE rates are substantially reduced so that the far side opening is much smaller than the actual pattern, thereby rendering the cross section bowl-shaped geometry. An Au contact of 200 nm thickness was evaporated onto the topside of the membrane, which filled the pore with Au. The sample was then immediately transferred into a solution to self-assemble the active electronic component. The sample was then rinsed, quickly loaded into a vacuum chamber, and mounted onto a liquid nitrogen cooling stage for the bottom Au electrode evaporation, where 200 nm Au was evaporated. The devices were then diced into individual chips, bonded onto packaging sockets and loaded into a variable temperature cryostat and conductivity measured.[13]

Conductivity of these oligo(phenylene ethynylene)s molecular scale wires and devices is hypothesized to arise from transfer of electrons through the π-orbital backbone that extends over the entire molecule. When the phenyl rings of the phenylene ethynylenes oligomers are planar, the π-orbital overlap of the molecule is continuous. Thus transfer over the entire molecule is achieved; electrons can freely flow between metal contacts, and conductivity is maximized. Moreover, if the phenyl rings become perpendicular with respect to each other, the π-orbitals between said phenyl rings become orthogonal. The discontinuity of the π-orbital network in the perpendicular arrangement does not allow for free flow of electrons through the molecular scale wire, thus conductivity is greatly decreased, Figure 3.[28]



31
(3-ph)



32
(2-ph)

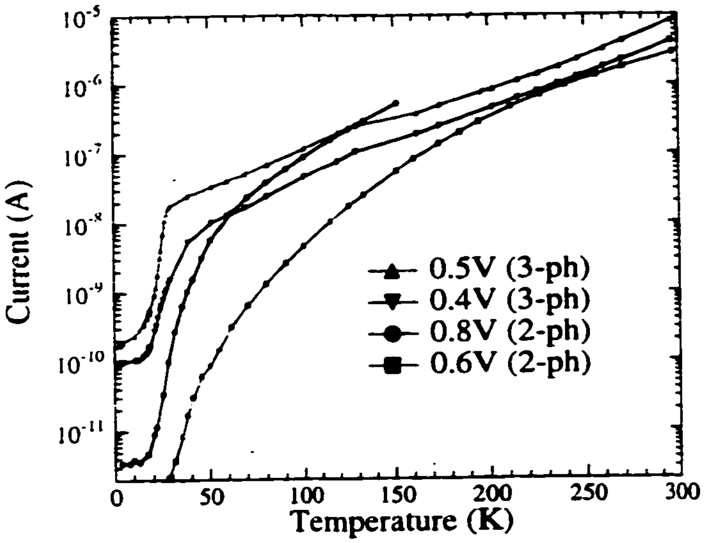


Figure 3: Plot of current versus temperature of molecules **31** and **32**.

According to Figure 3, **31** and **32** show a decrease in conductance between 20 and 40 K in the temperature-current plots.[29] At lower temperatures, phenylene ethynylenes have the tendency to fishbone pack whereas the phenyl rings are perpendicular to each other, decreasing the π-orbital overlap therefore lowering their conductivity, as seen in Figure 3.[28] As the SAM is heated, its kinetic energy allows the bonds to spin thus overcoming any activation barrier to rotation in the molecules. This movement permits the phenyl subunits to attain planarity and conduction occurs.[28]

This phenomenon of the altering conductivity by changing the degree of a molecule's π-orbital overlap led to the concept of molecular scale wires that will be able to act as molecular scale gates. The use of a molecular scale wire that will be able to conduct in the ground state and have no conductivity in the "perturbed" state, and the converse, would allow these wires to act as molecular scale switches and devices. These devices will allow us to perform any logical function that can be translated in Boolean logic, the basic language of all computers. The use of an electric field that is perpendicular to the SAM will allow us to control the conductivity of the molecular scale device (Figure 4).

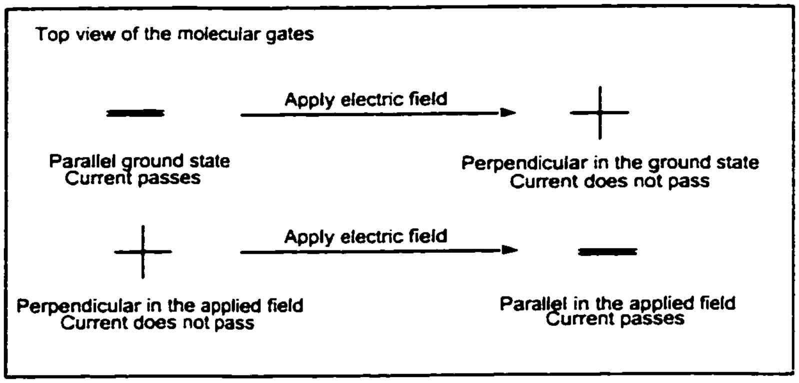

Top view of the molecular gates
Apply electric field
Parallel ground state
Current passes
Perpendicular in the ground state
Current does not pass
Apply electric field
Perpendicular in the applied field
Current does not pass
Parallel in the applied field
Current passes

Figure 4: Schematic of the molecular scale wire gate.

Testing of Molecular Scale Device Controller Type I

The first molecular scale switch, controller type I, that we decided to synthesize would be "on" in the ground state and "off" in the perturbed state (Figure 4). Controller type I is similar to the molecular scale wires that have been synthesized previously;

however, the interior phenyl ring possesses a large dipole moment that will orient itself with an electric field. By creating an electric field perpendicular to the SAM in the nanopore device, we will be able to manipulate the interior phenyl ring to be perpendicular to the other adjacent phenyl rings. This will cause orthogonality in the π-orbital overlap between neighboring phenyl rings, and thus conductance will decrease.

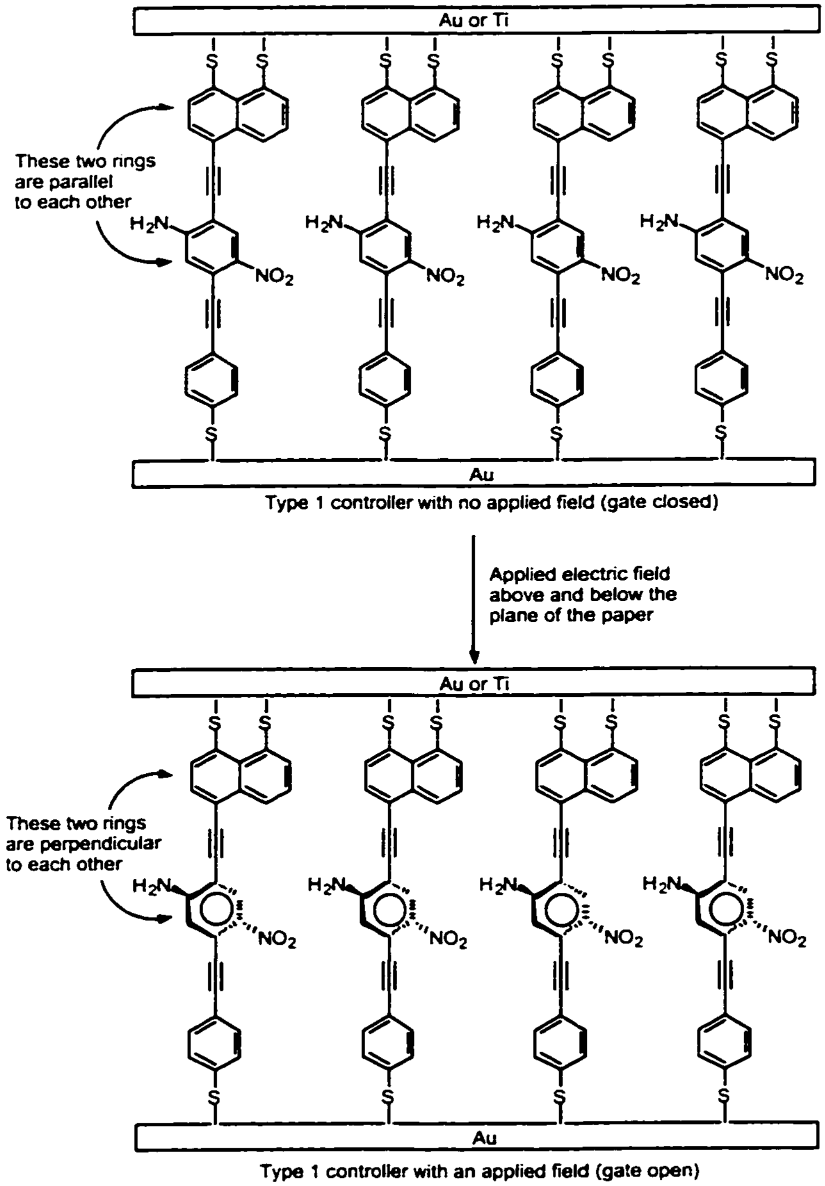
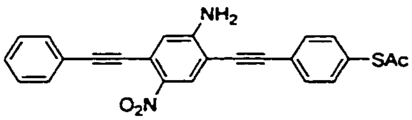

Au or Ti
S
These two rings are parallel to each other
H_2N
NO_2
Au
Type 1 controller with no applied field (gate closed)
Applied electric field above and below the plane of the paper
Au or Ti
These two rings are perpendicular to each other
H_2N
NO_2
Au
Type 1 controller with an applied field (gate open)

Figure 5: Schematic of a controller type I

The nanopore device with an electric field perpendicular to the SAM is currently being fabricated, thus the molecular scale controllers type I have not yet been tested as switching devices. Yet, it is necessary to determine the effects of electron withdrawing and electron donating groups on the conductivity of the molecular scale wire.



5

Compound **5** was then tested in the nanopore, in the absence of an external electric field, to determine its electronic characteristics. A series of control experiments were performed with alkanethiol-derived SAMs, silicon nitride membranes without pores, and membranes with pores but without molecules. Both the Au–alkanethiolate–Au junctions and the Au-silicon nitride membrane–Au junctions showed current levels at the noise limit of the apparatus (< 1 pA) for both bias polarities at both room and low temperatures. The Au-Au junctions gave ohmic I(V) characteristics with very low resistances. A device containing a SAM of conjugated molecules similar to **5** but not bearing the nitroamine functionalities was fabricated and measured in nearly identical conditions [30] and did not exhibit any non-linear I(V) behavior (Figure 2).

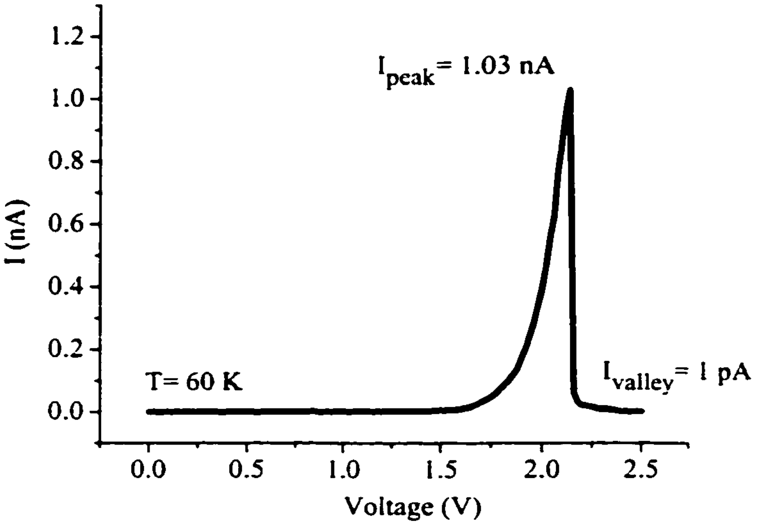


Figure 6: I(V) characteristics of an Au-(**5**)-Au device at 60 K.

Typical I(V) characteristics of an Au-(**5**)-Au device at 60 K are shown in Figure 6. Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact and electron injection from the evaporated contact. Unlike previous devices that also used molecules to form the active region,[31] this device exhibits a robust and large negative differential resistance (NDR) with a valley-to-peak ratio (PVR) of 1030:1. Some device-to-device variations of peak voltage position (~×2) and peak current (~×4) were observed.[32] The I(V) curve is fully reversible upon change in bias sweep direction; for a given device, small fluctuations (~1% in voltage peak position and ~6% in peak current) were observed with consecutive positive and negative sweeps but could be attributed to temperature fluctuations of ~2K (within the experimental thermal stability). The performance exceeds that observed in typical solid-state quantum well resonant tunneling heterostructures.[33] In addition to the obvious size advantages for scaling, the intrinsic device characteristics (that is, the valley current shutoff) may be superior to that of solid-state devices. The intrinsic PVR of the molecule may be considerably greater than that reported here, because the valley currents observed (on the order of picoamperes) are comparable to typical leakage currents in the silicon nitride. All of the devices examined exhibit peak voltage position and current magnitude shifts with temperature.[13]

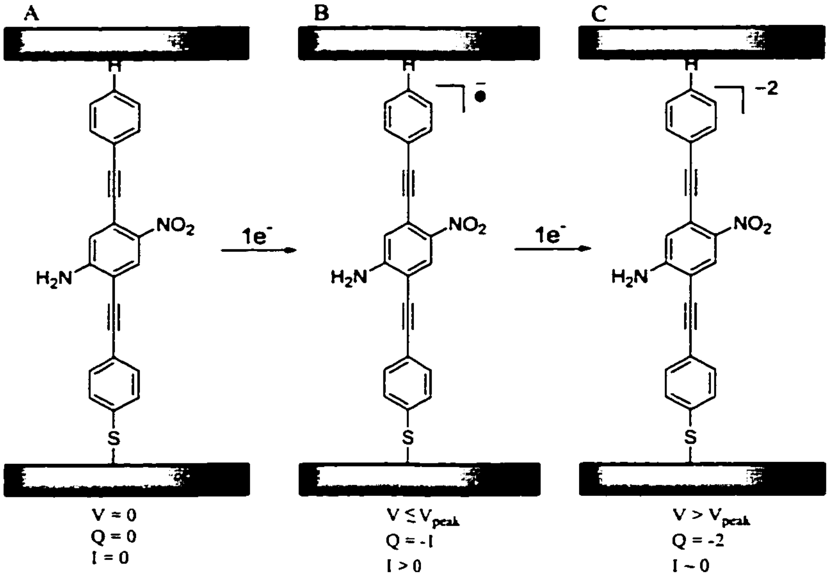


Figure 7: Potential mechanism for the NDR effect. As voltage is applied, the molecules in the SAM (A) undergo a one-electron reduction to form the radical anion (B) that provides a conductive state. Further increase of the voltage causes another one-electron reduction to form the dianion, insulating state (C).

A candidate mechanism for the NDR is a two-step reduction process that modifies charge transport through the molecule, as illustrated in Figure 7. As the voltage is increased, the molecule initially undergoes a one-electron reduction, thereby supplying a charge carrier for electron flow through the system (although the nitro moiety is the most electron-withdrawing group in the molecule, the charge is likely dispersed throughout the entire molecule). A further increase in voltage causes a second-electron reduction with subsequent blocking of the current. The width of the I(V) peak (~ 0.7 V) correlates well with the difference between the one-electron and two-electron peak reduction potentials (Ep_2-Ep_1= ΔEp = 0.63 V and 0.68 V for **5** with Z = SCH_3 and Z = H, respectively).[34] The NDR behavior is absent in the control molecule (no amine or nitro moieties)[30] and no electrochemical reduction peaks are observed over the corresponding voltage range.

Density functional theory (DFT) calculations on the lowest unoccupied molecular orbitals (LUMO) with respect to the reduction potential of a compound similar to **5** have been performed, Figure 8.[18] In the ground state (Q=0), the LUMO extends over most of the compound except for portions of the bottom phenyl ring which disrupts the continuity of the π-orbital network and therefore conduction is curtailed. As the voltage is increased across this compound, a voltage is attained when this compound is reduced with a single electron (Q= -1), the molecular orbital is perturbed allowing for the LUMO to extend over the entire molecule and conduction occurs. By further increasing the potential, the compound is reduced again with a second single electron that again perturbs the LUMO. In this reduction state (Q= -2), the LUMO does not extend over the entire compound and conduction ceases. A possible explanation of the gradual conduction commencing compared to ceasing may be due to electrons having the ability to tunnel between orbitals in the Q=0 state whereas the discontinuity, tunneling distance, in the LUMO of the Q= -2 state is too great for tunneling to occur.

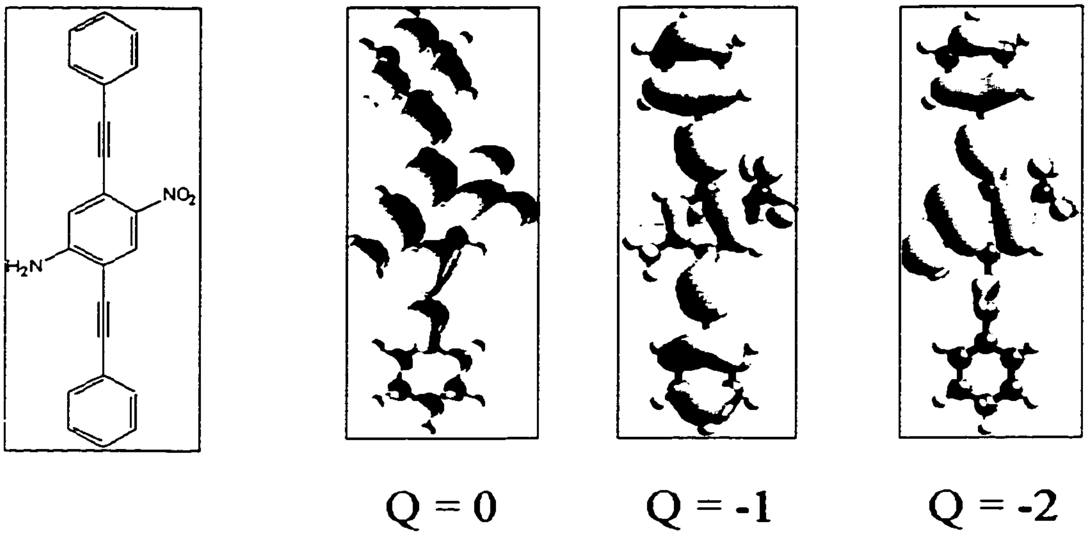

NO2
H2N
Q = 0
Q = -1
Q = -2

Figure 8: DFT Calculations for the Reduction Potentials of Compound **5**.

Additionally, we demonstrate here charge storage in a self-assembled nanoscale molecular device 1) that is operated as a random access memory, 2) with practical thresholds and output under ambient operation, and 3) with the ability to be scaled to the single molecule level.

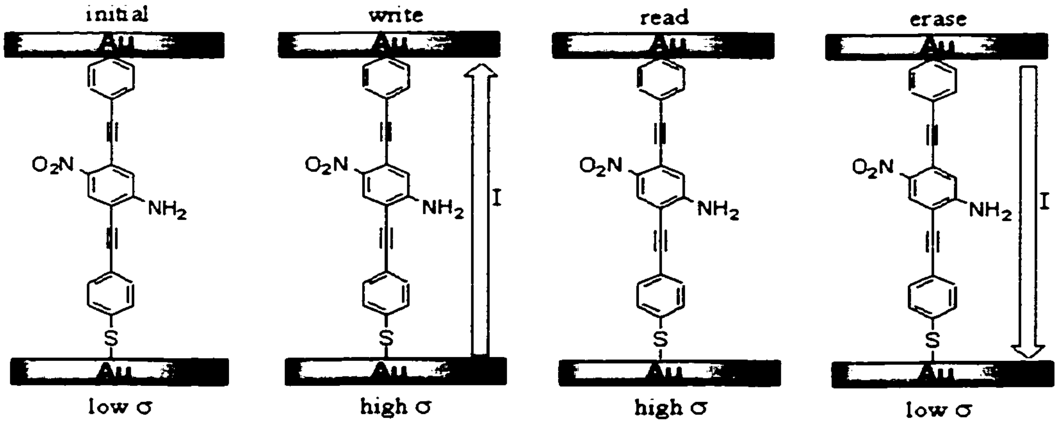
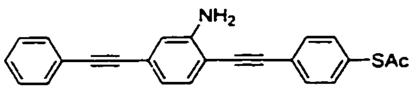
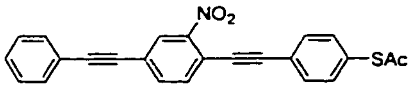

initial
write
read
erase
Au
O2N
NH2
S
I
low σ
high σ
high σ
low σ

Figure 9: Write, Read, and Erase sequences for the compound **5** use as random access memory.

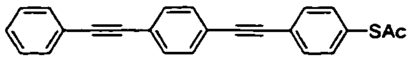
The memory device operates by the storage of a high or low conductivity state. Figure 9 shows the write, read, and erase sequence for **5**. An initially low conductivity state (low σ) is changed (written) into a high conductivity state (high σ) upon application of a voltage pulse. The direction of current that flows during this "write" pulse is diagrammed. The high σ state persists as a stored "bit", which is unaffected by successive read pulses.



12



33



34

Compounds with the nitro moieties **5** and **33** are observed to change conductivity state, whereas the amine only compound **12** and an unfunctionalized oligo(phenylene ethynylene) **34** do not exhibit storage. In the following, we first describe the characteristics obtained by linear voltage sweeps (so as to generate I(V) plots). Second we demonstrate the same effects and a circuit using voltage pulses.[14]

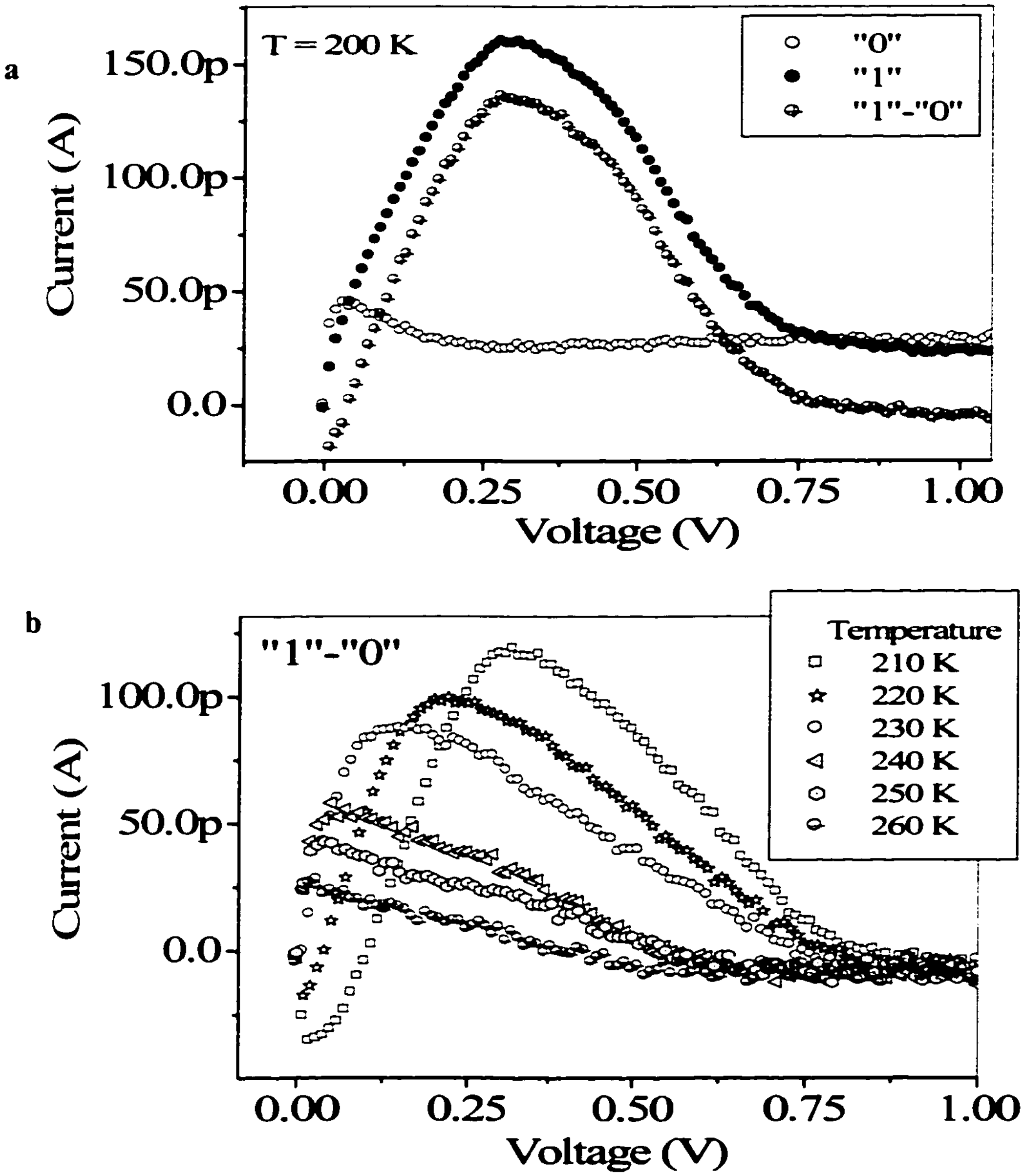


Figure 10: I(V) characteristics of an Au-(**5**)-Au device. **a**) The device at 200 K. "0" denotes the initial state, "1" the stored written state, and "1"-"0" the difference of the two states. Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact. **b**) Difference curves ("1"-"0") as a function of temperature.

Figure 10a shows the I(V) characteristics[35] of a Au-(5)-Au device at 200 K initially (defined as "0") and after (defined as "1") a write pulse, as well as the difference between the two (defined as "1"-"0"). Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact. The device initially probed with a positive voltage exhibits a low conductivity state. Subsequent positive sweeps show a high conductivity state with I(V) characteristics identical to the previous values ("1"). Device bias swept in the reverse bias direction causes the I(V) to be identically reset to the initial, "0" I(V) characteristic. The characteristics are repeatable to high accuracy and device degradation is not observed. This ability to program, read, and refresh the state of the molecular device accomplishes the functionality of a random access memory (RAM). Figure 10b shows the difference characteristic ("1"-"0") of compound **5** as a function of temperature. The peak current difference decreases approximately linear with increasing temperature over the range illustrated.[14]

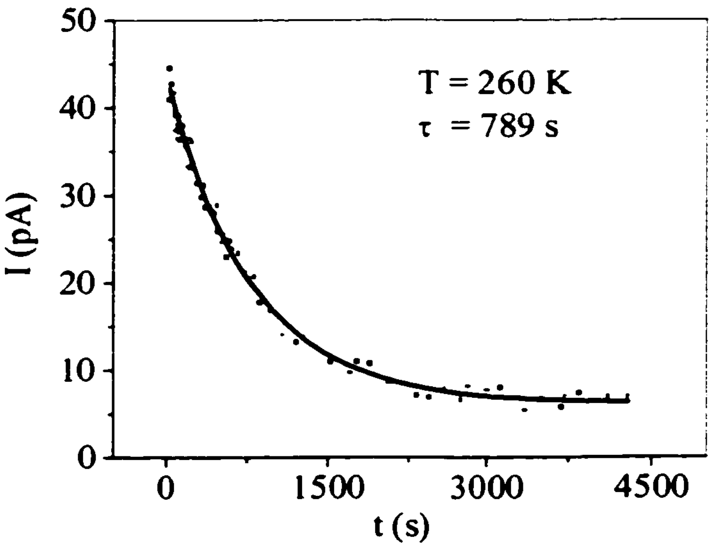


Figure 11: Bit retention as a function of time and temperature. Bit retention for (**5**) exhibits an exponential decay with a time constant (τ) of 790 seconds at 260 K.

A characteristic bit retention time was obtained by measuring the stored high conductivity state at various times intervals after programming the Au-(**5**)-Au device. After an initial write bias sweep, the peak current of the stored state "1" exhibits an exponential decay with a time constant (τ) of approximately 800 seconds at 260 K (Figure 11).

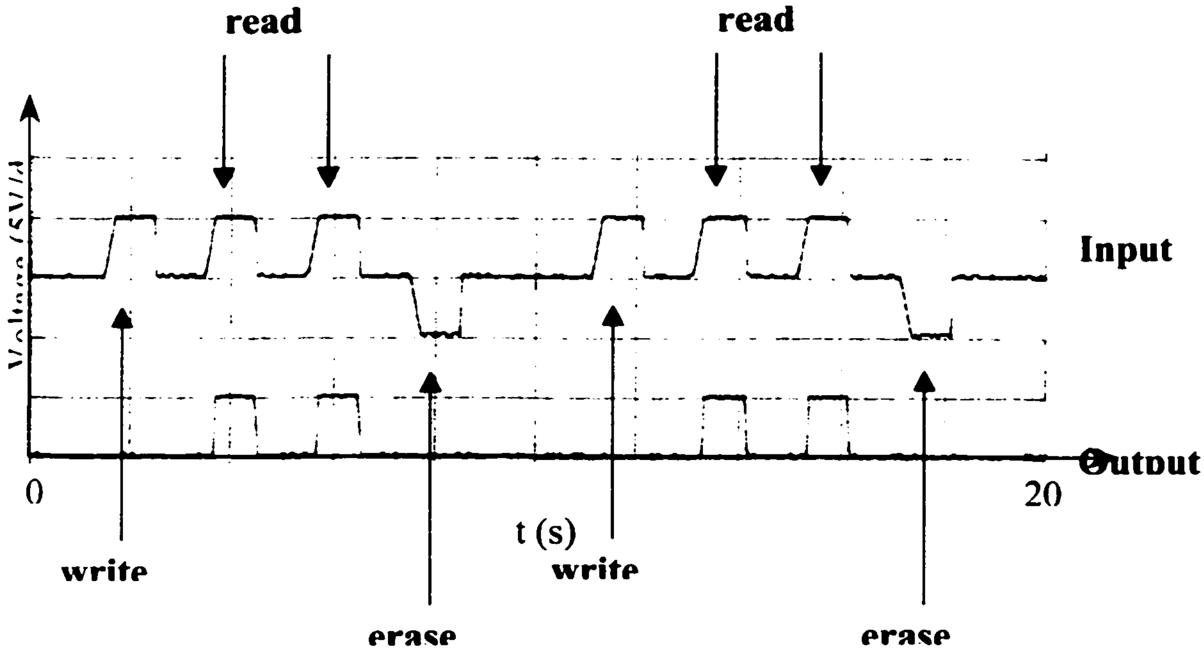
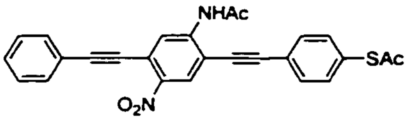


Figure 12: Measured logic diagram of the molecular random access memory (mRAM) compound **8**.

Figure 12 is a measured logic diagram demonstrating a SRAM cell using compound **33** containing a nitro moiety only at ambient temperature. To convert the stored conductivity to standard voltage conventions, the output of the device was dropped across a resistor, sent to a comparator, and inverted and gated with the "read" pulse. The upper trace shown in Figure 12 is an input waveform applied to the device, and the lower is the RAM cell output. The first positive pulse configures the state of the cell by writing a bit, and the second and third positive pulses read the cell. The third pulse (and subsequent read pulses, not shown here for simplicity) demonstrates that the cell is robust and continues to hold the state (up to the limit of the bit retention time). This demonstration highlights the dramatically long bit retention time. The negative pulse erases the bit, resetting the cell. The second set of 4 pulses repeats this pattern, and many hours of continuous operation have been observed with no degradation in performance.[14] There are no indications in the characteristics observed in this study that limitations exist for scaling the number of molecules in the active region of the device to one, assuming that an appropriate fabrication scheme can be identified.

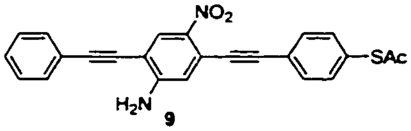
To further explore the mechanism of this molecular NDR and mRAM phenomenon, numerous similar molecules have been synthesized. Compound **7** differs from NDR molecule **5** in that it possesses an acetamide rather than an amine moiety.



6

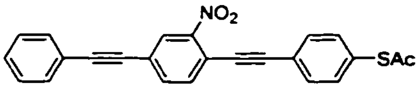
After conductivity testing in the nanopore, compound **7** exhibited the NDR effect, yet, a smaller valley to peak ratio of 200:1 at 60 K.

To determine if the orientation of the dipole moment relative to the SAM surface affected the electronic characteristics, molecule **9** was synthesized. This compound possesses a dipole that is directed towards the thioacetyl terminus that is opposite of the dipole in compound **5**. Currently, no conductivity tests have been performed on this compound.



9

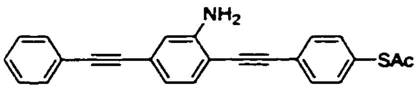
To determine if the NDR effect is influenced solely by an electron withdrawing or donating moiety on the interior phenyl ring or by the presence of both groups the following compounds have been synthesized.

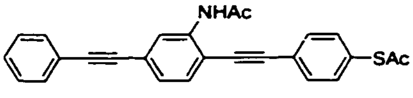


33

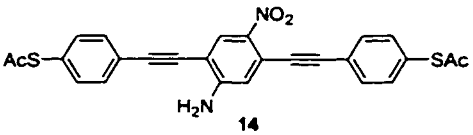
David Price, Jr. synthesized the nitro only containing molecular scale device in our laboratory. It remarkably showed both NDR and mRAM capabilities at room temperature. Memory effects were observed in devices with the molecules having only the nitro moiety **33**, although in this case the storage was of a *low* conductivity state, opposite to that of compound **5**. The details of the mechanism that causes a high conductivity state in **5** and a low conductivity state in **33** is presently under investigation.[29]

To determine the contribution of and electron donating moiety to its electrical properties compounds **12** and **13** were synthesized. Compound **12** demonstrated no NDR effects or mRAM properties.[14] Therefore, it is hypothesized that the nitro group is the necessary moiety for the development of molecular scale devices that show the NDR effect and mRAM properties.

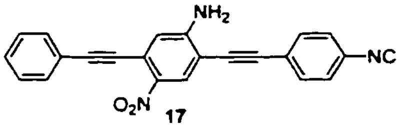

12


13

Similar to molecular scale device **12**, the acetamide adduct was synthesized. Currently, there have been no electrical conductivity studies performed on compound **13**, yet, it is hypothesized that this compound will not demonstrate the NDR effect. A two terminal molecular scale device that is similar to NDR compound **5** has been synthesized for the attachment between two gold particles, yet, no conductivity tests have been performed on this compound.

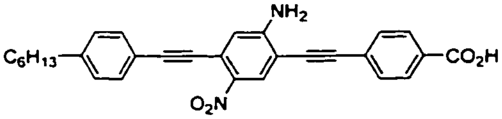

14

The conduction diminishing contact resistance barrier between the organic wire-sulfur-gold has been studied in detail over the last few years.[15,36-39] To reduce this conduction barrier, the sulfur has been replaced with more metallic Se and Te termini to allow for greater overlap of the compounds LUMO and the gold's Fermi levels. Nonetheless, it was determined that neither the selenium nor tellurium alligator clip significantly reduced the barrier height.[39]



17

Recently it has been discovered that the use of an isonitrile as the contact between the organic molecular scale wire and the metal probe would significantly reduce the conduction barrier,[40] and would allow an increase in the conductivity of the molecular scale wires. Therefore molecular scale device **17** with an isonitrile attachment moiety was synthesized. Compound **17** is currently being tested for NDR and mRAM properties.



22

Currently, the formation of a SAM is the method of attachment of these molecular scale wires to the metal probe and devices. An additional method of preparing ordered monolayers of molecular devices is the use of Langmuir-Blodgett films.[21] Therefore, a compound with hydrophilic and hydrophobic subunits with the central core of the NDR molecule **5** was synthesized. Electrical conductivity tests are currently being performed on **22**.

Testing of Molecular Scale Device Controller Type II

Molecular device controller type II will not conduct in the ground state but will conduct in the "perturbed" state. We envision the compound in Figure 13 acting as a controller type II. In the ground state, the biphenyl ring system will be non-planar due to steric interactions. This will cause the π-orbitals of the molecular device to be non-planar thus decreasing the electrical conductivity of this device. In an electric field, the molecular scale device will exist more in the planarized zwitterionic resonance form that will allow the π-orbitals to be parallel and conductance will occur.

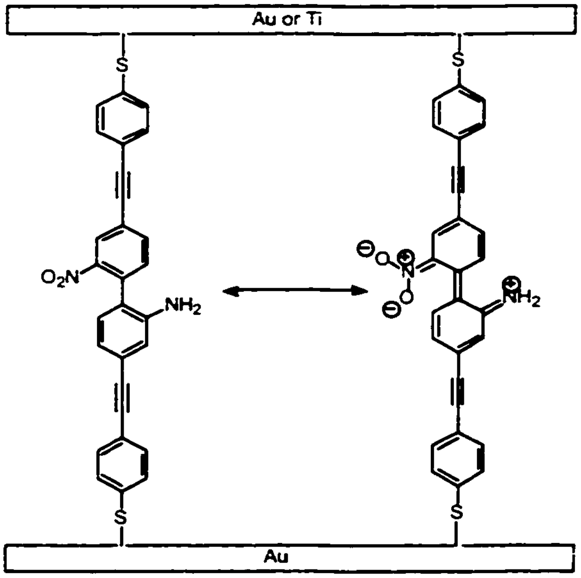
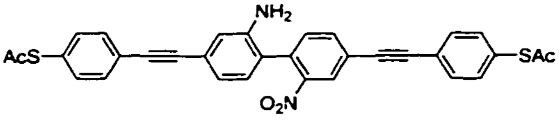


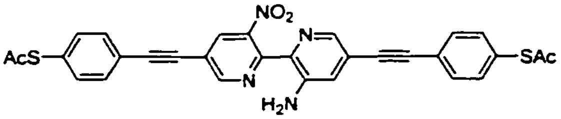
Figure 13: Schematic of Molecular Device Controller Type II

It is not imperative that the molecular controller type II be entirely planar in the perturbed state. There will be steric interactions between the amino/nitro moieties and the phenyl protons on the adjacent ring that may not allow the system to achieve planarity. Though, in the perturbed state, the SAM will be more planar which will permit more π-orbital overlap, thus its conductivity will be greater. The increased conductivity in the perturbed state, compared to the ground state, will allow this material to function as a molecular scale switch. Therefore, compound **26** was synthesized.



26

An additional molecular switch II was synthesized based on a pyridine ring system, eq 10. The pyridine ring system may allow for a greater degree of planarity in the zwitterionic form due to the decreased steric interactions between the nitrogen and the nitro or amino moieties compared to the carbon-hydrogen interaction with the same.



30

Due to the difficulties in fabrication of the nanopore with an electrical field perpendicular to the SAM formed, conductivity and switching studies on compounds **26** and **30** have not yet been performed.

Summary

This chapter has summarized the great utility of highly conjugated oligo(phenylene ethynylene)s in the field of electronics. We have demonstrated that organic material can possess NDR and mRAM capabilities and may significantly affect the electronics industry that would allow for the further miniaturization of computing devices. The use of highly conjugated organic materials has the ability to enhance the electronic properties of many devices and therefore improve the lives of many.

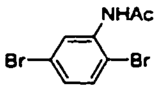
Experimental

General. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. All reagents and starting materials were purchased from Aldrich, Acros, Fischer, Fluka, and Alfa Aesar if not otherwise stated. Alkyllithium reagents were obtained from FMC. Pyridine, methyl iodide, triethylamine, and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Toluene and benzene were distilled over CaH_2. Methylene chloride and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine and *N, N*-diisopropylethylamine was distilled over CaH_2. MeOH was dried over oven dried 3 Å molecular sieves. ^1H NMR spectra were recorded at 300, 400, or 500 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively or at 400 and 500 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively or at 400 MHz on Oxford Instruments 400 MHz NMR using Brüker XWIN NMR processing program. The ^{13}C NMR spectra were recorded at 75, 100, or 125 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively at 100 and 125 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively or at 125 MHz on Oxford Instruments 400 MHz NMR using Brüker XWIN NMR processing program. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0-ppm $CDCl_3$ resonance as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. Gas chromatography experiments were performed on a

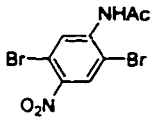
Hewlett-Packar GC model 5890A equipped with an Alltech column (cat # 932525, serial # 9059) 25 m × 0.25 mm D × 0.2 mm. Gravity column chromatography, silica gel plugs, and flash chromatography were preformed using 230-400 mesh silica gel from EM Science. Thin layer chromatography was preformed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Combustion analyses were obtained from Atlantic Microlab, Inc., P. O. Box 2288, Norcross, GA 30091.

General Procedure for the coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).[41] To an oven dried round bottom flask equipped with a water cooled West condenser or screw capped pressure tube with a magnetic stirbar were added the aryl halide, bis(triphenylphosphine)palladium(II) chloride (3-5 mol % per halide), and copper(I) iodide (6-10 mol % per halide). Triphenylphosphine was used in some reactions to keep the palladium in solution. The vessel was then sealed with a rubber septum under a N_2 atmosphere. A co-solvent system of THF, benzene, or methylene chloride was added at this point depending on the solubility of the aryl halide. Then base, either triethylamine or *N,N*-diisopropylethylamine, was added and finally the terminal alkyne (1-1.5 mol % per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was then quenched with water, a saturated solution of NH_4Cl, or brine. The organic layer was diluted with methylene chloride or Et_2O and washed with water, a saturated solution of NH_4Cl, or brine (3×). The combined aqueous layers were extracted with methylene chloride or Et_2O (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each material.

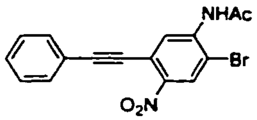
General procedure for the deprotection of trimethylsilyl protected alkynes (Method A). The silylated alkyne was dissolved in methanol and potassium carbonate was added. The mixture was stirred overnight before poured into water. The solution was extracted with ether or ethyl acetate and washed with brine. After drying over magnesium sulfate the solvent was evaporated *in vacuo* to afford pure products. **(Method B).** The silylated alkyne was dissolved in pyridine in a plastic vessel. A mixed solution of 49% hydrofluoric acid and 1.0 M tetrabutylammonium fluoride in THF was added at room temperature. The solution was stirred for 15 min and quenched with silica gel. The mixture was poured into water and extracted with ether. The extract was washed with brine and dried over magnesium sulfate. After filtration the solvent was evaporated *in vacuo*. The crude products were purified by a flash chromatography on silica gel. Eluents and other slight modifications are described below for each material.



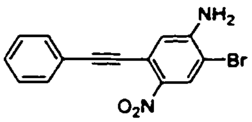
2,5-Dibromoacetanilide (AMR-II-45, 151, 161).[17] To a 500 mL round bottom flask equipped with a magnetic stirbar and a West condenser were added 2,5-dibromoaniline (1.38 g, 55.0 mmol), acetic anhydride (50 mL), and water (50 mL). The reaction mixture was allowed to heat to reflux for 12 h. The resultant mixture was cooled to ambient temperature and poured into water (500 mL). The precipitate was collected by filtration and further washed by water. The reaction afforded 14.25 g (88 % yield) of the desired material. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (br s, 1 H), 7.60 (br s, 1 H), 7.36 (d, *J*=8.5 Hz, 1 H), 7.08 (dd, *J*=8.5, 2.4, Hz, 1 H), 2.22 (s, 3 H).



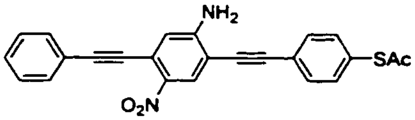
2,5-Dibromo-4-nitroacetanilide (2, AMR-II-46).[17] To a oven dried 500 mL round bottom flask equipped with a magnetic stirbar were added sulfuric acid (50 mL), and nitric acid (50 mL) and the reaction mixture was cooled to 0 °C. 2,5-Dibromoacetonilide (14.25 g, 48.65 mmol) was added and the reaction mixture was allowed to stir for 2.5 h. Upon completion, ice (300 g) was added slowly to the reaction mixture. The reaction mixture was filtered and the solid collected. The desired material was purified by flash liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product)= 0.77. The reaction afforded 11.27 g (69 % yield) of the desired material. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1 H), 8.19 (s, 1 H), 7.76 (br s, 1 H), 2.30 (s, 3 H).



2-Bromo-4-nitro-5-(phenylethynyl)acetanilide (3, AMR-II-49, III-11). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2,5-Dibromo-4-nitroacetanilide (3.0 g, 8.88 mmol) was coupled to phenylacetylene (0.98 mL, 8.88 mmol) as described above using copper(I) iodide (0.17 g, 0.89 mmol), bis(triphenylphosphine)palladium(II) chloride (0.25 g, 0.44 mmol), triphenylphosphine (0.47 g, 1.78 mmol), *N,N*-diisopropylethylamine (6.18 mL, 35.52 mmol), and THF (25 mL) in an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar. The reaction mixture was allowed to react at room temperature for 1 d then was heated to 50 °C for 12 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.60. The reaction afforded 1.79 g (56% yield, first crop) of the desired product. IR (KBr) 3261.5, 3097.4, 2215.4, 1671.8, 1553.8, 1533.3, 1502.6, 1379.5, 1333.3, 1261.5, 1092.3, 1020.5, 892.3, 851.3, 753.8, 687.2, 651.3 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1 H), 8.39 (s, 1 H), 7.80 (br s, 1 H), 7.66-7.60 (m, 2 H), 7.43-7.36 (m, 3 H), 2.32 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.30, 139.81, 132.20, 129.49, 129.03, 128.49, 124.87, 122.21, 119.88, 117.49, 111.00, 98.64, 84.81, 25.33. HRMS calcd $C_{16}H_{11}N_2O_3Br$: 357.9953. Found: 357.9948.

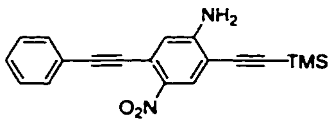


2-Bromo-4-nitro-5-(phenylethynyl)aniline (AMR-II-55, 233, 273, III-5, 15, 23). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. To a 100 mL round bottom flask equipped with a magnetic stirbar 2-bromo-4-nitro-5-(phenylethynyl)acetanilide (0.33 g, 0.92 mmol), potassium carbonate (0.64 g, 4.6 mmol), methanol (15 mL), and methylene chloride (15 mL) was added. The reaction was allowed to stir at room temperature for 1 h. The reaction mixture was quenched with water and extracted with methylene chloride (3 ×). The organic layers were combined and dried over magnesium carbonate. Solvents were removed in vacuo. No further purification needed. The reaction afforded 0.29 g (100% yield) of the titled compound as a yellow solid. IR (KBr) 3476.9, 3374.4, 3159.0, 1656.4, 1615.4, 1559.0, 1379.5, 1307.7, 1138.5, 1102.6, 892.3, 748.7, 687.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.74-7.68 (m, 2 H), 7.52-7.46 (m, 3 H), 7.06 (s, 1 H), 4.93 (br s, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.55, 139.41, 132.02, 130.45, 129.25, 128.46, 122.46, 120.17, 118.38, 106.86, 96.94, 85.46. HRMS calcd: 317.9828. Found: 317.9841.



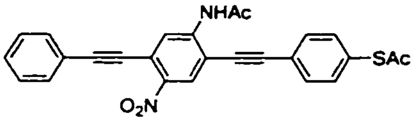
2′-Amino-4,4′-diphenylethynyl-5′-nitro-1-thioacetylbenzene (5, AMR-II-69, 253). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-

nitro-5-(phenylethynyl)aniline (0.10 g, 0.30 mmol) was coupled to 1-thioacetyl-4-ethynylbenzene (0.10 g, 0.56 mmol) as described above using copper(I) iodide (0.01 g, 0.03 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), triphenylphosphine (0.02 g, 0.06 mmol), *N,N*-diisopropylethylamine (0.24 mL, 1.40 mmol), and THF (10 mL) in an oven dried round screw capped pressure tube equipped with a stirbar. The reaction mixture was allowed to react at 80 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.26. An additional hexanes wash gave pure yellow crystals of the desired compound, 0.80 g (67 % yield). IR (KBr) 3374.4, 3138.5, 2205.1, 1384.6, 1312.8, 1246.2, 1112.8, 825.6, 753.8, 692.3, 615.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 7.59 (m, 2 H), 7.55 (d, *J*=8.0 Hz, 2 H), 7.42 (d, *J*=8.2 Hz, 2 H), 7.38 (m, 3 H), 6.92 (s, 1 H), 4.89 (br s, 2 H), 2.45 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 193.03, 150.99, 139.53, 134.36, 132.12, 132.08, 130.24, 129.23, 129.19, 128.441, 123.21, 122.55, 121.06, 118.01, 106.88, 97.66, 96.53, 85.98, 84.89, 30.51. HRMS calcd $C_{24}H_{16}N_2O_3S$: 412.0882. Found: 412.0882.

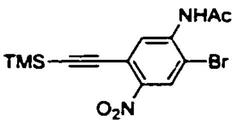


4-Nitro-3-phenylethynyl-6-trimethylsilylethynylaniline (AMR-II-235). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-nitro-5-(phenylethynyl)aniline (0.26 g, 0.83 mmol) was coupled to trimethylsilylacetylene (0.17

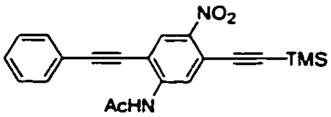
mL, 1.25 mmol) using copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), *N,N*-diisopropylethylamine (0.58 mL, 3.32 mmol), and THF (10 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.72. The reaction afforded 0.22 g (81 % yield) of the desired compound. IR (KBr) 3465.06, 3350.39, 3214.34, 2958.03, 2360.06, 2341.17, 2146.27, 1625.20, 1539.10, 1507.32, 1305.69, 1247.56, 1199.99, 1091.12, 878.19, 843.71, 756.00, 663.28, 472.37 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.65-7.60 (m, 2 H), 7.43-7.38 (m, 3 H), 6.91 (s, 1 H), 4.87 (br s, 2 H), 0.31 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.80, 139.68, 132.47, 130.77, 129.62, 128.85, 122.95, 121.37, 118.22, 107.50, 103.95, 99.08, 97.83, 86.32, 0.30. HRMS calcd $C_{19}H_{18}N_2O_2Si$: 334.1138. Found: 334.1135.



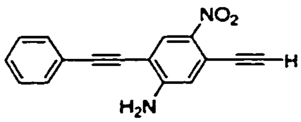
2′-Acetamido-4,4′-diphenylethynyl-5′-nitro-1-thioacetylbenzene (6, AMR-II-67). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-nitro-5-(phenylethynyl)acetanilide (0.10 g, 0.28 mmol) was coupled to 1-thioacetyl-4-ethynylbenzene (0.08 g, 0.45 mmol) as described above using copper(I) iodide (0.01 g, 0.02 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.01 mmol), triphenylphosphine (0.01 g, 0.04 mmol), *N,N*-diisopropylethylamine (0.19 mL, 1.12 mmol), and THF (10 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 80 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.40. The compound was further purified by a hexanes wash to give 0.10 g (82 % yield) of the desired compound as bright yellow crystals. IR (KBr) 3138.5, 2205.1, 1384.6, 1333.3, 1241.0, 1117.9, 953.8, 897.4, 825.6, 753.6, 687.2, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (s, 1 H), 8.29 (s, 1 H), 8.06 (br s, 1 H), 7.62 (m, 2 H), 7.57 (d, *J*=8.4 Hz, 2 H), 7.46 (d, *J*=8.5 Hz, 2H), 7.38 (m, 3 H), 2.64 (s, 3 H), 2.32 (s, 3 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 192.77, 168.29, 143.82, 142.02, 134.51, 132.23, 132.17, 130.17, 129.47, 128.61, 128.46, 123.57, 122.27, 122.21, 120.70, 111.15, 99.43, 98.68, 85.55, 83.51, 30.58, 25.33. HRMS calcd $C_{26}H_{18}N_2O_4S$: 454.0987. Found: 454.0987.



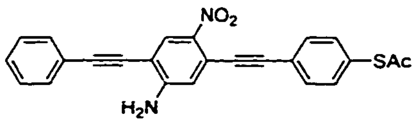
2-Bromo-4-nitro-5-(trimethylsilylethynyl)acetanilide (AMR-II-165). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2,5-Dibromo-4-nitroacetanilide (4.00 g, 11.84 mmol) was coupled to trimethylsilylacetylene (1.30 mL, 11.8 mmol) as described above using copper(I) iodide (0.22 g, 1.18 mmol), bis(triphenylphosphine)palladium(II) chloride (0.41 g, 0.59 mmol), *N,N*-diisopropylethylamine (8.25 mL, 47.36 mmol), and THF (80 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 70 °C for 2 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 diethyl ether/hexanes as the eluent. R_f (product): 0.43. The reaction afforded 1.46 g (35 % yield, 54 % based on a recovered 1.44 g of starting material) of the desired product. IR (KBr) 3384.6, 3107.7, 3056.4, 2964.1, 2143.6, 1717.9, 1559.0, 1523.1, 1492.3, 1446.2, 1379.5, 1333.3, 1246.2, 1225.6, 1097.4, 846.2, 764.1, 712.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1 H), 8.29 (s, 1 H), 7.75 (br s, 1 H), 2.30 (s, 3 H), 0.27 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.38, 145.60, 140.82, 129.90, 126.63, 120.52, 112.46, 106.70, 100.03, 26.45, 0.93. HRMS Calcd $C_{13}H_{15}BrN_2O_3Si$: 354.0035. Found: 354.0034.



2-(Phenylethynyl)-4-nitro-5-(trimethylsilylethynyl)acetanilide (7, AMR-II-169). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-nitro-5-(trimethylsilylethynyl)acetanilide (1.20 g, 3.38 mmol) was coupled to phenylacetylene (0.56 mL, 5.07 mmol) as described above using copper(I) iodide (0.06 g, 0.34 mmol), bis(triphenylphosphine)palladium(II) chloride (0.12 g, 0.17 mmol), *N,N*-diisopropylethylamine (2.36 mL, 13.52 mmol), and THF (25 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.38. The reaction afforded 1.00 g (79 % yield) of the desired product. IR (KBr) 3384.6, 3128.2, 2953.8, 2215.4, 2153.8, 1707.7, 1543.6, 1523.1, 1497.4, 1456.4, 1384.6, 1338.5, 1225.6, 1169.2, 1112.8, 1051.3, 846.2, 748.7, 687.2, 620.5 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1 H), 8.21 (d, *J*=0.03 Hz, 1 H), 8.07 (br s, 1 H), 7.57-7.52 (m, 2 H), 7.47-7.39 (m, 3 H), 2.30 (s, 3 H), 0.29 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.35, 145.49, 142.99, 132.82, 131.01, 129.94, 129.34, 125.26, 122.25, 121.06, 112.98, 107.23, 100.90, 100.76, 83.10, 26.45, 0.96. HRMS Calcd $C_{21}H_{20}N_2O_3Si$: 376.1243. Found: 376.1235.

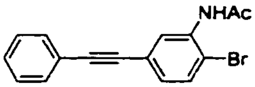


2-(Phenylethynyl)-4-nitro-5-(ethynyl)acetanilide (AMR-II-189). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 2-(Phenylethynyl)-4-nitro-5-(trimethylsilylethynyl)acetanilide (0.10 g, 0.27 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.19 g, 1.35 mmol), methanol (15 mL), and methylene chloride (15 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.



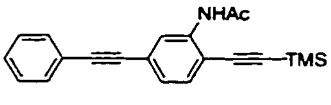
1-Thioacetyl-4(5′-amino-1′-(ethynyl)phenyl-2′-nitro-4′-(phenylethynyl)benzene (9, AMR-II-191). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-(Phenylethynyl)-4-nitro-5-(ethynyl)acetanilide (0.08 g, 0.27 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.09 g, 0.32 mmol) as described above using copper(I) iodide (0.005 g, 0.01 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.01 mmol), *N,N*-diisopropylethylamine (0.20 mL, 1.08 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 70 °C for 12 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/ hexanes as the eluent. R_f (product): 0.32. The reaction afforded 0.09 g (82 % yield) of the desired product as a yellow solid which turned yellowish-green upon standing. IR (KBr) 3466.7, 3364.1, 2205.1, 1702.6, 1615.4, 1548.7, 1507.7, 1476.9, 1307.7, 1246.2, 1117.9, 948.7, 912.8, 871.8, 820.5, 748.7, 682.1 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.61 (½ABq, *J*=8.4 Hz, 2H), 7.55 (m, 2 H), 7.41

(½Abq, J=8.4 Hz, 2 H), 7.41-7.35 (m, 3 H), 6.90 (s, 1 H), 4.93 (br s, 2 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.09, 150.93, 139.33, 134.98, 134.13, 132.46, 131.55, 130.06, 129.07, 128.49, 123.69, 121.94, 120.25, 117.91, 107.50, 97.51, 96.26, 87.50, 83.16, 30.45. HRMS Calcd $C_{24}H_{16}N_2O_3S$: 412.0882. Found: 412.0883.

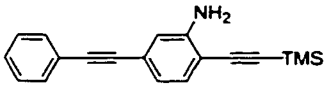


2-Bromo-5-(phenylethynyl)acetanilide (AMR-II-163). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2,5-Dibromoacetanilide (6.00 g, 17.76 mmol) was coupled to phenylacetylene (1.95 mL, 17.76 mmol) as described above using copper(I) iodide (0.34 g, 1.78 mmol), bis(triphenylphosphine)palladium(II) chloride (0.62 g, 0.89 mmol), *N,N*-diisopropylethylamine (12.37 mL, 71.04 mmol), and THF (75 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 2.5 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.38. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 hexanes/ethyl acetate as the eluent. R_f (product): 0.50. The reaction afforded 1.79 g (32 % yield, 42 % based on a recovered 0.69 g of starting material) of the desired compound as a white solid. IR (KBr) 3282.1, 3159.0, 1661.5, 1559.0, 1507.7, 1461.5, 1405.1, 1379.5, 1271.8, 1107.7, 1066.7, 1015.4, 964.1, 892.3, 861.5, 820.5, 748.7, 682.1, 610.3 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.66 (br s, 1 H), 7.92 (br s, 1 H), 7.55-7.49

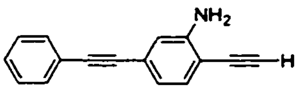
(m, 2 H), 7.41-7.37 (m, 3 H), 7.32 (½ABq, *J*=8.3 Hz, 1 H), 7.20 (½ABq d, *J*= 6.4, *J*=1.8 Hz, 1 H), 2.25 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.15, 140.81, 133.62, 132.61, 130.32, 129.80, 127.70, 124.93, 123.33, 123.15, 111.69, 98.63, 84.65, 26.32. HRMS Calcd $C_{16}H_{12}BrNO$: 313.0102. Found: 313.0107.



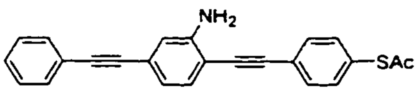
5-Phenylethynyl-2-(trimethylsilylethynyl)acetanilide (11, AMR-II-167). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-5-(phenylethynyl)acetanilide (0.91 g, 2.90 mmol) was coupled to trimethylsilylacetylene (0.47 mL, 4.35 mmol) as described above using copper(I) iodide (0.06 g, 0.29 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.15 mmol), *N,N*-diisopropylethylamine (2.02 mL, 11.60 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 70 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.33. The reaction afforded 0.81 g (84 % yield) of the desired compound as an airy yellow foam after drying in a vacuum atmosphere. IR (KBr) 3394.9, 3138.5, 2953.8, 2143.6, 1702.6, 1553.85, 1553.8, 1523.1, 1410.3, 1384.6, 1271.8, 1246.2, 1169.2, 1112.8, 1015.4, 846.2, 753.8, 687.2, 620.5 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.53 (br s, 1 H), 7.91 (br s, 1 H), 7.55-7.49 (m, 2 H), 7.43-7.36 (m, 4 H), 7.15 (dd, *J*= 6.6, 1.5 Hz, 1 H), 2.24 (s, 3 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.09, 139.72, 132.62, 132.49, 130.27, 129.79, 128.06, 125.58, 123.63, 123.24, 112.98, 105.68, 99.09, 97.67, 85.26, 26.33, 1.28. HRMS Calcd $C_{21}H_{21}BrNOSi$: 331.1392. Found: 331.1391.



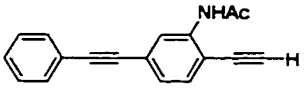
5-Phenylethynyl-2-(trimethylsilylethynyl)aniline (AMR-II-203). To a 100 mL round bottom flask equipped with a magnetic stirbar was charged with 5-phenylethynyl-2-(trimethylsilylethynyl)acetanilide (0.25 g, 0.75 mmol), hydrochloric acid (15 mL, 1.5 M), and THF (15 mL). The reaction mixture was heated to reflux for 2.5 h. The reaction progress was monitored by TLC. The reaction was quenched and extracted with water (3×) and diluted with methylene chloride. The organic layers were combined and dried over magnesium sulfate. Volatiles were removed in vacuo. Crude ^{1}H NMR and TLC showed two inseparable products with similar amine and aromatic resonances. Therefore, the crude reaction mixture was reacted further without purification.



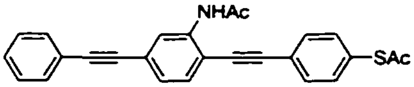
5-Phenylethynyl-2-(ethynyl)aniline (AMR-II-205). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 5-Phenylethynyl-2-(trimethylsilylethynyl)aniline (0.22 g, 0.75 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.52 g, 3.75 mmol), methanol (15 mL), and methylene chloride (15 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.



1-Thioacetyl-4(4′-(phenylethynyl)-2′-amino-1′-(ethynyl)phenyl)benzene (12, AMR-II-207). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 5-Phenylethynyl-2-(ethynyl)aniline (0.16 g, 0.75 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.25 g, 0.90 mmol) as described above using copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), *N,N*-diisopropylethylamine (0.53 mL, 3.00 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 45 °C for 12 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:3 diethyl ether/hexanes as the eluent. R_f (product): 0.40. The reaction afforded 0.28 g (43% yield, 2 steps) of the desired compound as a bright yellow solid. IR (KBr) 3138.5, 2205.1, 1702.6, 1610.3, 1384.6, 1117.9, 943.6, 825.6, 753.8, 692.3, 615.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 4 H), 7.42-7.31 (m, 6 H), 6.92-6.87 (m, 2 H), 4.32 (br s, 2 H), 4.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.66, 148.20, 134.72, 132.40, 131.75, 128.89, 128.86, 128.84, 128383, 124.60, 124.10, 123.32, 121.49, 117.14, 108.58, 96.57, 91.32, 89.72, 85.78, 30.48. HRMS Calcd $C_{24}H_{17}NOS$: 367.1031. Found: 367.1032.

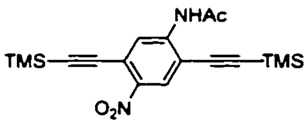


5-Phenylethynyl-2-(ethynyl)acetanilide (AMR-II-185). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 5-Phenylethynyl-2-(trimethylsilylethynyl)acetanilide (0.20 g, 0.60 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.25 g, 1.80 mmol), methanol (15 mL), and methylene chloride (15 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.



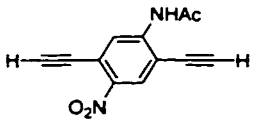
1-Thioacetyl-4(4′-(phenylethynyl)-2′-acetamide-1′-(ethynyl)phenyl)benzene (13, AMR-II-187). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 5-Phenylethynyl-2-(ethynyl)acetanilide (0.16 g, 0.60 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.20 g, 0.72 mmol) as described above using copper(I) iodide (0.01 g, 0.06 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.03 mmol), *N,N*-

diisopropylethylamine (0.42 mL, 2.40 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 70 °C for 12 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 ethyl acetate/ hexanes as the eluent. R_f (product): 0.35. The reaction afforded 0.12 g (50 % yield, 2 steps) of the desired compound as a off white solid. IR (KBr) 3138.5, 2933.3, 1702.6, 1656.4, 1543.6, 1379.5, 1261.5, 1112.8, 1010.3, 948.7, 882.1, 820.5, 748.7, 682.1, 610.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (br s, 1 H), 7.96 (br s, 1 H), 7.58-7.52 (m, 4 H), 7.46 (½ABq, *J*=7.8 Hz, 1 H), 7.42-7.37 (m, 5 H), 7.23 (½ABq d, *J*= 8.1, 1.4 Hz, 1 H), 2.43 (s, 3 H), 2.27 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.62, 168.51, 139.39, 134.70, 132.48, 132.02, 131.88, 129.52, 129.09, 129.00, 126.87, 124.41, 124.25, 122.45, 122.27, 112.45, 98.38, 91.06, 90.61, 84.24, 30.48, 25.10. HRMS Calcd $C_{26}H_{19}NO_2S$: 410.1215. Found: 410.1212.

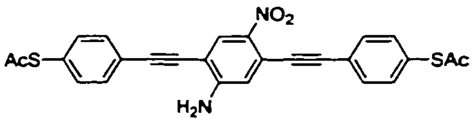


4-Nitro-2,5-bis(trimethylsilylethynyl)acetanilide (AMR-II-165, 209). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2,5-Dibromo-4-nitroacetanilide (0.60g, 1.78 mmol) was coupled to trimethylsilylacetylene (0.78 mL, 7.12 mmol) as described above using copper(I) iodide (0.07 g, 0.37 mmol), bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.18 mmol), *N,N*-

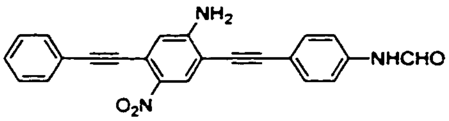
diisopropylethylamine (2.48 mL, 14.24 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 diethyl ether/hexanes as the eluent. R_f (product): 0.80. The reaction afforded 0.63 g (95 % yield; 0.26 g of material as the product with the deprotected amino moiety instead of the acetamide) of the desired product. IR (KBr) 3374.4, 3117.9, 2964.1, 2143.6, 1723.1, 1610.3, 1543.6, 1502.6, 1456.4, 1400.0, 1379.5, 1333.3, 1251.3, 1220.5, 1112.8, 882.1, 846.2, 759.0, 620.5 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72 (s, 1 H), 8.11 (s, 1 H), 8.07 (br s, 1 H), 2.25 (s, 3 H), 0.31 (s, 9 H), 0.26 (s, 9 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ169.27, 145.23, 143.53, 129.21, 124.94, 121.27, 112.68, 107.86, 107.26, 100.70, 98.57, 26.25, 1.08, 0.94. HRMS Calcd $C_{18}H_{24}N_2O_3Si_2$: 372.1325. Found: 372.1332.



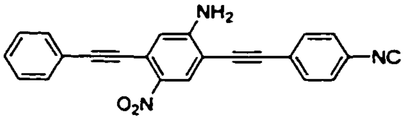
4-Nitro-2,5-di(ethynyl)aniline (AMR-II-211). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 4-Nitro-2,5-di(trimethylsilylethynyl)acetanilide (0.60 g, 1.61 mmol) was deprotected to the terminal alkyne using potassium carbonate (2.22 g, 16.10 mmol), methanol (40 mL), and methylene chloride (40 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.



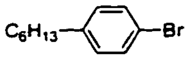
4-Nitro-2,5-di(4′-thioacetyl(phenylethynyl))aniline (14, AMR-II-213). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 4-Nitro-2,5-di(ethynyl)aniline (0.30 g, 1.61 mmol) was coupled to 1-iodo-4-thioacetylbenzene (1.09 g, 3.86 mmol) as described above using copper(I) iodide (0.06 g, 0.32 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.16 mmol), *N,N*-diisopropylethylamine (2.25 mL, 12.88 mmol), and THF (40 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 50 °C for 2 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f (product):0.52. The reaction afforded 0.47g (60 % yield, 2 steps) of the desired compound as a bright yellow solid. IR (KBr) 3476.9, 3364.1, 3117.9, 1687.2, 1625.6, 1543.6, 1507.7, 1476.9, 1384.6, 1307.7, 1246.2, 1117.9, 1010.3, 948.7, 825.6, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 7.62 (½ABq, *J*=8.2 Hz, 2 H), 7.56 (½ABq, *J*=8.4 Hz, 2 H), 7.44 (½ABq, *J*=4.4 Hz, 2 H), 7.42 (½ABq, *J*=4.2 Hz, 2 H), 6.92 (s, 1 H), 4.90 (br s, 2 H), 2.45 (s, 3 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.00, 192.91, 150.99, 134.26, 134.25, 134.25, 134.13, 134.11, 132.45, 132.04, 130.16, 123.64, 123.09, 120.52, 118.01, 107.00, 96.59, 96.45, 87.44, 84.79, 30.44, 30.42. HRMS Calcd $C_{24}H_{17}NOS$: 487.0786. Found: 487.0792.



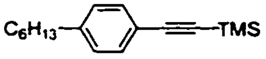
2′-Amino-4,4′-diphenylethynyl-1-formamido-5′-nitrobenzene (16, AMR-II-237,275, III-17). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-4-ethynylphenyl-5-nitroaniline (0.26 g, 0.83 mmol) was coupled to 1-ethynyl-4-formamidobenzene (0.15 g, 1.00 mmol) as described above using copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.03 g, 0.04 mmol), *N,N*-diisopropylethylamine (0.58 mL, 3.32 mmol), and THF (25 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 70 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f (product): 0.09. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of ethyl acetate as the eluent. R_f (product): 0.63. The reaction afforded an impure product of 0.23 g. The crude reaction product was taken on to the next synthetic step.



2′-Amino-4,4′-diphenylethynyl-5′-nitrobenzenisonitrile (17, AMR-II-263, 277, III-3,19,31).[20] To an oven dried 100 mL round bottom flask equipped with a stirbar and a West condensor 2′-Amino-4,4′-diphenylethynyl-1-formamido-5′-nitrobenzene (0.04, 0.10 mmol), triphenylphosphine (0.09 g, 0.33 mmol), triethylamine (0.04 mL, 0.39 mmol), carbontetrachloride (0.03 mL, 0.31 mmol), and methylene chloride (10 mL) were added. The reaction was heated to 60 °C for 5 h. The reaction mixture was cooled and quenched with water and extracted with methylene chloride (3×). Organic layers were combined and dried over $MgSO_4$. Volatiles were removed in vacuo. The crude reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and ethyl acetate as the eluent. R_f (product): 0.85. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.30. The reaction afforded 0.03 g (83 % yield, 2 steps) of the desired material. IR (KBr) 3450.62, 3358.15, 2925.78, 2855.52, 2200.00, 2114.03, 1618.06, 1542.38, 1506.39, 1432.51, 1367.16, 1309.39, 1246.34, 1203.57, 1144.72, 1097.07, 995.30, 835.22, 749.25, 470.10 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$) δ 8.32 (s, 1 H), 7.68-7.55 (m, 4 H), 7.45-7.37 (m, 5 H), 6.97 (s, 1 H), 4.89 (br s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.38, 133.03, 132.52, 132.07, 130.82, 129.74, 129.03, 128.89, 127.11, 126.98, 123.92, 122.86, 121.80, 118.54, 106.73, 98.30, 95.78, 86.36, 86.16. HRMS Calcd $C_{23}H_{13}N_3O_2$: 363.1008. Found: 363.1008.

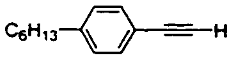


4-Bromo-1-*n*-hexylbenzene (AMR-I-261, 268).[22] In an 125 mL Erlenmeyer flask, bromine (0.52 mL, 10 mmol) was absorbed on neutral, Brockmann grade I alumina (10 g). 1-Phenylhexane (1.88 mL, 10 mmol) was absorbed on neutral alumina (10 g) in a second 125 mL Erlenmeyer flask. The contents of both flasks were combined in a 250 mL Erlenmeyer flask equipped with a magnetic stirbar. The reaction was complete within 1 min when the dark orange color of the bromine became light yellow. The solid mass was then poured in a column that contained a short plug of silica gel. The desired product was eluted with methylene chloride to give 2.58 g (100 % yield) of the desired clear oil. According to ^{1}H NMR, there was a ratio of products; 80:15:>5 (desired product: starting material: ortho substituted product). Isolation of the desired material was deemed to be more facile after the subsequent step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J*=8.2 Hz, 2 H), 7.03 (d, *J*=8.2 Hz, 2 H), 2.54 (t, *J*=7.5 Hz, 2 H), 1.60 (p, *J*=7.1 Hz, 2 H), 1.38-1.24 (m, 8 H), 0.92-0.84 (m , 3 H).

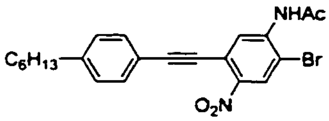


1-*n*-Hexyl-4-(trimethylsilylethynyl)benzene (AMR-I-266, 275, II-245). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 4-Bromo-1-*n*-

hexylbenzene (7.23 g, 30.0 mmol) was coupled to trimethylsilylacetylene (5.94 mL, 42.0 mmol) as described above using copper(I) iodide (0.69 g, 3.6 mmol), bis(triphenylphosphine)palladium(II) chloride (0.84 g, 1.2 mmol), triphenylphosphine (1.57 g, 6.0 mmol), triethylamine (30.36 mL. 300 mmol), and THF (30 mL) in a large oven dried pressure tube equipped with a magnetic stirbar. The reaction was sealed under a N_2 atmosphere and was heated to 85 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and hexanes as the eluent. The reaction afforded 5.26 g (68 % yield) of the desired material. IR (KBr) 2923.1, 2851.3, 2158.2, 1923.1, 1507.7, 1461.5, 1405.1, 1246.2, 1220.5, 861.5, 835.9, 753.8, 600.0 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J=8.0 Hz, 2 H), 7.07 (d, J=8.1 Hz, 2 H), 2.56 (t, J=7.7 Hz, 2 H), 1.62-1.50 (m, 2 H), 1.28 (br s, 8 H), 0.86 (br t, 3 H), 0.22 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.48, 131.75, 128.18, 120.17, 105.36, 93.15, 35.95, 31.76, 31.24, 28.95, 22.68, 14.18, 0.17. HRMS calcd $C_{17}H_{26}Si$: 258.1804. Found: 258.1793.

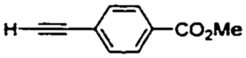


1-*n*-Hexyl-4-(ethynyl)benzene (AMR-I-270, II-6, 239, 255). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 1-*n*-Hexyl-4-(trimethylsilylethynyl)benzene (0.18 g, 0.7 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.48 g, 3.5 mmol), methanol (10 mL), and methylene chloride (10 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.

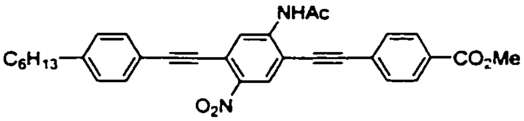


2-Bromo-4-nitro-5-(4′-*n*-hexylphenylethynyl)acetanilide (19, AMR-II-257). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2,5-Dibromo-4-nitroacetanilide (1.42 g, 4.21 mmol) was coupled to 1-ethynyl-4-*n*-hexylbenzene (0.95 g, 3.83 mmol) as described above using copper(I) iodide (0.02 g, 0.08 mmol), bis(triphenylphosphine)palladium(II) chloride (0.07 g, 0.38 mmol), *N,N*-diisopropylethylamine (2.69 mL, 15.38 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of methylene chloride as the eluent. R_f (product): 0.58. The reaction afforded 0.52 g (31% yield, 2 steps) of the desired material. IR (KBr) 3276.65, 3086.57, 3016.72, 2926.07, 2852.18, 2213.34, 1671.79, 1592.84, 1560.91, 1534.12, 1500.11, 1460.89, 1389.78, 1337.01, 1260.89, 1093.45, 1020.52, 894.33, 813.73, 743.88, 631.04, 464.48, 442.99 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$) δ 8.83 (s, 1 H), 8.39 (s, 1 H), 7.81 (br s, 1 H), 7.35 (ABq, J=8.3 Hz, Δv=110.6 Hz, 4 H), 2.65 (t,

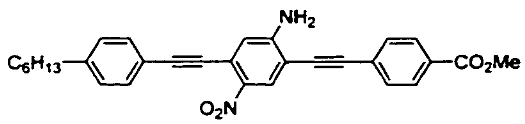
J=7.6 Hz, 2 H), 2.33 (s, 3 H), 1.63 (p, J=7.8, 6.1, 2 H), 1.40-1.22 (m, 6 H), 0.93 (t, J= 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.83, 145.36, 144.28, 140.22, 132.55, 129.38, 129.03, 125.18, 120.44, 119.69, 111.21, 99.49, 84.76, 36.43, 32.08, 31.53, 29.32, 25.49, 22.99, 14.49. HRMS Calcd $C_{22}H_{23}Br^{79}N_2O_3$: 442.0892. Found: 442.0895.



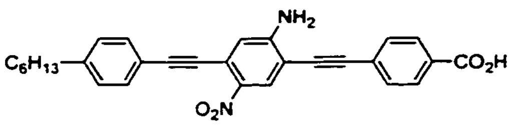
Methyl-4-ethynylbenzoate (20, AMR-II-259). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. Methyl-4-(trimethylsilylethynyl)benzoate (0.75 g, 3.23 mmol)was deprotected to the terminal alkyne via the procedure described above using potassium carbonate (2.23 g, 16.15 mmol), methanol (50 mL), and methylene chloride (50 mL). The mixture, in a round bottom flask, was stirred at room temperature for 2 h. Extraction of the product followed the procedure described previously to yield 0.488 g of the desired product that was immediately reacted in the next step.



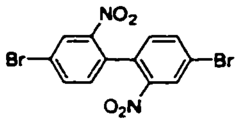
Methyl 2′-acetamido-4,-4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate(AMR-II-261). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromo-5-(4′-*n*-hexylphenylethynyl)-4-nitroacetanilide (0.23 g, 0.52 mmol) was coupled to 1-ethynyl-4-methyl benzoate (0.11 g, 0.68 mmol) as described above using copper(I) iodide (0.01 g, 0.05 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.03 mmol), *N,N*-diisopropylethylamine (0.36 mL, 2.08 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of methylene chloride as the eluent. R_f (product): 0.20. The reaction afforded 0.26 g (96 % yield) of the desired material. IR (KBr) 3426.99, 3286.07, 2926.72, 2844.78, 2361.19, 2334.33, 2194.63, 1722.66, 1671.72, 1602.42, 1546.11, 1494.92, 1426.27, 1407.39, 1339.77, 1276.39, 1173.17, 1105.95, 760.00 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$) δ 8.86 (s, 1 H), 8.33 (s, 1 H), 8.06 (br s, 1 H), 7.85 (ABq, *J*=6.8 Hz, Δv=188.8 Hz, 4 H), 7.35 (ABq, *J*=8.2 Hz, Δv=170.20 Hz, 4 H), 3.98 (s, 3 H), 2.66 (t, *J*=7.6 Hz, 2 H), 2.35 (s, 3 H), 1.65 (p, *J*=7.8, 6.1 Hz, 2 H), 1.40-1.37 (m, 6 H), 0.93 (t, *J*=6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.70, 166.52, 145.43, 144.23, 142.39, 132.65, 132.03, 131.37, 130.30, 129.15, 129.03, 126.09, 123.95, 121.65, 119.74, 111.04, 100.61, 98.76, 85.46, 85.05, 52.86, 36.45, 32.08, 31.54, 29.32, 25.56, 22.99, 14.48. HRMS Calcd $C_{32}H_{30}N_2O_5$: 522.2155. Found: 522.2147.



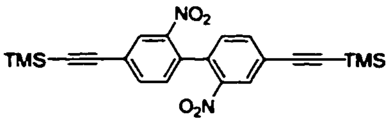
Methyl 2′-amino-4,-4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate (21, AMR-II-267). To a 100 mL round bottom flask equipped with a magnetic stirbar methyl 2′-acetamido-4,-4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate (0.10 g, 0.19 mmol), potassium carbonate (0.16 g, 1.15 mmol), methanol (15 mL), and methylene chloride (15 mL) were added. The reaction mixture was allowed to react at room temperature for 1 h. The reaction was quenched with water and extracted with methylene chloride (3×). Organic layers were combined and dried over $MgSO_4$. Volatiles were removed in vacuo. No further purification was needed. The reaction afforded 0.09 g (99 % yield) of the desired material. IR (KBr) 3475.47, 3362.54, 2914.63, 2850.15, 2205.37, 1706.79, 1629.40, 1596.36, 1543.77, 1519.70, 1426.27, 1316.01, 1290.51, 1279.59, 1173.73, 1141.49, 1114.87, 760.00, 679.40, 614.93, 469.85 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$) δ 8.31 (s, 1 H), 7.85 (ABq, J= 8.6 Hz, $\Delta\nu$=182.9 Hz, 4 H), 7.36 (ABq, J=8.2 Hz, $\Delta\nu$=129.83 Hz, 4 H), 6.95 (s, 1 H), 4.92 (br s, 2 H), 3.96 (s, 3 H), 2.64 (t, J=7.6 Hz, 2 H), 1.65 (p, J=7.7, 6.8 Hz, 2 H), 1.36-1.27 (m, 6 H), 0.91 (t, J=7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.74, 151.42, 145.13, 139.96, 132.46, 131.92, 130.77, 130.64, 130.10, 129.00, 127.11, 121.96, 120.01, 118.38, 106.80, 98.72, 96.69, 86.51, 85.81, 52.75, 36.42, 32.08, 31.56, 29.32, 22.99, 14.47. HRMS Calcd $C_{30}H_{28}N_2O_4$: 480.2049. Found: 480.2050.



2′-Amino-4,-4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoic acid (22, AMR-II-269).[23] To a 250 mL round bottom flask equipped with a magnetic stirbar methyl 2′-amino-4,-4′-diphenylethynyl-4′′-*n*-hexyl-5′-nitrobenzoate (0.07 g, 0.15 mmol), lithium hydroxide (0.02, 0.75 mmol), methanol (9 mL), methylene chloride (5 mL), and water (3 mL) were added. The reaction mixture was allowed to stir at room temperature for 2.5 d. The reaction was quenched with water and extracted with methylene chloride (3×). The yellow aqueous phases were combined and acidified to pH=3 where upon a yellow solid precipitated. The solid material was collected on a fritted funnel. The collected solid reaction mixture was purified by gravity column chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.10. The reaction afforded 0.065 g (94 % yield) of the desired material. IR (KBr) 3460.77, 3378.60, 2957.49, 2921.54, 2844.51, 2207.7, 1580.98, 1542.74, 1428.19, 1385.56, 1307.71, 1242.23, 1108.70, 774.89, 646.51, 615.69, 456.49 cm^{-1}. ^{1}H NMR (400 MHz, MeOH) δ 8.22 (s, 1 H), 7.72 (ABq, *J*=8.5 Hz, Δν=142.14 Hz, 4 H), 7.38 (ABq, *J*=8.2 Hz, Δν=97.07 Hz, 4 H), 6.99 (s, 1 H), 2.61 (t, *J*=7.6 Hz, 2 H), 1.69-1.59 (m, 2 H), 1.42-1.28 (m, 6 H), 0.96-0.86 (m, 3 H).

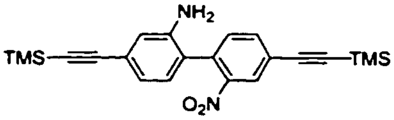


4,4′-Dibromo-2,2′-dinitrobiphenyl (AMR-II-81).[24] In a large oven dried screw capped tube equipped with a magnetic stirbar 2,2′-dinitrobiphenyl (2.44 g, 10.0 mmol) and silver acetate (4.01 g, 24.0 mmol) were added. Glacial acetic acid (20 mL), sulfuric acid (2.03 mL, 38.0 mmol), and bromine (1.54 mL, 30.0 mmol) were sequentially added and the reaction vessel was sealed. The reaction vessel was heated to 80 °C for 16 h. The reaction mixture was cooled and was poured into ice water. The solid material was then collected by filtration. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.58. The reaction afforded 1.43 (36 % yield) of the desired material as a yellow solid. IR (KBr) 3097.4, 2861.5, 1523.1, 1384.6, 1338.5, 1271.8, 1241.0, 1148.7, 1092.3, 1000.0, 892.3, 835.9, 764.1, 723.1, 697.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J*=2.0 Hz, 2 H), 7.81 (dd, *J*=2.0, 8.2 Hz, 2 H), 7.15 (d, *J*=8.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.07, 136.34, 131.76, 131.69, 127.81, 122.66. HRMS Calcd $C_{12}H_6Br_2N_2O_4$: 399.8694. Found: 399.8675.

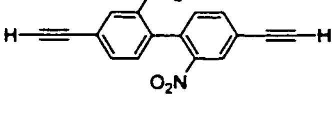


2,2′-Dinitro-4,4′-bis(trimethylsilylethynyl)biphenyl (24, AMR-II-125). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 4, 4′-Dibromo-2,2′-

dinitrobiphenyl (1.50 g, 3.73 mmol) was coupled to trimethylsilylacetylene (1.32 mL, 9.33 mmol) as described above using copper(I) iodide (0.07 g, 0.37 mmol), bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.19 mmol), triphenylphosphine (0.20 g, 0.75 mmol), triethylamine (1.62 mL, 14.92 mmol), and THF (25 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.55. The reaction afforded 1.44 g (88 % yield) of the desired compound as a very viscous yellow liquid. IR (KBr) 3743.6, 3651.3, 3076.9, 2953.8, 2892.3, 2153.8, 2061.8, 1943.6, 1876.9, 1805.1, 1610.4, 1523.3, 1477.1, 1405.3, 1338.6, 1256.6, 1215.6, 1143.8, 1092.5, 1000.2, 928.4, 851.5, 759.2, 692.5, 641.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J*=1.6 Hz, 2 H), 7.71 (dd, *J*=6.2, 0.7 Hz, 2 H), 7.20 (d, *J*=6.9 Hz, 2 H), 0.19 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.76, 136.22, 133.26, 130.71, 128.04, 124.97, 101.67, 98.74, -0.07. HRMS Calcd $C_{22}H_{24}N_2O_4Si_2$: 436.1275. Found: 436.1281.

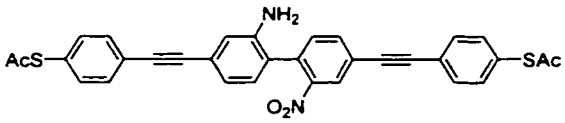


2-Amino-2′-nitro-4,4′-bis(trimethylsilylethynyl)biphenyl (25, AMR-II-153).[25] 2,2′-Dinitro-4,4′-bis(trimethylsilylethynyl)biphenyl (0.70 g, 1.60 mmol), glacial acetic acid (15 mL), and THF (15 mL) were charged to a 100 mL round bottom flask equipped with a magnetic stirbar and a West condenser. The reaction mixture was allowed to heat to reflux. Iron powder (0.20, 3.52 mmol) was carefully added to the refluxing reaction mixture. The reaction mixture was allowed to reflux for 2 h while being monitored by TLC. The reaction mixture was cooled, quenched with water, and filtered through filter paper to remove unreacted iron. The filtrate was extracted with brine (3×) and diluted with methylene chloride. Organic layers were combined and dried over magnesium chloride. Volatiles were removed in vacuo. The crude reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/ hexanes as the eluent. R_f (product): 0.68. The reaction afforded 0.13 g (21 % yield, 33 % based on a recovered 0.26 g of starting material) of the desired material. IR (KBr) 3469.7, 3382.5, 2953.8, 2154.7, 1617.1, 1529.9, 1479.1, 1413.7, 1346.2, 1242.5, 848.4, 759.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J*=1.7 Hz, 1 H), 7.68 (dd, *J*=7.8, 1.6 Hz, 1 H), 7.36 (d *J*= 7.8 Hz, 1 H), 6.93-6.86 (m, 3 H), 3.49 (s, 2 H), 0.28 (s, 9 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.08, 143.25, 135.73, 132.67, 132.41, 128.92, 127.58, 124.33, 124.19, 123.13, 122.56, 118.91, 104.72, 101.77, 98.24, 94.43, 0.09, -0.12. HRMS Calcd $C_{22}H_{26}N_2O_2Si_2$: 406.1533. Found: 406.1532.



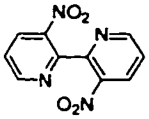
2-Amino-2′-nitro-4,4′-diethynylbiphenyl (AMR-II-155). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 2-Amino-2′-nitro-

4,4′-ditrimethylsilylethynylbiphenyl (0.13g, 0.33 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.46 g, 3.30 mmol), methanol (10 mL), and methylene chloride (10 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.

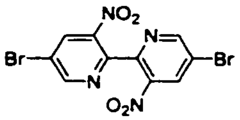


2-Amino-2′-nitro-4,4′-di(1-thioacetyl(phenylethynyl))biphenyl (26, AMR-II-157). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Amino-2′-nitro-4,4′-diethynylbiphenyl (0.09 g, 0.33 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.22 g, 0.79 mmol) as described above using copper(I) iodide (0.02 g, 0.10 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.03 mmol), *N,N*-diisopropylethylamine (0.46 mL, 2.64 mmol), and THF (10 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 50 °C for 2 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.55. The reaction afforded 0.11 g (61 % yield, 2 steps) of the desired compound as a bright yellow solid. IR (KBr) 3128.2, 2924.8, 2859.4, 1718.8, 1348.6, 1261.1, 1108.5, 948.7, 825.2,

614.5 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, *J*=1.2 Hz, 1 H), 7.78 (dd, *J*=6.2, 1.6 Hz, 1 H), 7.58 (dd, *J*=6.6, 1.8 Hz, 2 H), 7.54 (d, *J*=8.6 Hz, 2 H), 7.46-7.36 (m, 5 H), 7.02-6.94 (m, 3 H), 3.59 (s, 2 H), 2.45 (s, 3 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.26, 192.96, 149.29, 143.50, 135.56, 134.24, 134.14, 132.74, 132.66, 132.44, 132.36, 132.26, 132.14, 129.17, 128.02, 127.35, 124.42, 124.22, 124.09, 123.21, 122.38, 118.631, 91.64, 90.84, 88.86, 88.12, 30.48, 30.42. HRMS Calcd $C_{32}H_{22}N_2O_4S_2$: 563.1099. Found: 563.1094.

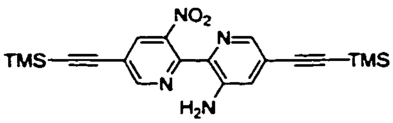


3,3′-Dinitro-2,2′-bipyridyl (AMR-II-219).[26] To a 250 mL round bottom flask equipped with a magnetic stirbar and a West condensor 2-chloro-3-nitropyridine (15.0 g, 94.61 mmol) and copper bronze (15.03 g, 236.53 mmol) were added. DMF (100 mL) was added and the reaction mixture was heated to reflux for 18 h. The reaction mixture was cooled and was filtered through a pad of celite. The filter cake was washed with boiling DMF. The filtrate was poured into 1000 mL of water and the desired material precipitated. The solid material was collected on a fritted funnel to give 3.57 g (35 % yield, first crop) of a golden brown solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.91 (dd, *J*=4.8, 1.5 Hz, 2 H), 8.60 (dd, *J*=8.3, 1.5 Hz, 2 H), 7.67 (dd, *J*=8.4, 4.8 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.52, 151.79, 144.33, 133.44, 124.65.

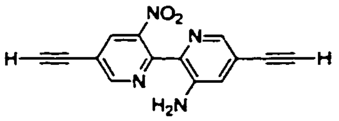


5,5′-Dibromo-3,3′-dinitro-2,2′-bipyridyl (28, AMR-II-225, 227).[27] To a 100 mL round bottom flask equipped with a magnetic stirbar 3,3′-dinitro-2,2′-bipyridyl (1.00 g, 4.06 mmol) was added. The starting material was dissolved in MeOH (50 mL) and CH_2Cl_2 (50 mL). In a separate 100 mL two necked round bottom flask was added KBr (9.66 g, 81.2 mmol) and then bromine (4.33 mL, 81.2 mmol) was slowly added. The KBr/Br_2 mixture was slowly transferred via cannula over 30 min to the first flask containing the bipyridine. The desired material precipitated and was collected on a fritted funnel. The collected solid was added to an oven dried pressure tube equipped with a magnetic stirbar and capped with a septum. Bromine (0.42 mL, 8.12 mmol) was added the septum was removed and the reaction vessel was quickly sealed with a screw cap then heated to 180 °C for 3 d. The reaction was cooled and poured into a solution of ice water. 1 M $NaHSO_3$ (aq) was added to react with any unreacted bromine. The solution was made alkaline with NaOH (s). The resulting solution was extracted with CH_2Cl_2 (4×). The organic layers were combined and dried over $MgSO_4$. Volatiles were removed in vacuo. The reaction mixture was purified by gravity liquid chromatography using silica gel as the stationary phase and 2:3 ethyl acetate/hexanes as the eluent mixture. R_f (product): 0.41. The reaction afforded 0.52 g (45 % yield). IR (KBr) 3425.07, 3059.70, 1578.41, 1544.96, 1428.03, 1345.68, 1232.84, 1104.05, 1027.57, 897.37, 879.49, 789.60, 749.49, 649.64, 551.72, 475.22 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J*=2.0 Hz, 2

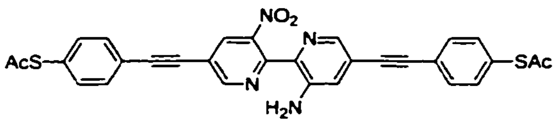
H), 8.67 (d, J= 2.1 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ154.26, 148.55, 143.76, 135.50, 120.86. HRMS Calcd $C_{10}H_4Br_2N_4O_4$: 401.8600. Found: 401.8603.



3-Amino-5,5′-ditrimethylsilylethynyl-3′-nitro-2,2′-bipyridyl (29, AMR-II-231). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 5,5′-dibromo-3,3′-dinitro-2,2′-bipyridyl (0.40 g, 1.41 mmol) was coupled to trimethylsilylacetylene (0.60 mL, 4.23 mmol) using copper(I) iodide (0.04 g, 0.23 mmol), bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.19 mmol), *N,N*-diisopropylethylamine (1.97 mL, 11.28 mmol), and THF (10 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.70. The reaction afforded 0.10 g of the desired amino/nitro compound and 0.03 g of the dinitro product. IR (KBr) 3442.55, 3261.82, 2957.58, 2899.86, 2144.38, 1594.75, 1561.95, 1394.84, 1248.80, 1214.22, 1182.60, 1091.00, 844.12, 757.63, 649.60 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J= 1.8 Hz, 1 H), 7.93 (d, J=1.7 Hz, 1 H), 7.36 (d, d=1.8 Hz, 1 H), 7.17 (d, J=1.7 Hz), 6.80 (br s, 2 H), 0.30 (s, 9 H), 0.29 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.28, 143.92, 140.67, 140.08, 137.78, 136.61, 127.51, 126.85, 120.64, 120.48, 102.09, 101.59, 99.24, 98.88, 0.25, 0.20. Additional formation of the 5,5′-ditrimethylsilylethynyl-3,3′-dinitro-2,2′-bipyridyl was seen and yielded 0.03 g of material. IR (KBr) 3080.74, 2952.35, 2890.73, 2156.35, 1591.44, 1542.61, 1448.33, 1386.02, 1359.38, 1249.87, 1185.73, 1021.40, 939.23, 908.42, 844.36, 809.63, 761.16, 642.57 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J*=1.8 Hz, 2 H), 8.56 (d, *J*=1.8 Hz, 2 H), 0.33 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.51, 149.38, 143.86, 135.69, 122.24, 103.78, 98.68, -0.05. HRMS Calcd $C_{20}H_{22}N_4O_4Si_2$: 438.1180. Found: 438.1180.



3-Amino-5,5′-ethynyl-3′-nitro-2,2′-bipyridyl (AMR-II-247). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 3-Amino-5,5′-ditrimethylsilylethynyl-3′-nitro-2,2′-bipyridyl (0.09 g, 0.23 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.32 g, 2.30 mmol), methanol (10 mL), and methylene chloride (10 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately used in the next step without additional purification or identification.



3-Amino-5,5′-di(4″,4‴-(thioacetyl)phenylethynyl)-3′-nitro-2,2′-bipyridyl (30, AMR-II-249). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 3-Amino-5,5′-ethynyl-3′-nitro-2,2′-bipyridyl (0.09 g, 0.23 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.16 g, 0.58 mmol) as described above using copper(I) iodide (0.01 g, 0.04 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.02 mmol), *N,N*-diisopropylethylamine (0.32 mL, 1.84 mmol), and THF (10 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 60 °C for 2 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and 3:7 ethyl acetate/ hexanes as the eluent. R_f (product): 0.35. The reaction afforded 0.073 g (54 % yield, 2 steps) of the desired compound as a bright yellow solid. IR (KBr) 3441.37, 3245.08, 2916.41, 2844.51, 2197.43, 1701.84, 1596.23, 1560.85, 1483.59, 1424.31, 1397.77, 1264.00, 1205.64, 1114.78, 1014.94, 949.28, 872.47, 824.84, 723.54, 605.42, 543.79, 466.76 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J*=1.8 Hz, 1 H), 8.04 (dd, *J*=1.8 Hz, 1 H), 7.56 (½ ABq, *J*=7.6 Hz, 2 H), 7.54 (½ ABq, *J*=7.8 Hz, 2 H), 7.45 (½ ABq, *J*=7.7 Hz, 4 H), 7.37 (d, *J*=3.7 Hz, 1 H), 7.26 (d, *J*=1.7 Hz, 1 H), 6.85 (br s, 2 H), 2.48 (s, 3 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, DMSO) δ193.54, 193.50, 156.42, 144.30, 140.33, 140.28, 136.21, 135.56, 134.78, 134.77, 132.56, 132.55, 129.66, 129.49, 126.88, 126.37, 124.11, 123.91, 120.52, 120.22, 92.42, 92.27, 88.19, 87.75, 30.53, 30.53.

References

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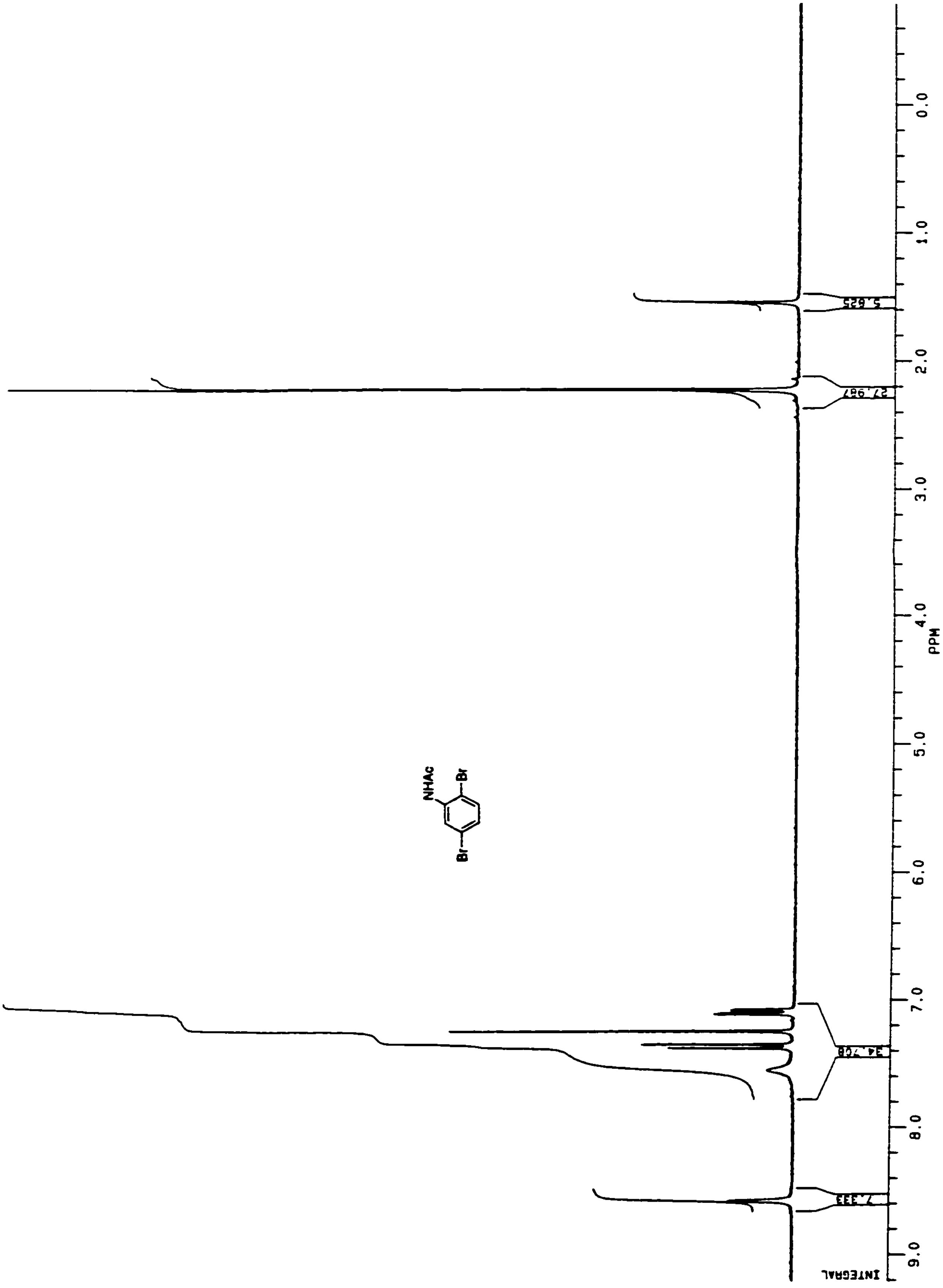
Spectral Section for

Chapter 1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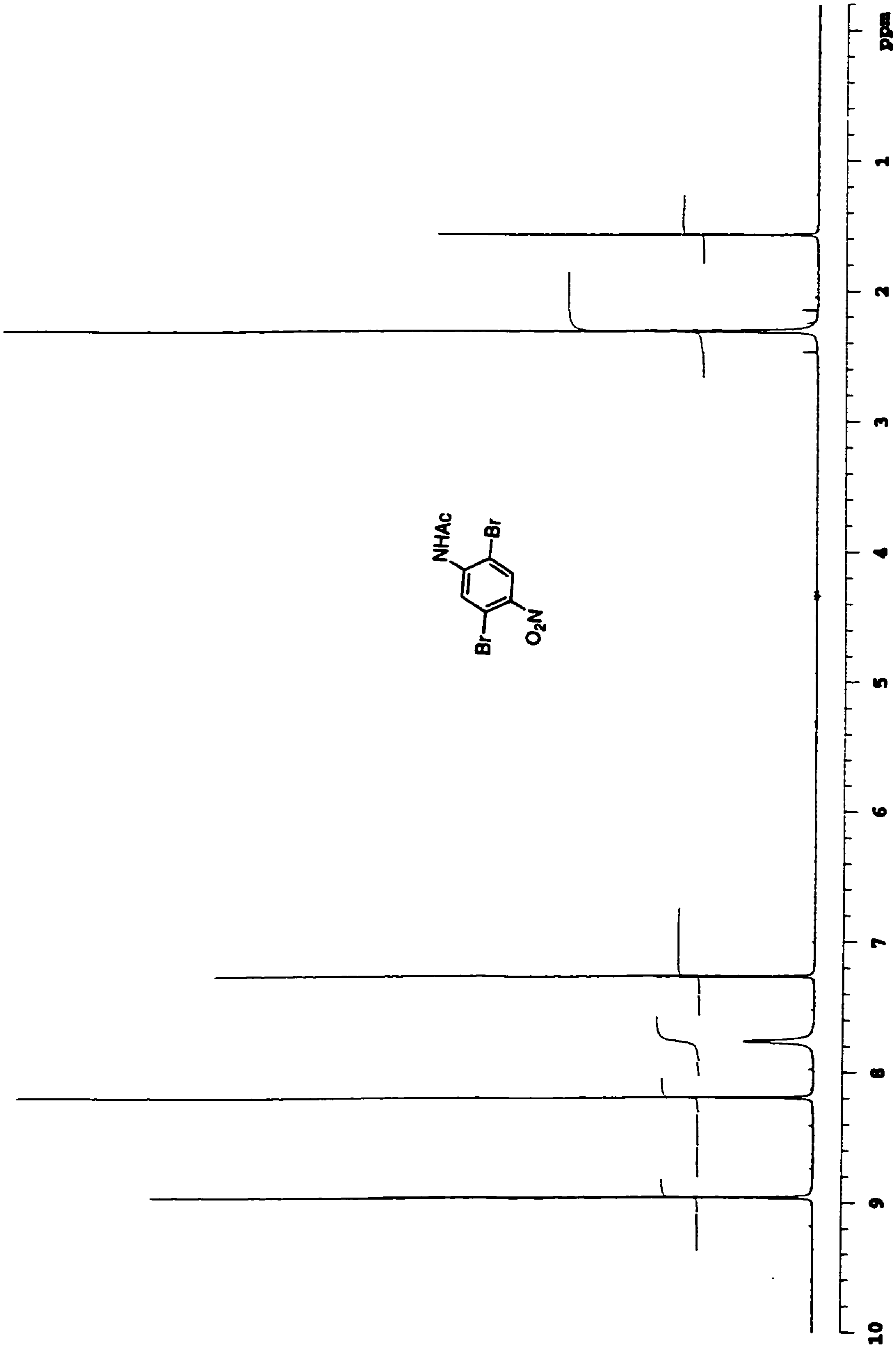
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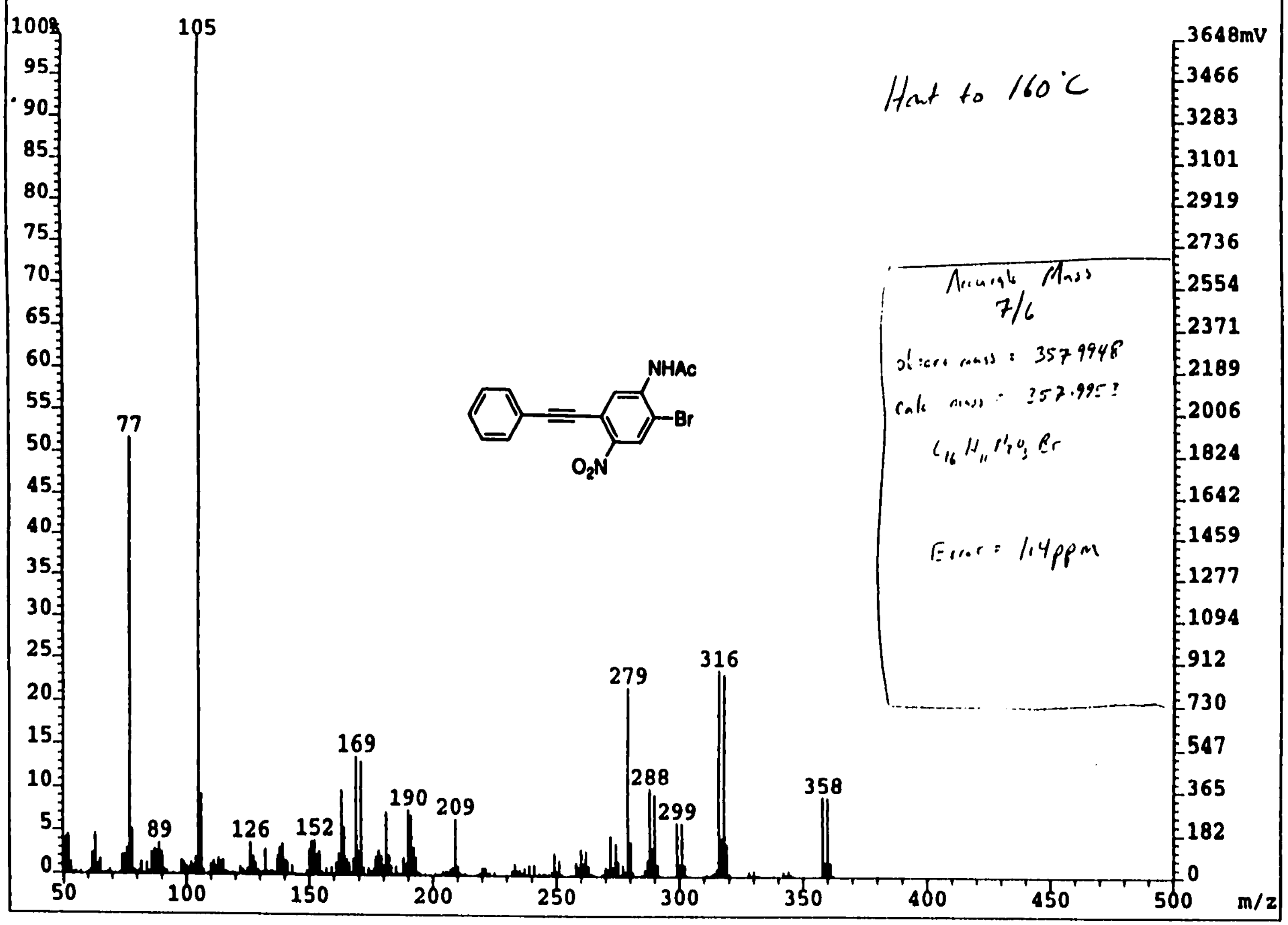

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7/6

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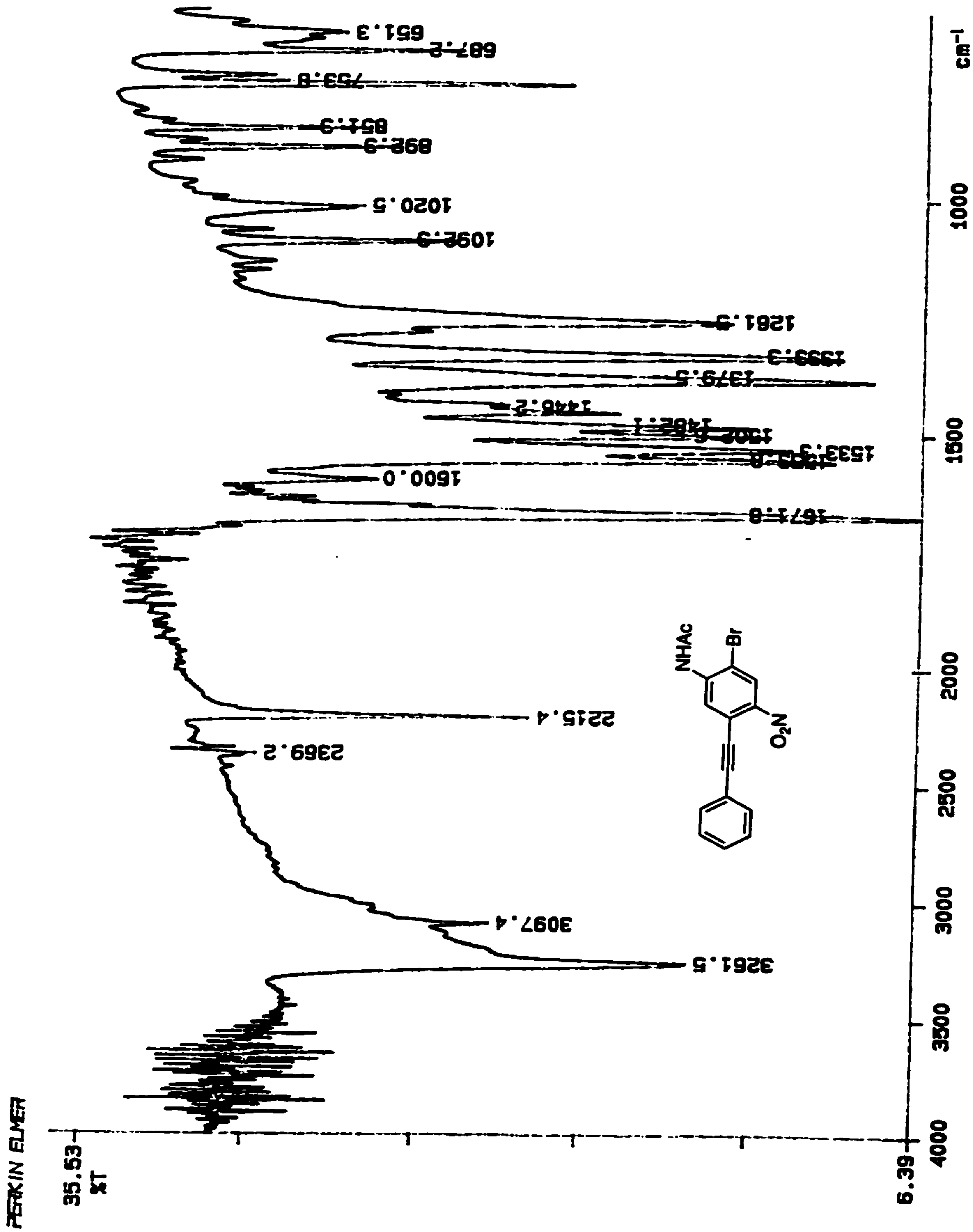
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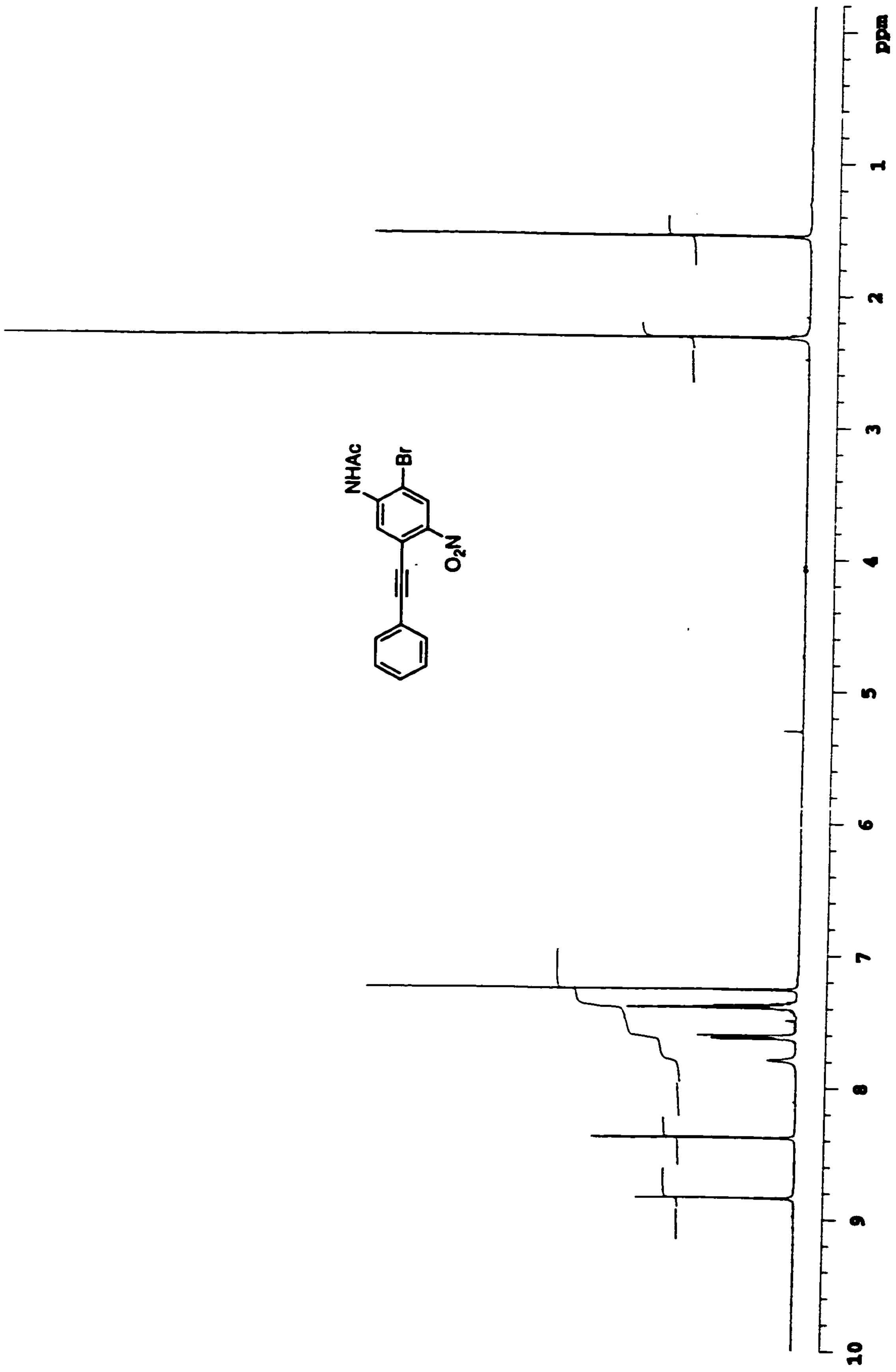
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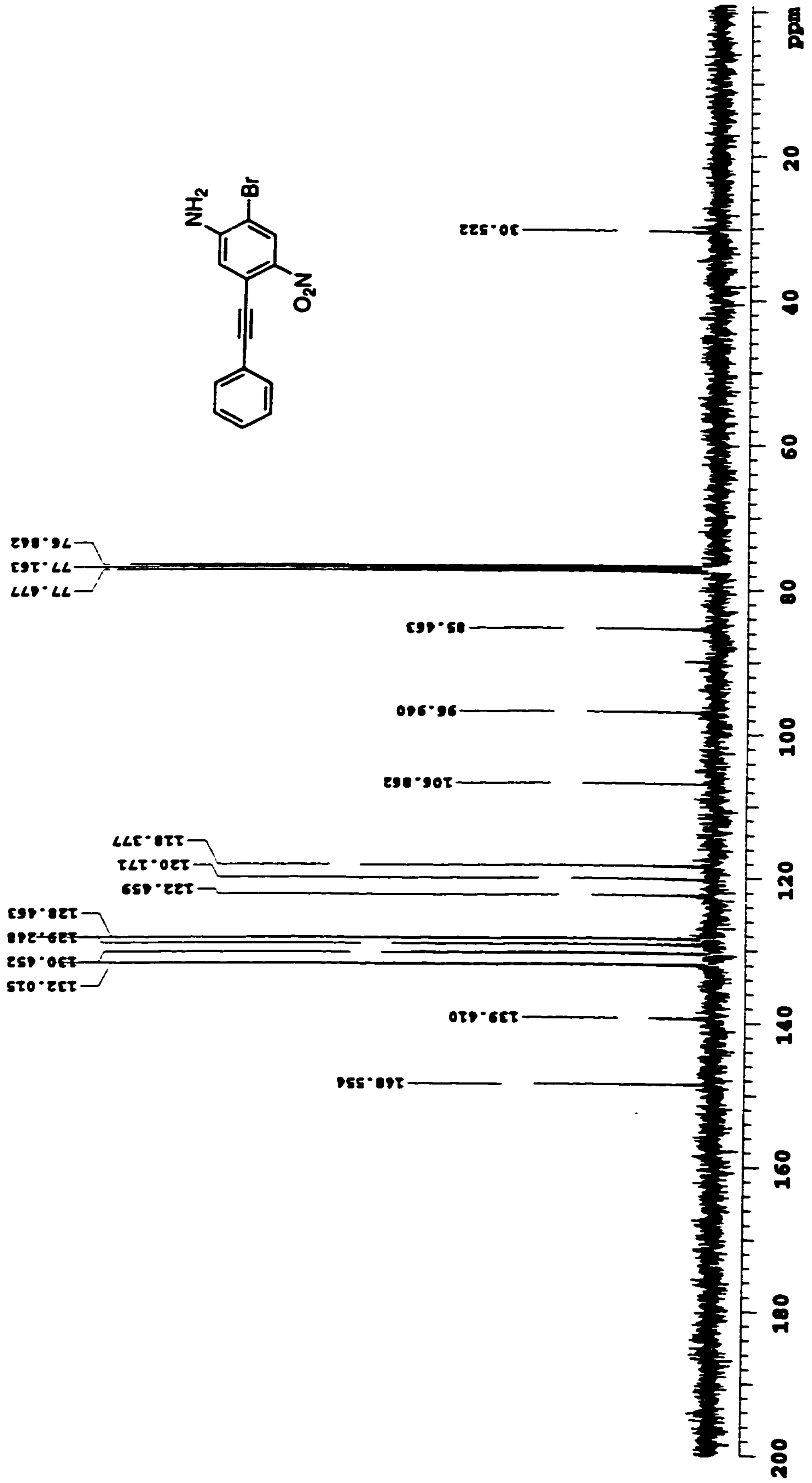
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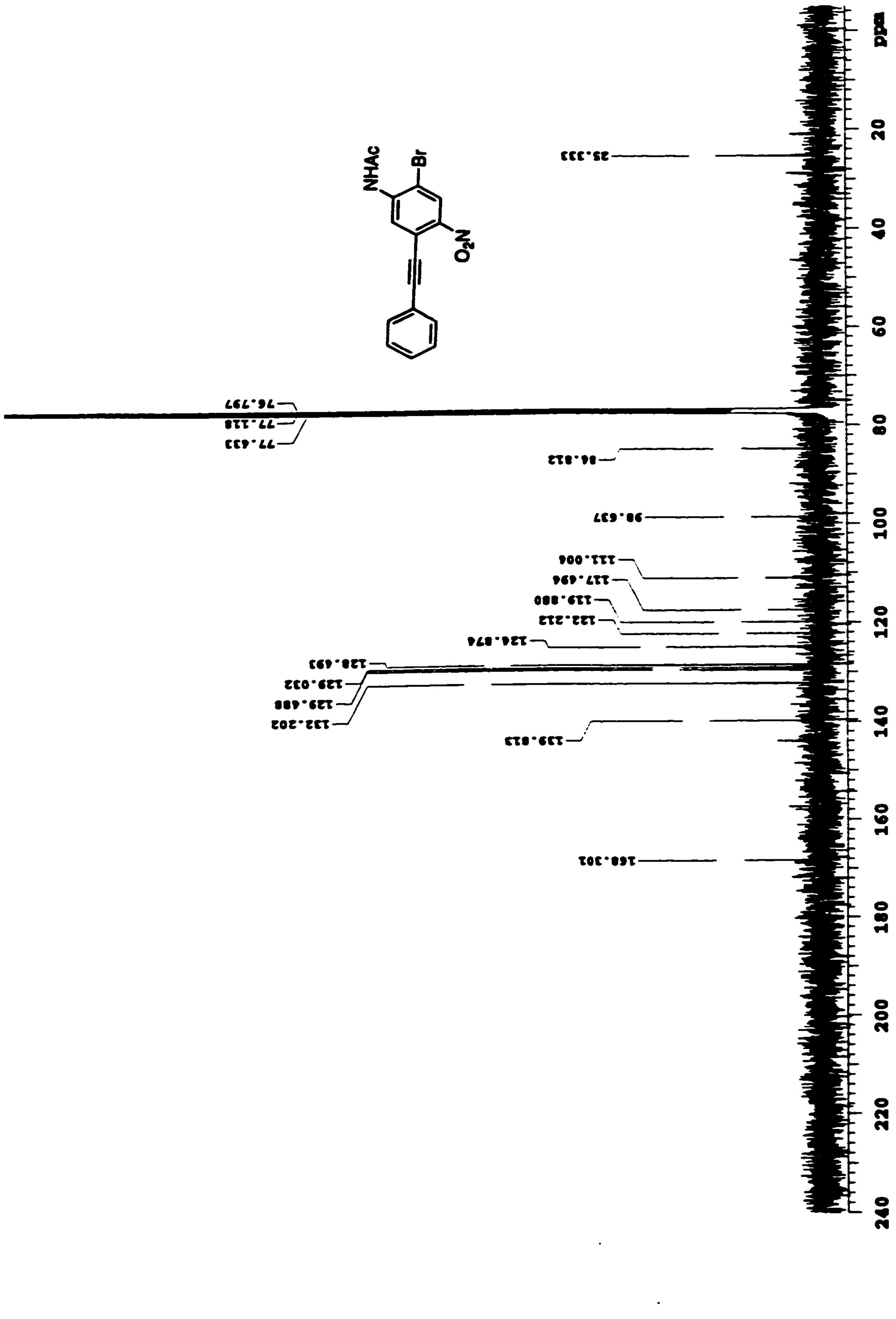
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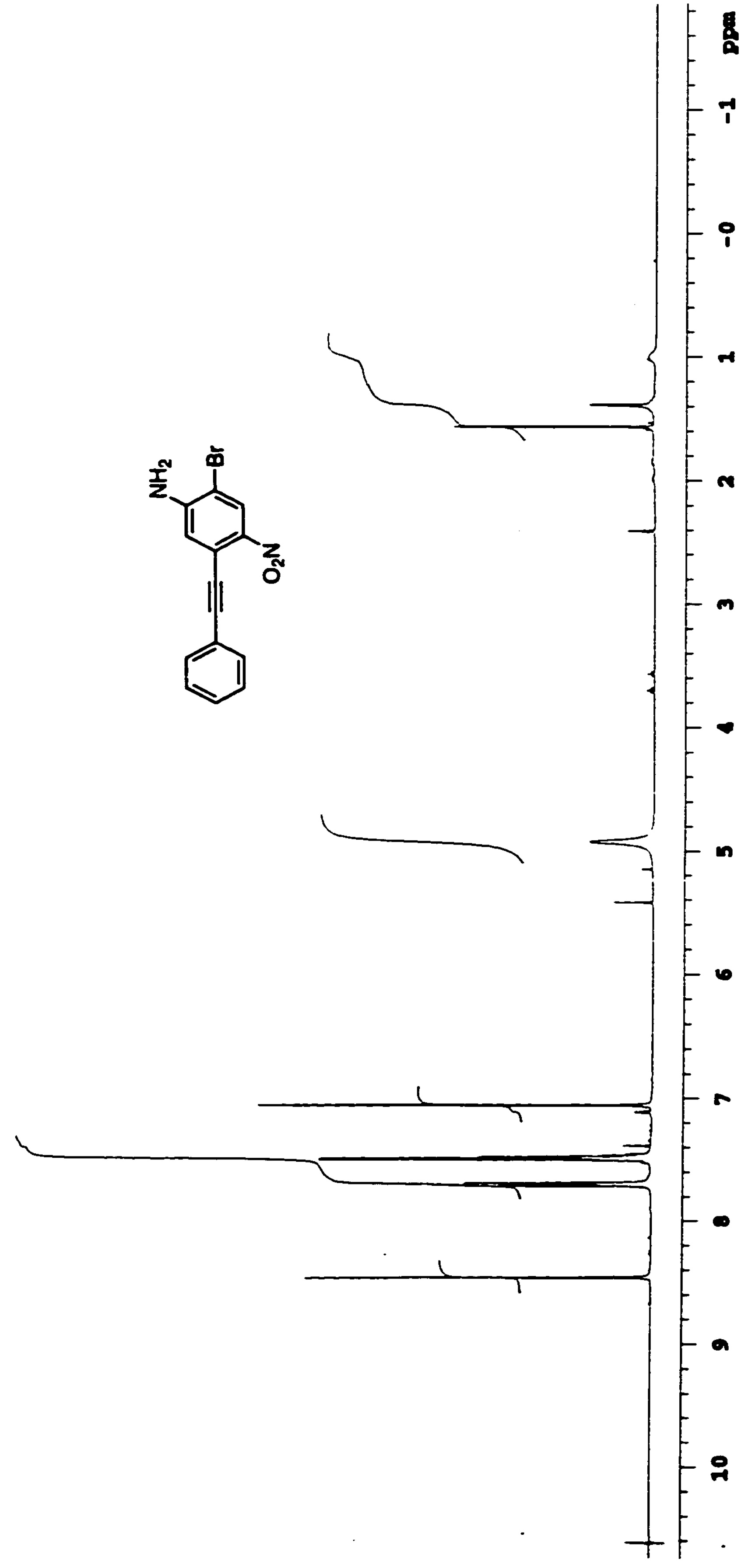
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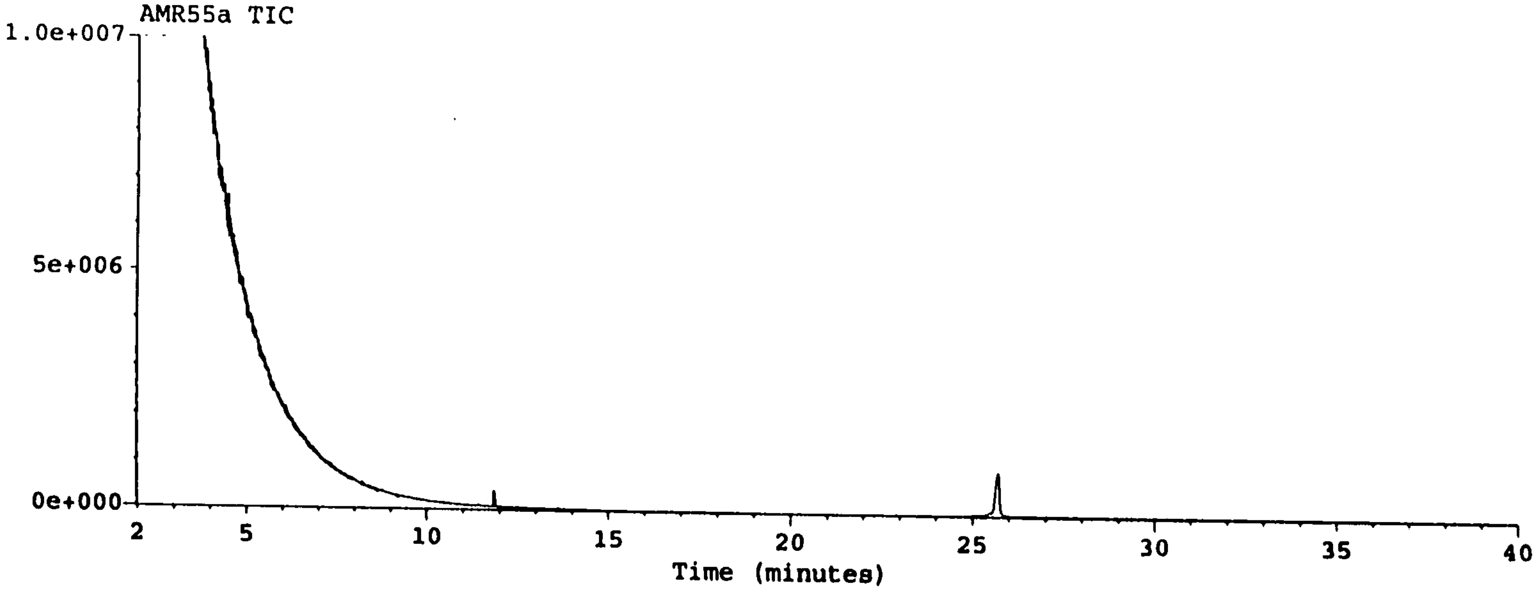

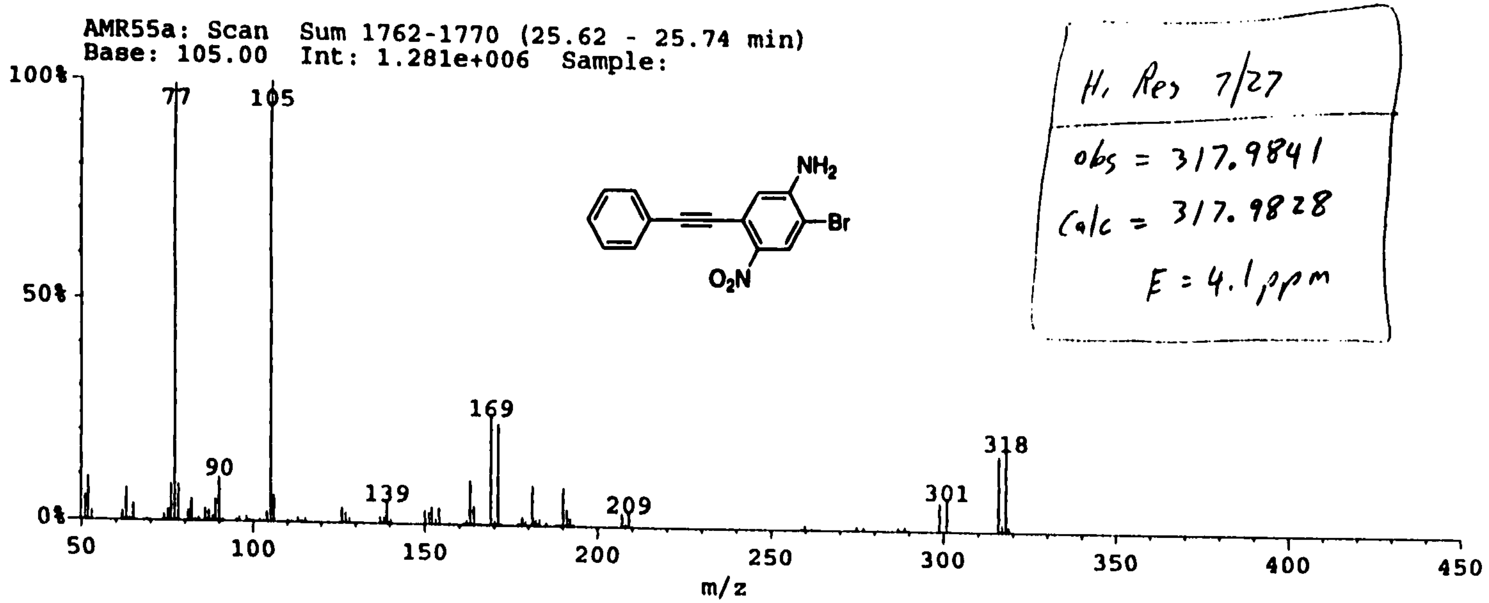

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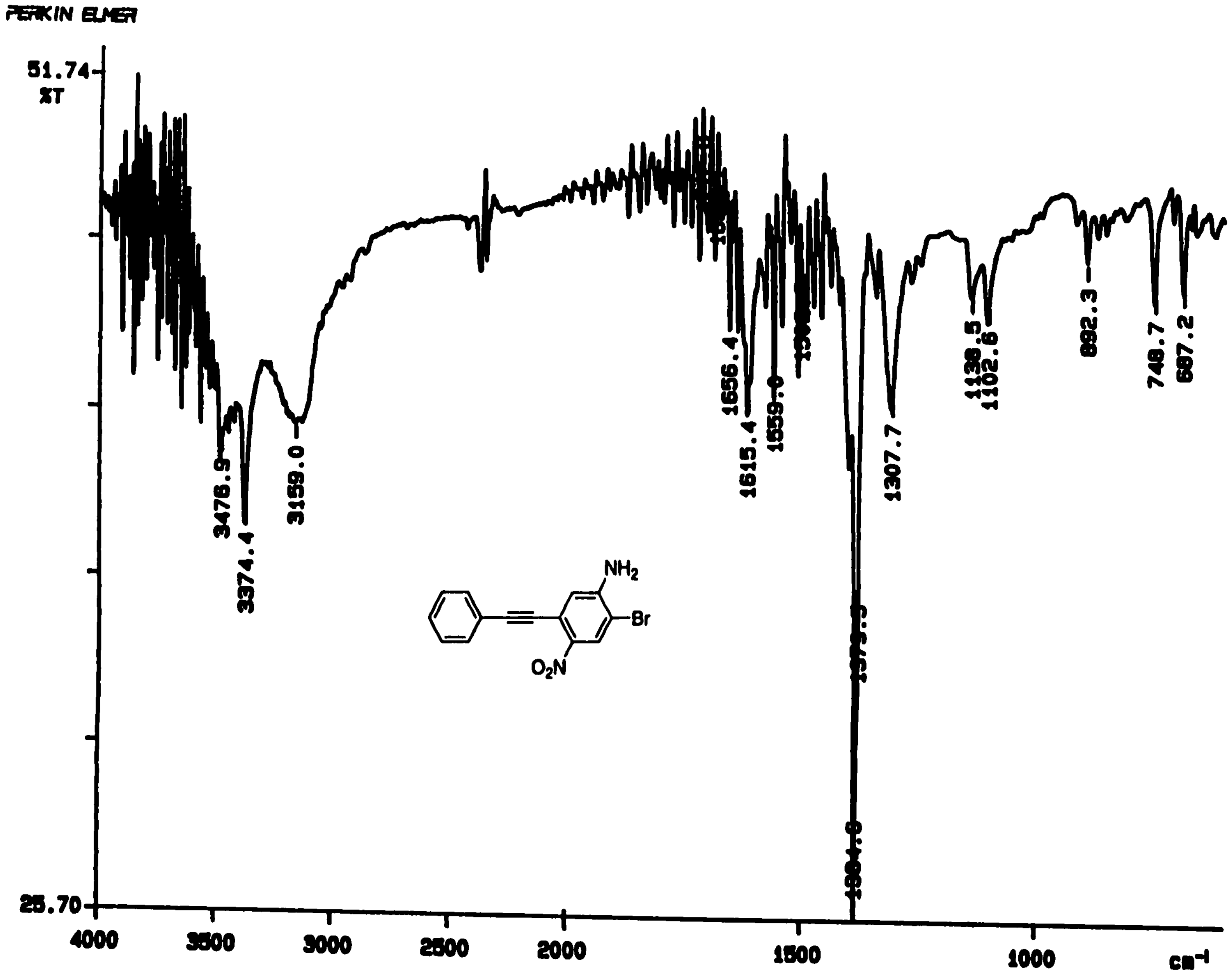
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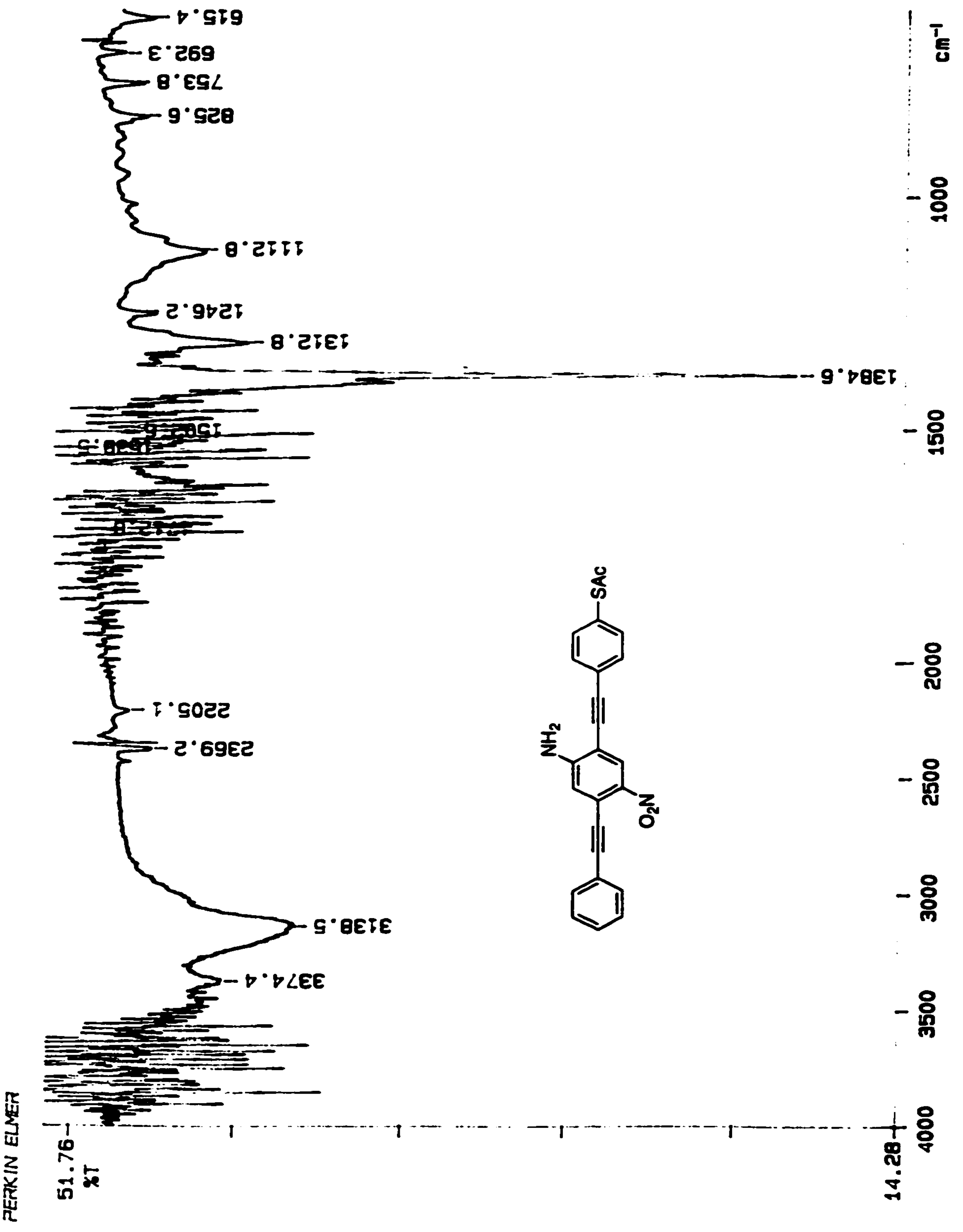
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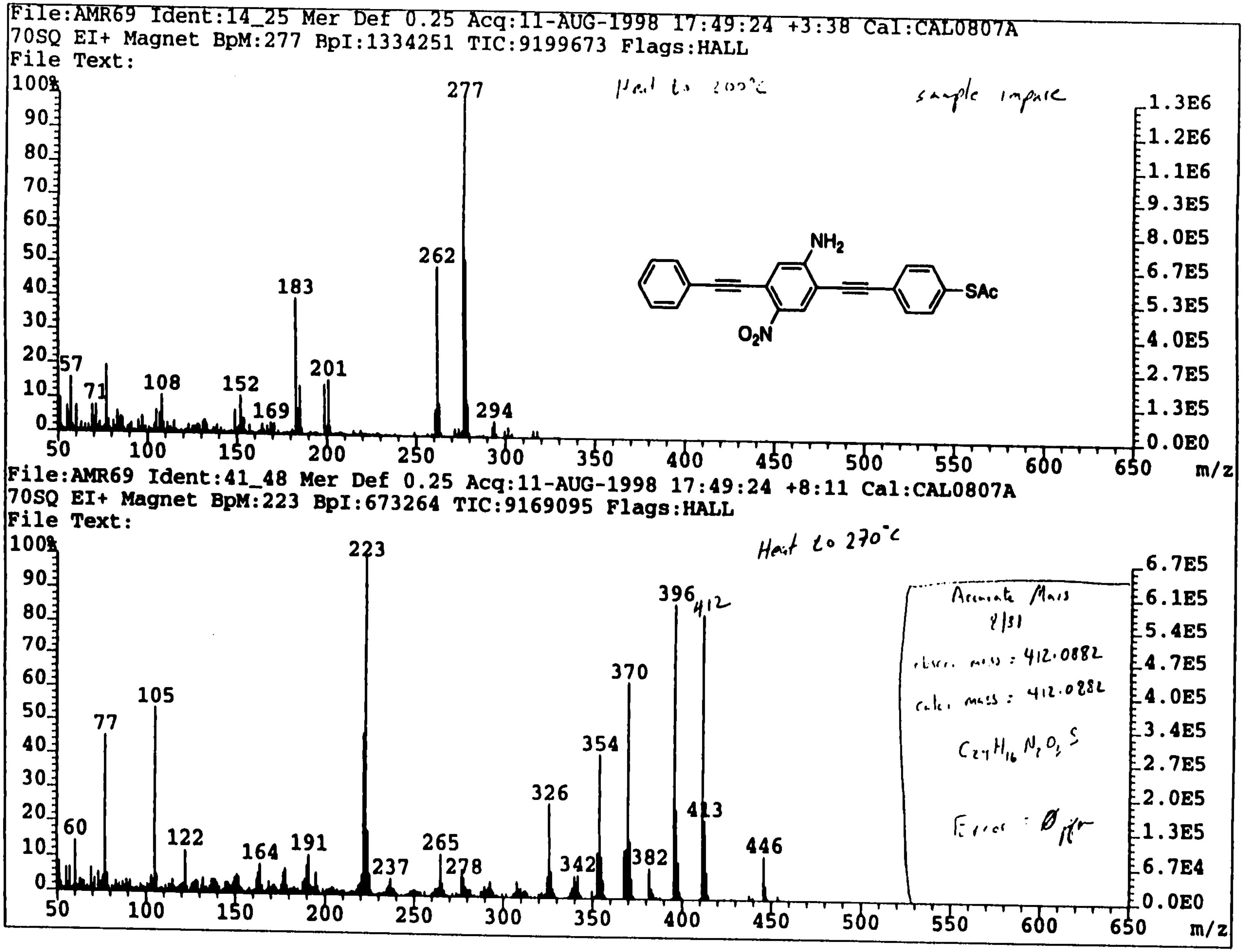

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8/31
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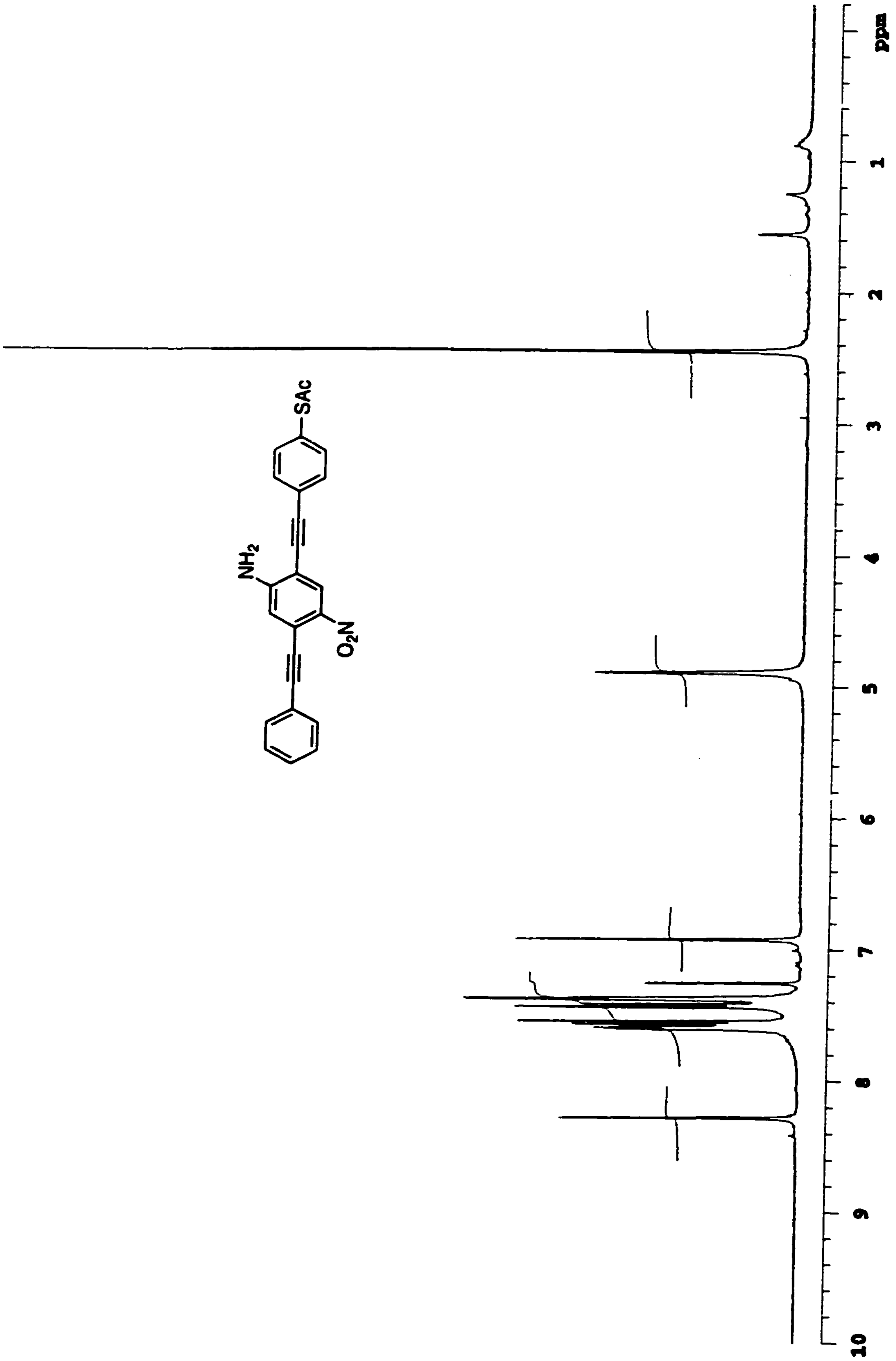
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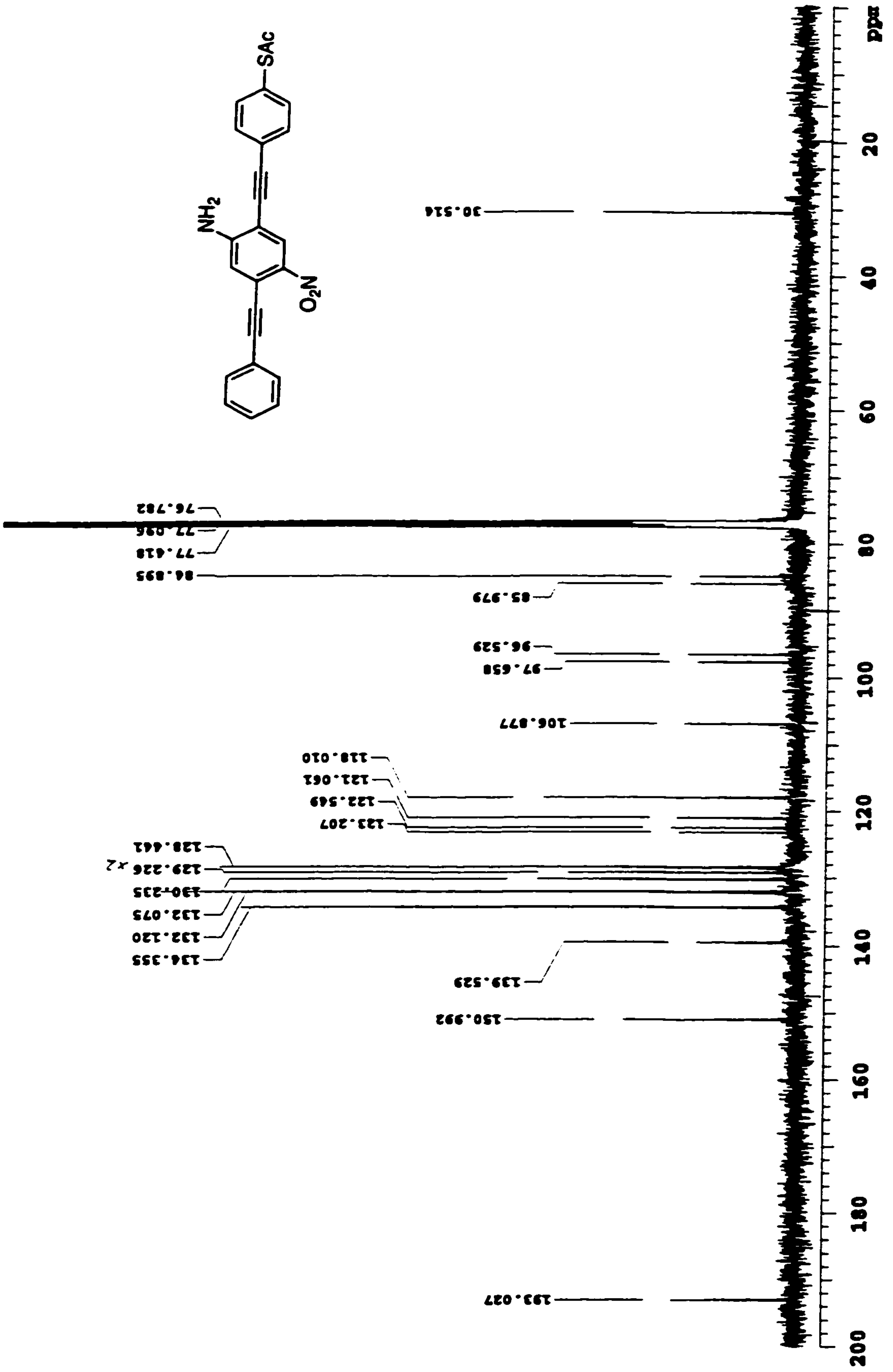
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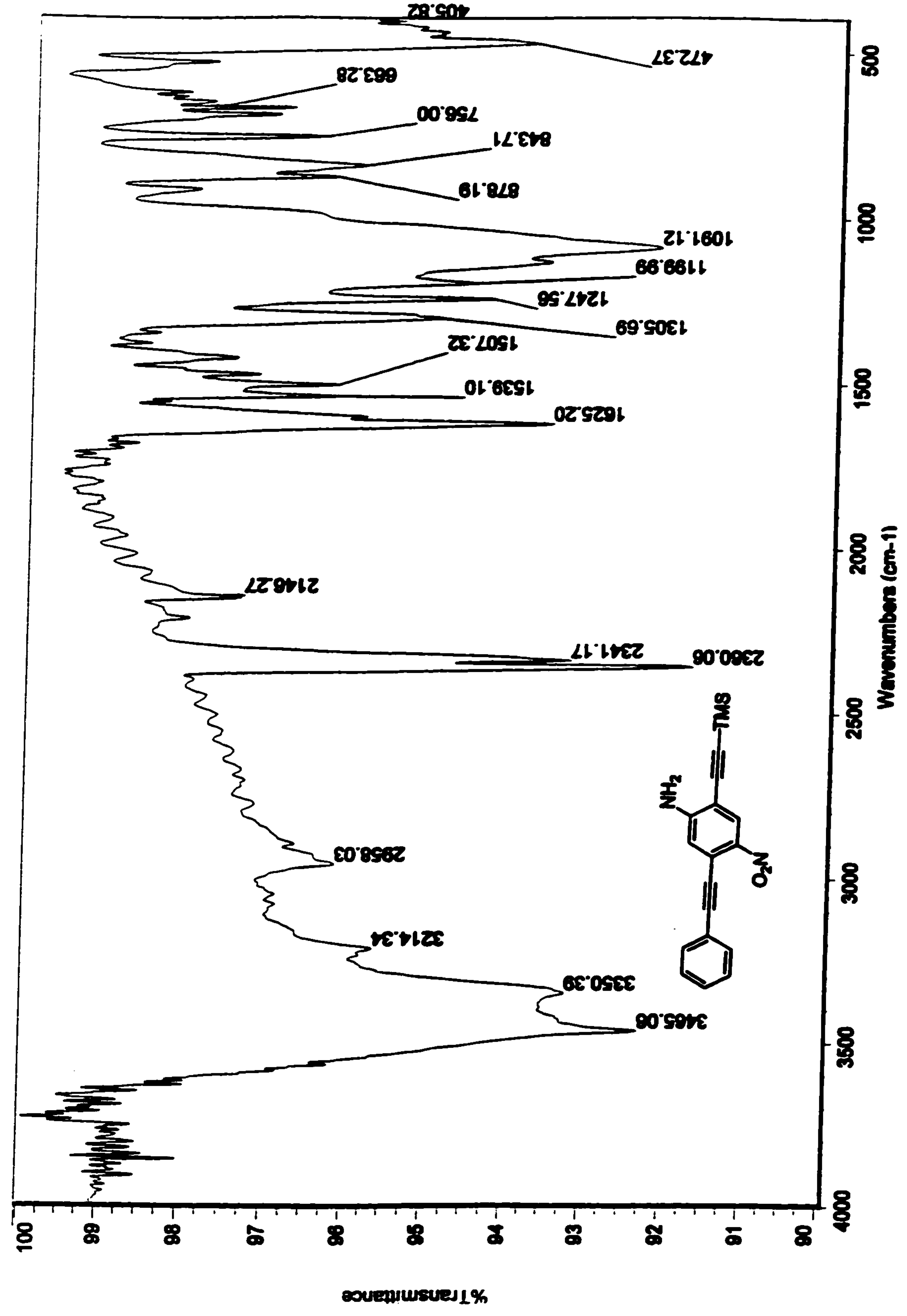
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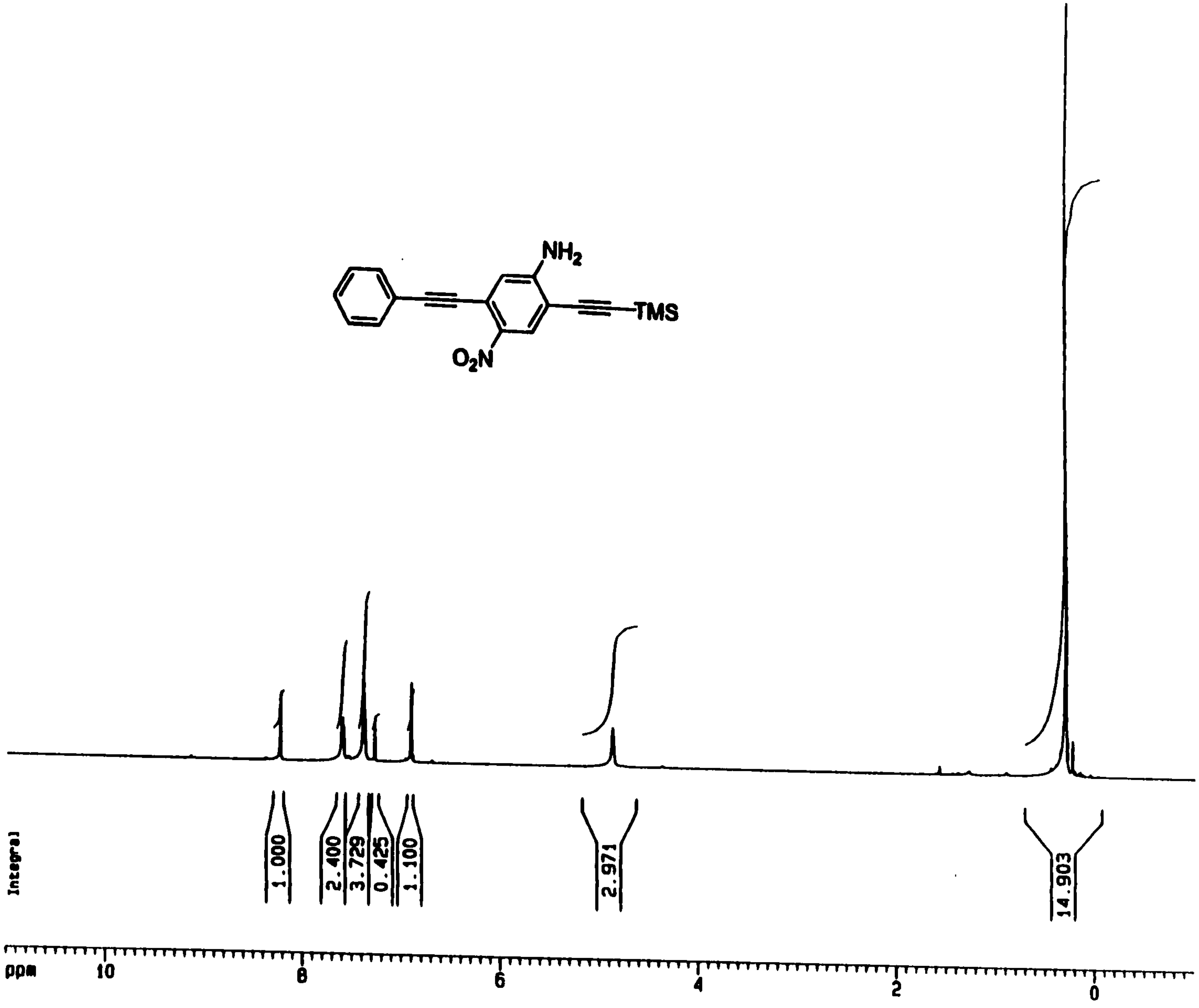
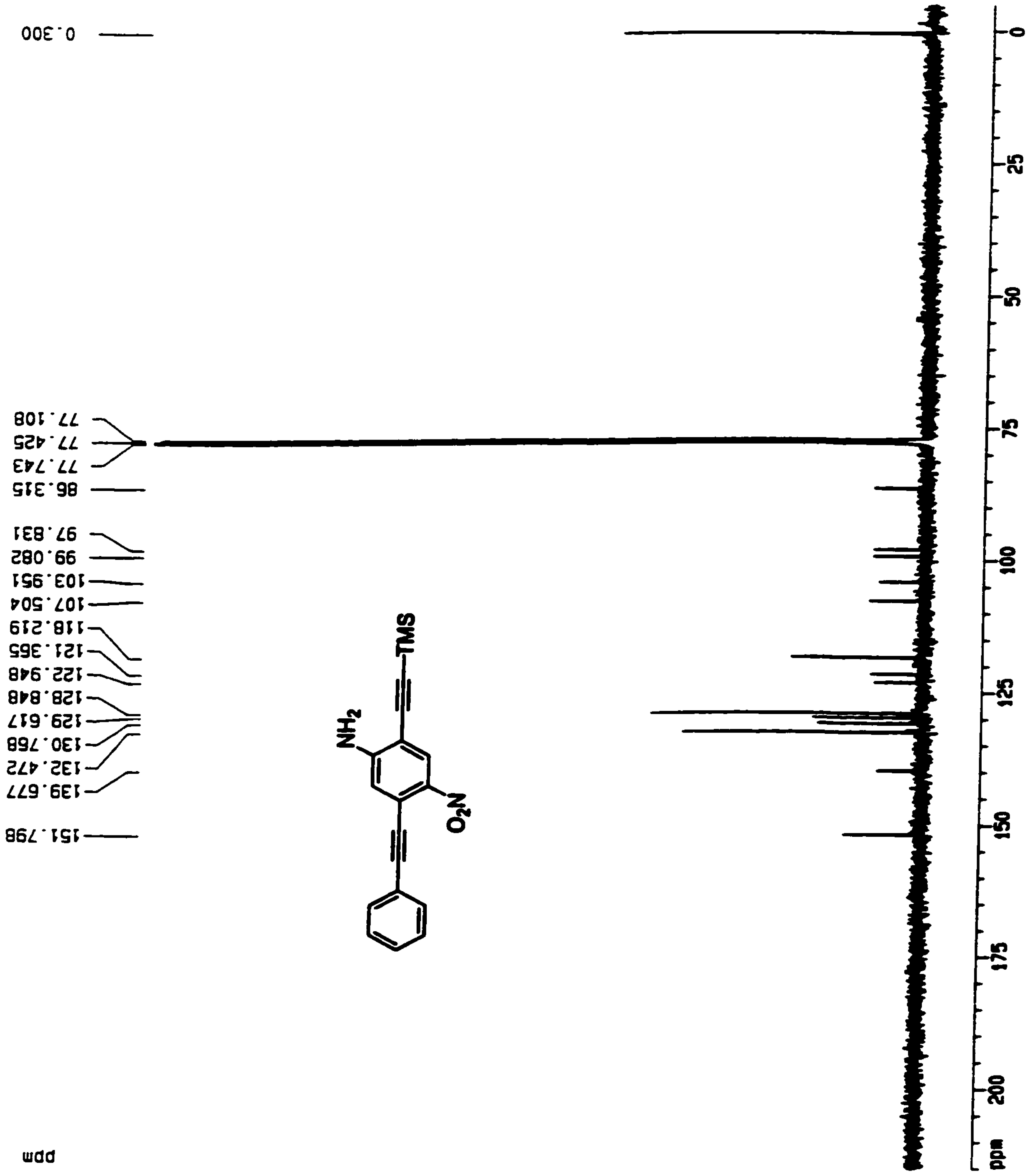
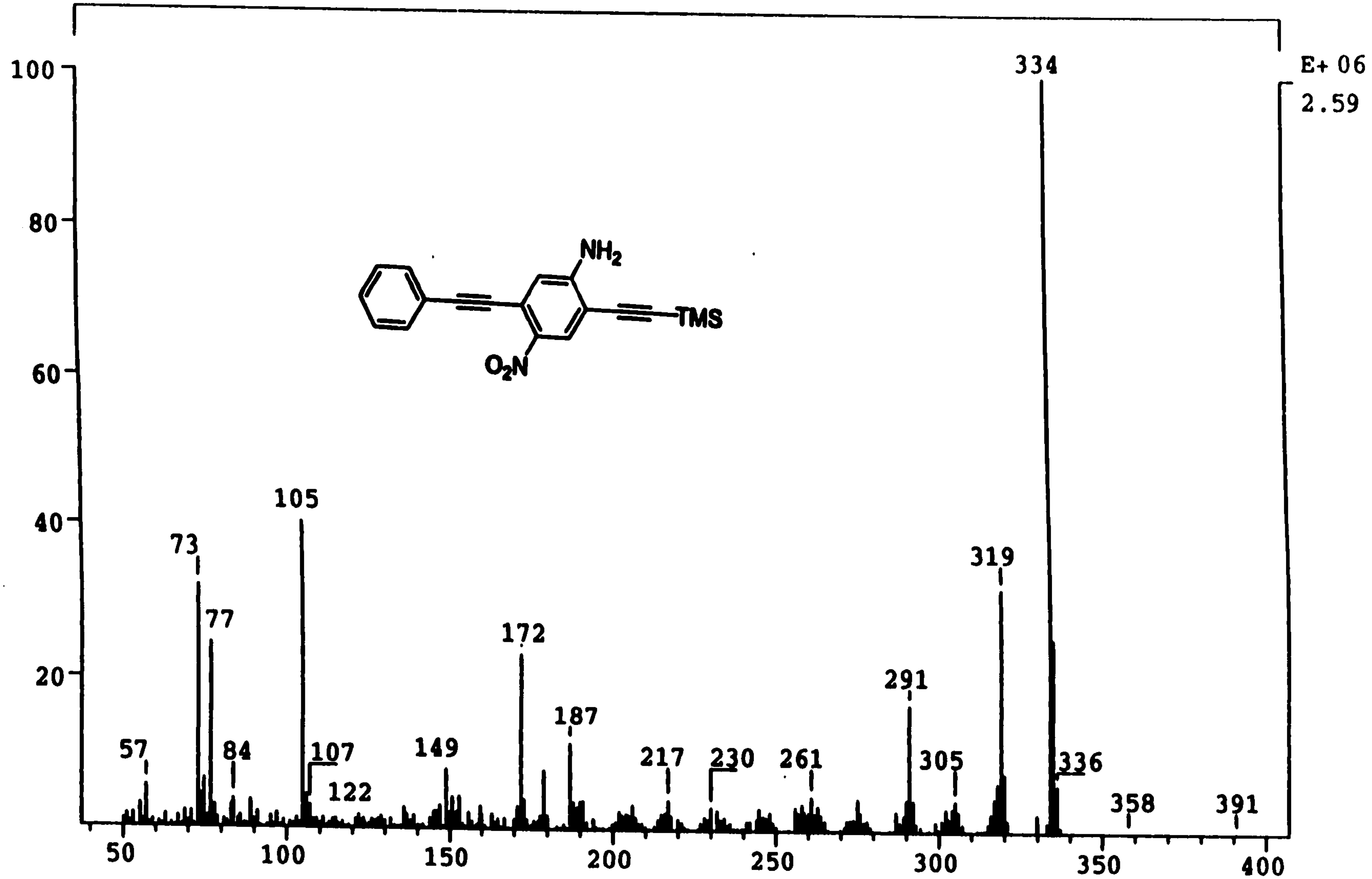
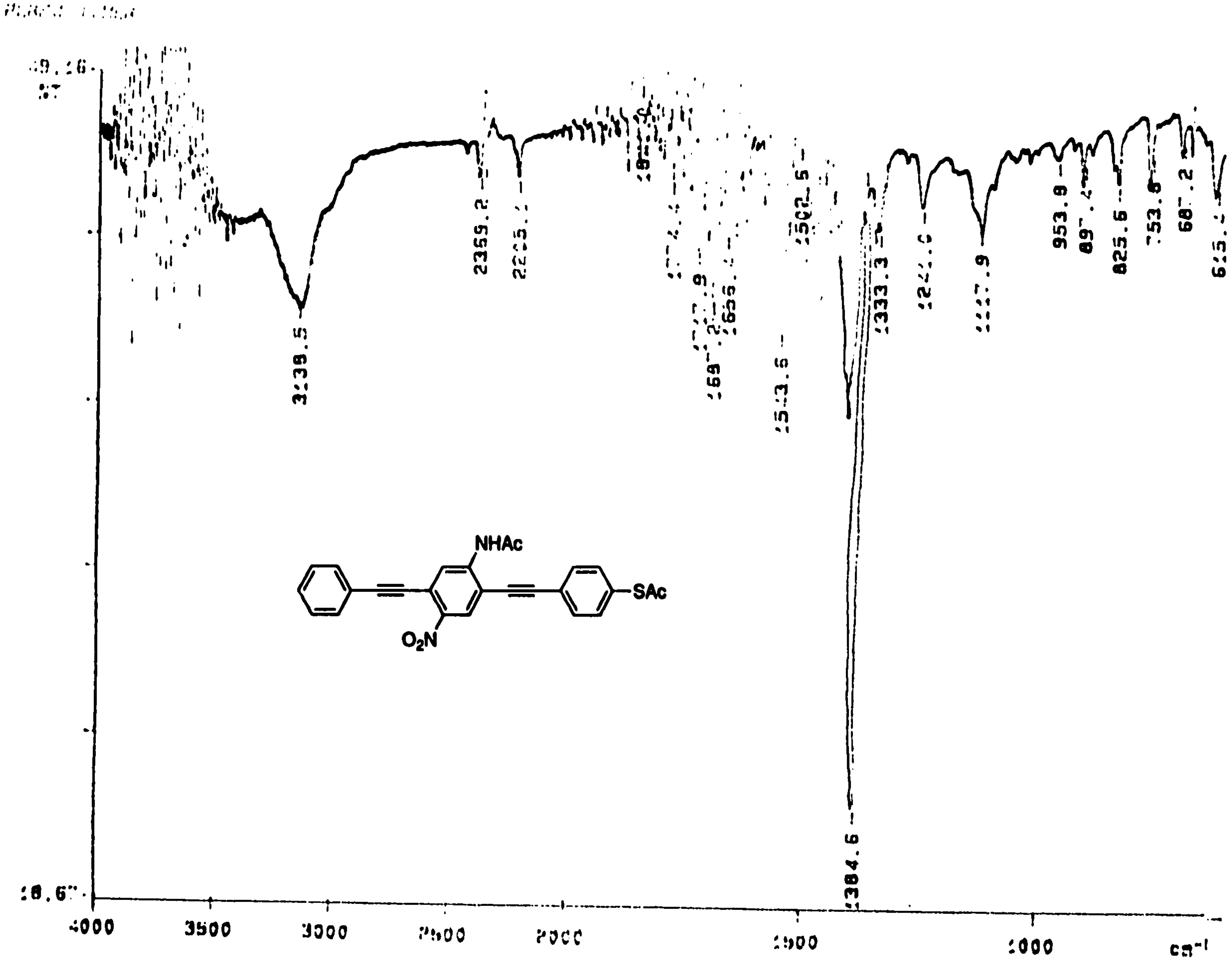
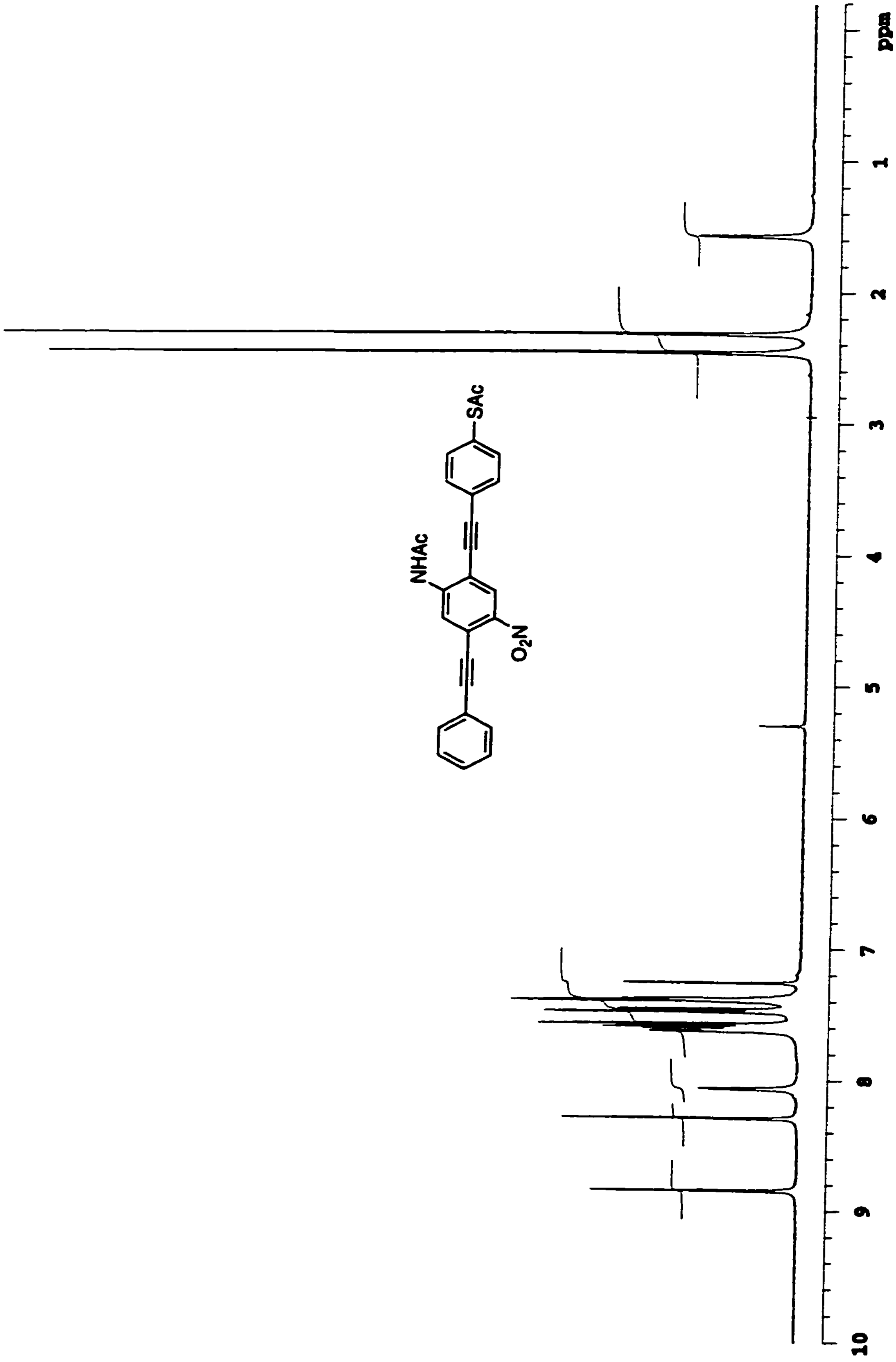
500
Wavenumbers (cm-1)

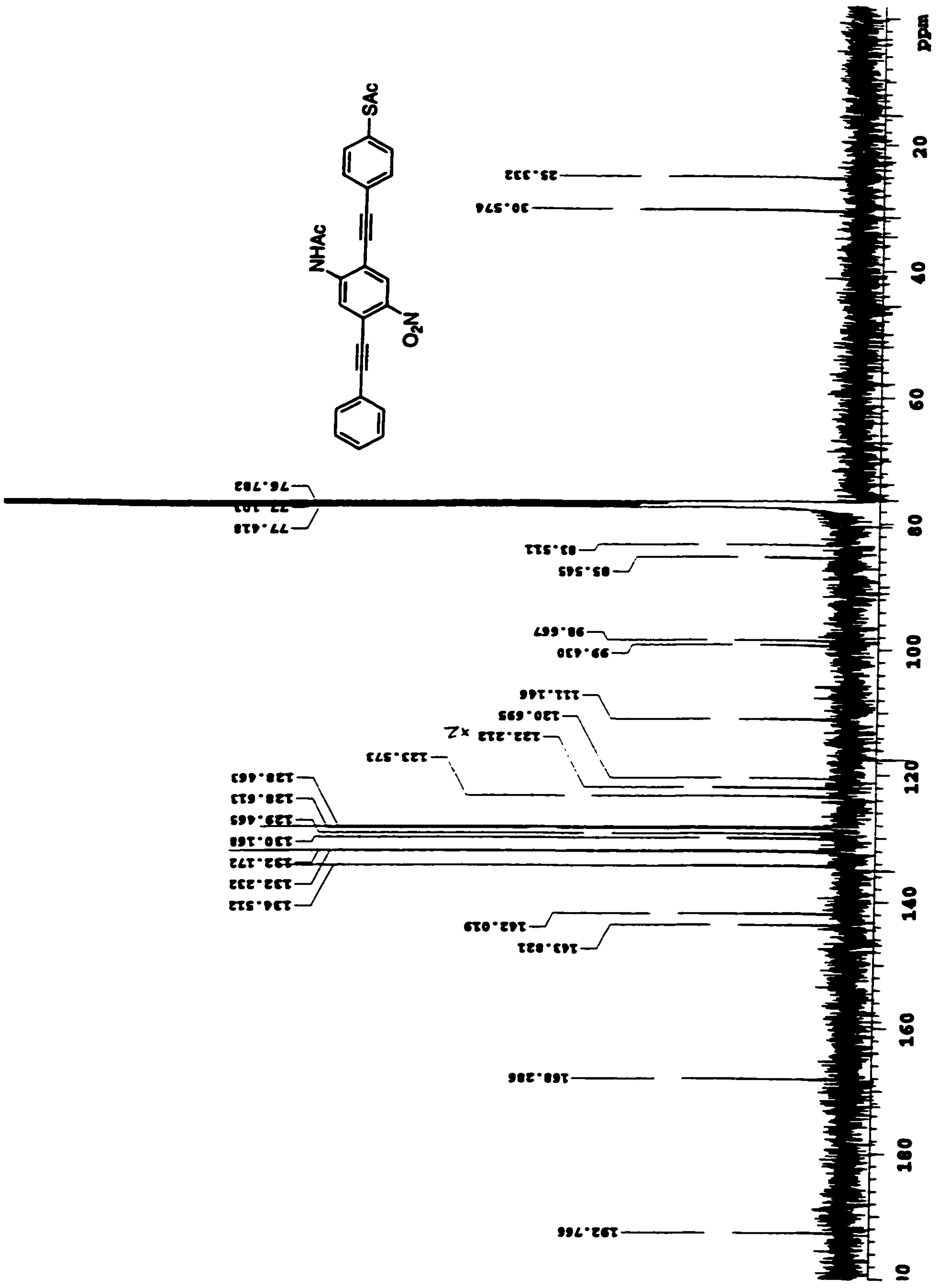

NH$_2$
TMS
O$_2$N
1.000
2.400
3.729
0.425
1.100
2.971
14.903
Integral
ppm
10
8
6
4
2
0

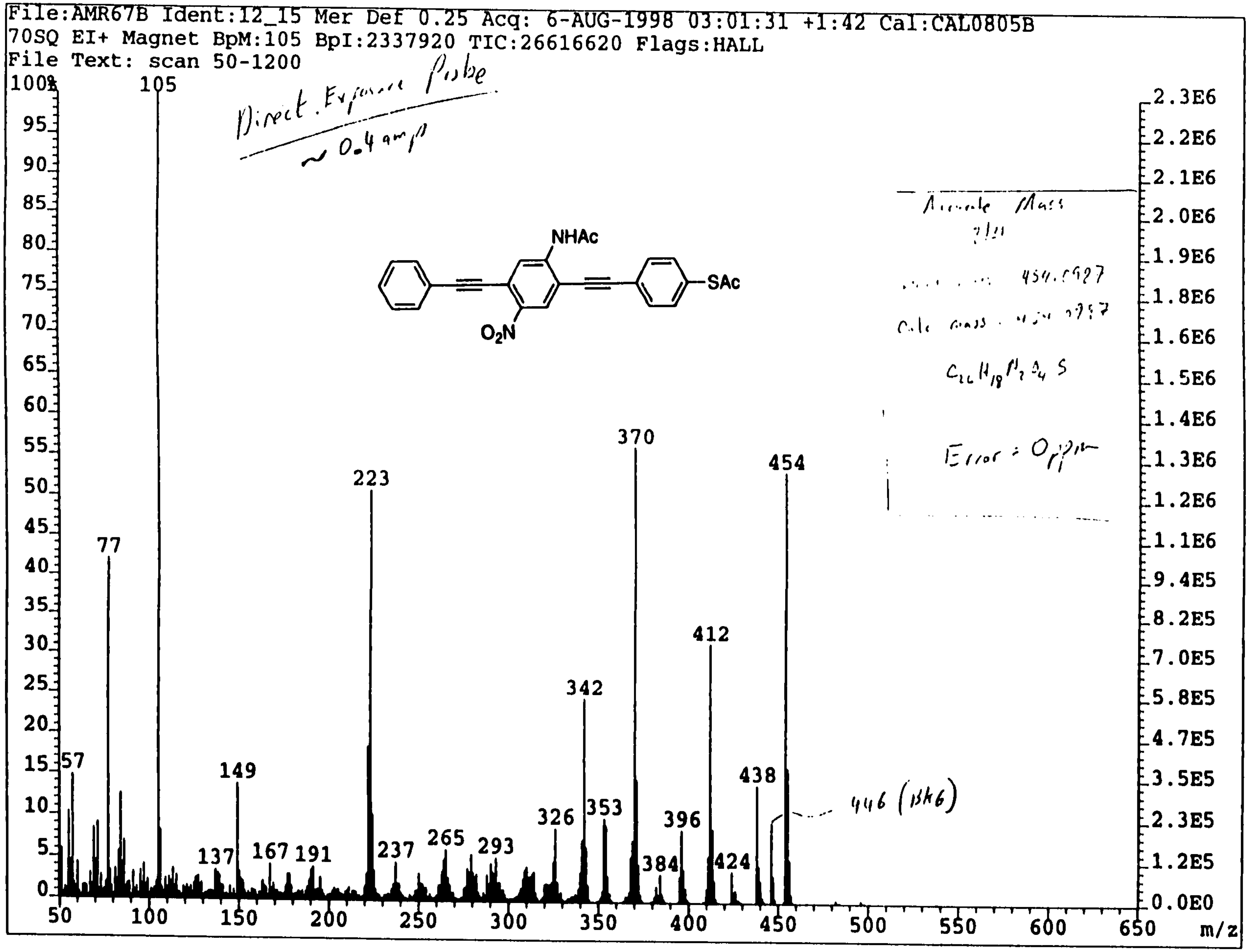

0.300
77.108
77.425
77.743
86.315
97.831
99.082
103.951
107.504
118.219
121.365
122.948
128.848
129.617
130.768
132.472
139.677
151.798
ppm
TMS
NH_2
O_2N
0
25
50
75
100
125
150
175
200
ppm

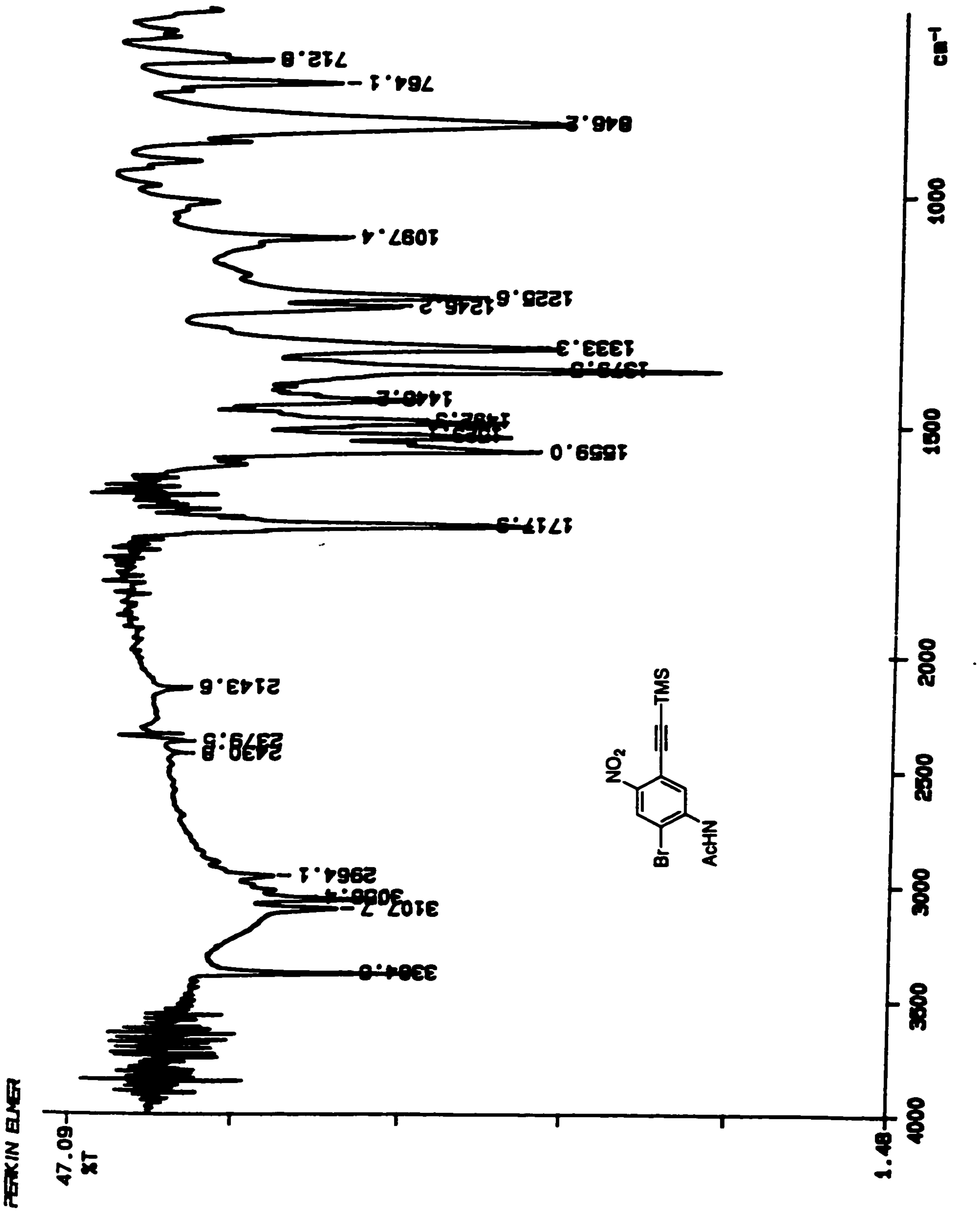

E+ 06
2.59
100
80
60
40
20
50
100
150
200
250
300
350
400
57
73
77
84
105
107
122
149
172
187
217
230
261
291
305
319
334
336
358
391
NH2
TMS
O2N

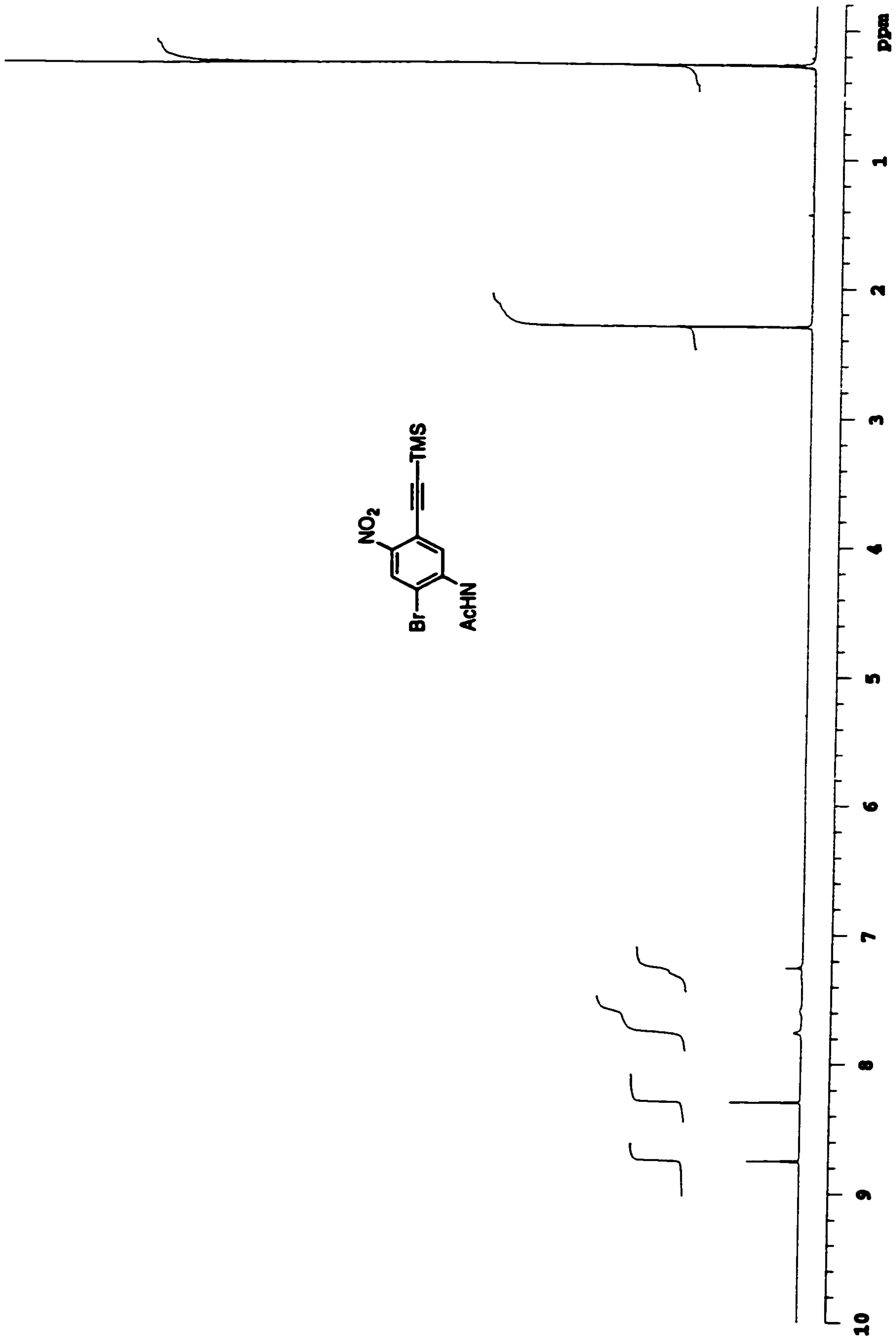

NHAc
SAc
O_2N
2359.2
1384.6
1333.3
953.9
825.6
753.8
4000
3500
3000
2500
2000
1500
1000
cm⁻¹

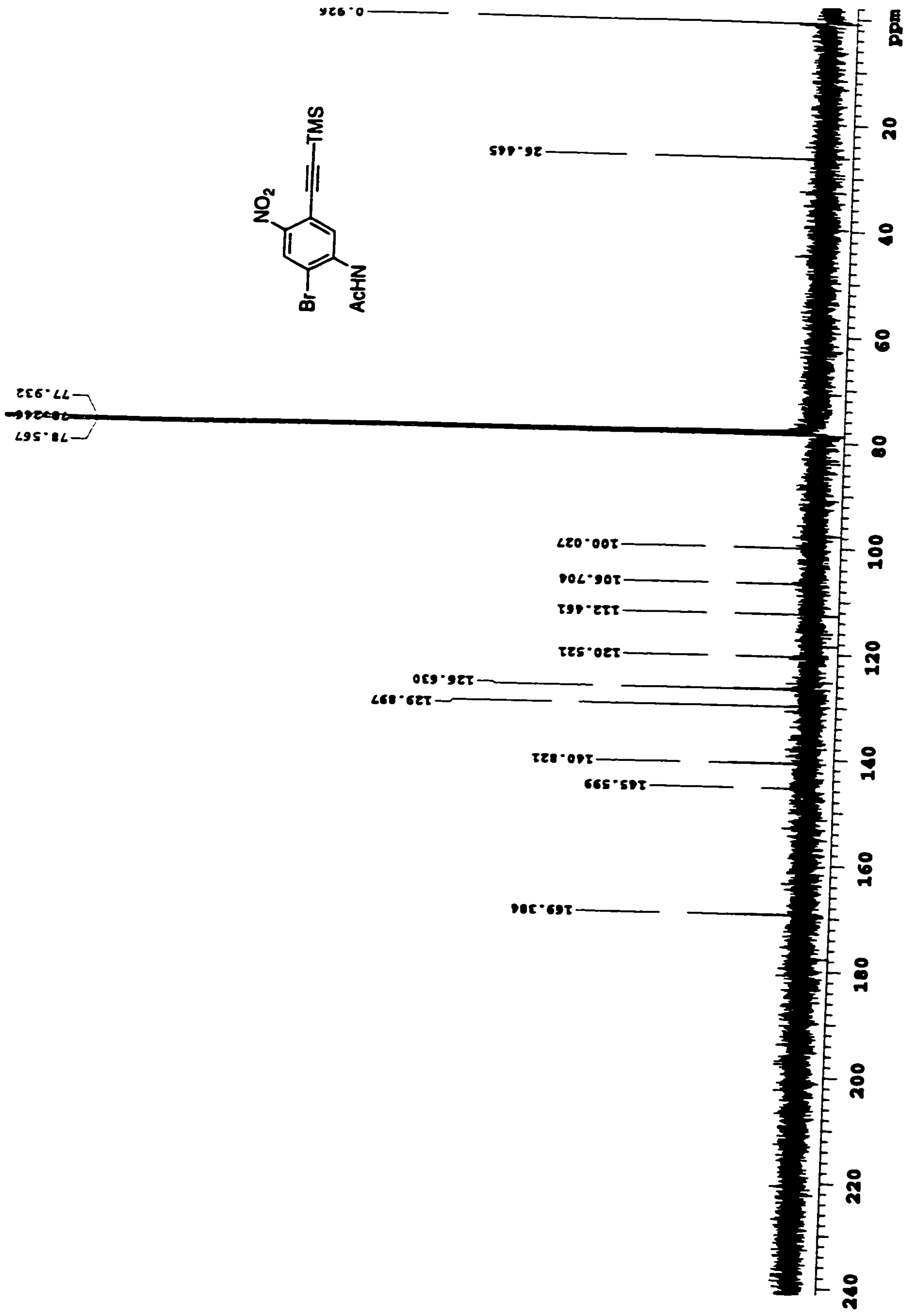

NHAc
SAc
O2N
ppm
1
2
3
4
5
6
7
8
9
10

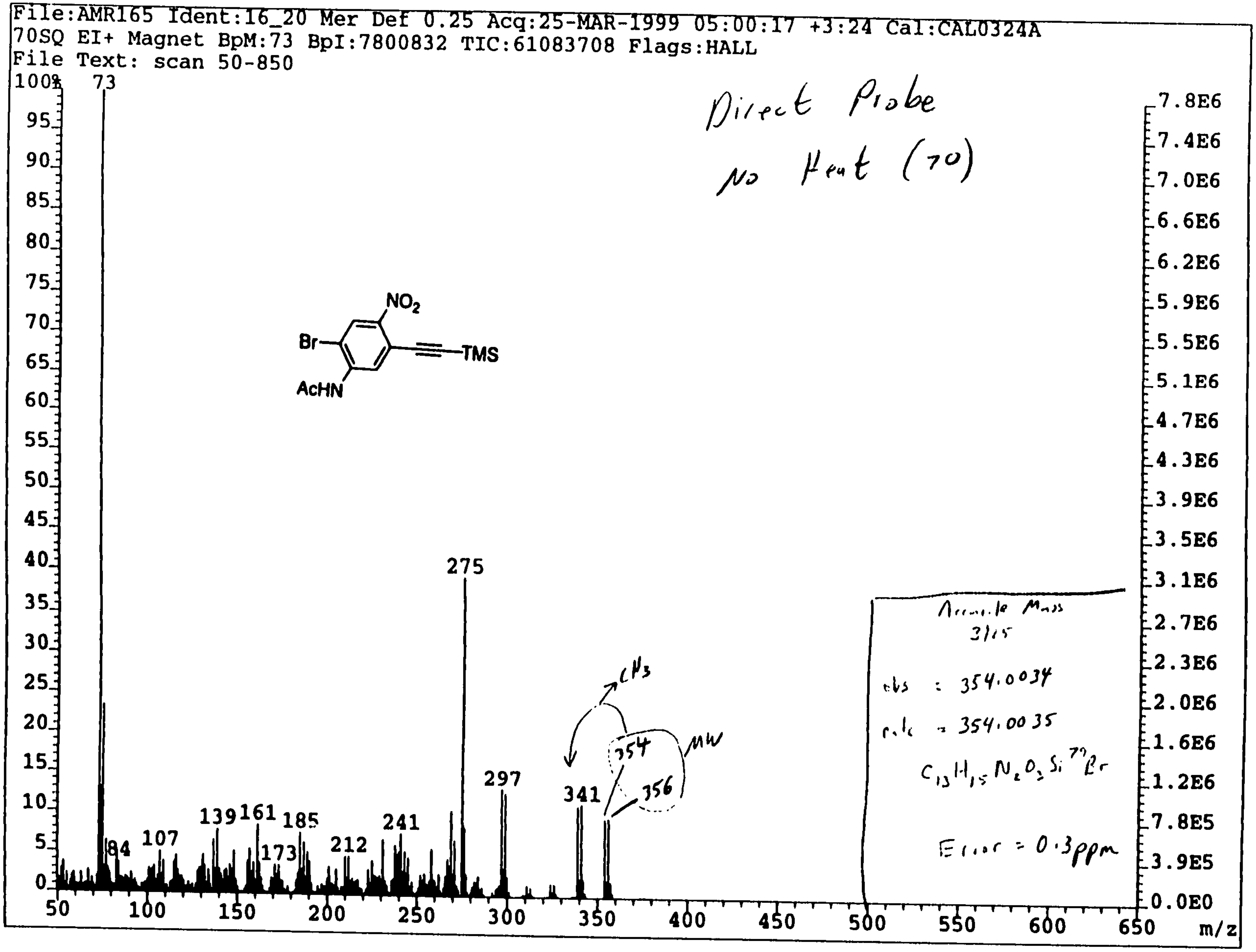

SAc
NHAc
O_2N
25.332
30.574
76.783
77.101
77.418
83.511
85.545
98.667
99.430
111.146
120.695
122.213 x2
123.573
128.463
128.613
129.465
130.168
132.172
133.332
134.512
142.019
143.821
168.286
192.766
ppm
20
40
60
80
100
120
140
160
180


File:AMR67B Ident:12_15 Mer Def 0.25 Acq: 6-AUG-1998 03:01:31 +1:42 Cal:CAL0805B
70SQ EI+ Magnet BpM:105 BpI:2337920 TIC:26616620 Flags:HALL
File Text: scan 50-1200
Direct Exposure Probe
~ 0.4 amp
NHAc
SAc
O2N
Accurate Mass
[illegible]
[illegible] 454.0987
Calc mass : 454.0987
C26H18N2O4S
Error = 0 ppm
446 (Bkg)
100%
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
2.3E6
2.2E6
2.1E6
2.0E6
1.9E6
1.8E6
1.6E6
1.5E6
1.4E6
1.3E6
1.2E6
1.1E6
9.4E5
8.2E5
7.0E5
5.8E5
4.7E5
3.5E5
2.3E5
1.2E5
0.0E0
105
77
57
149
137
167
191
223
237
265
293
326
342
353
370
384
396
412
424
438
454
50
100
150
200
250
300
350
400
450
500
550
600
650
m/z


PERKIN ELMER
47.09
%T
1.48
4000
3500
3000
2500
2000
1500
1000
cm-1
3384.0
3107.7
3088.4
2964.1
2430.8
2379.5
2143.6
1717.9
1559.0
1482.3
1440.2
1379.8
1333.3
1246.2
1225.6
1097.4
846.2
764.1
712.8
NO2
TMS
Br
AcHN


ppm
1
2
3
4
5
6
7
8
9
10
NO$_2$
TMS
Br
AcHN


NO$_2$
TMS
Br
AcHN
0.926
26.445
77.932
78.246
78.567
100.027
106.704
112.461
120.521
126.630
129.897
140.821
145.599
169.386
ppm
20
40
60
80
100
120
140
160
180
200
220
240



File:AMR165 Ident:16_20 Mer Def 0.25 Acq:25-MAR-1999 05:00:17 +3:24 Cal:CAL0324A
70SQ EI+ Magnet BpM:73 BpI:7800832 TIC:61083708 Flags:HALL
File Text: scan 50-850

Direct Probe
No Heat (70)

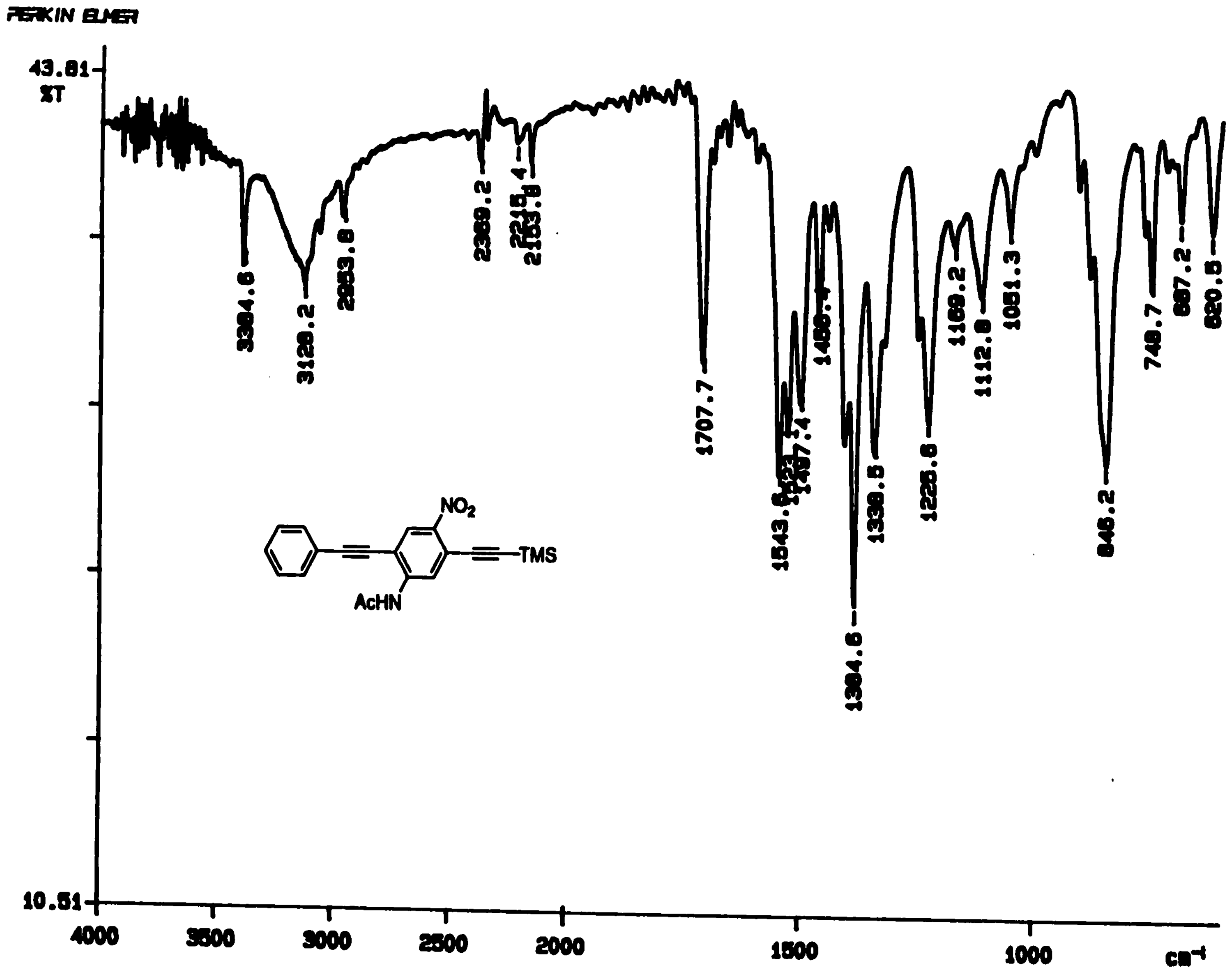
Accurate Mass
3/15

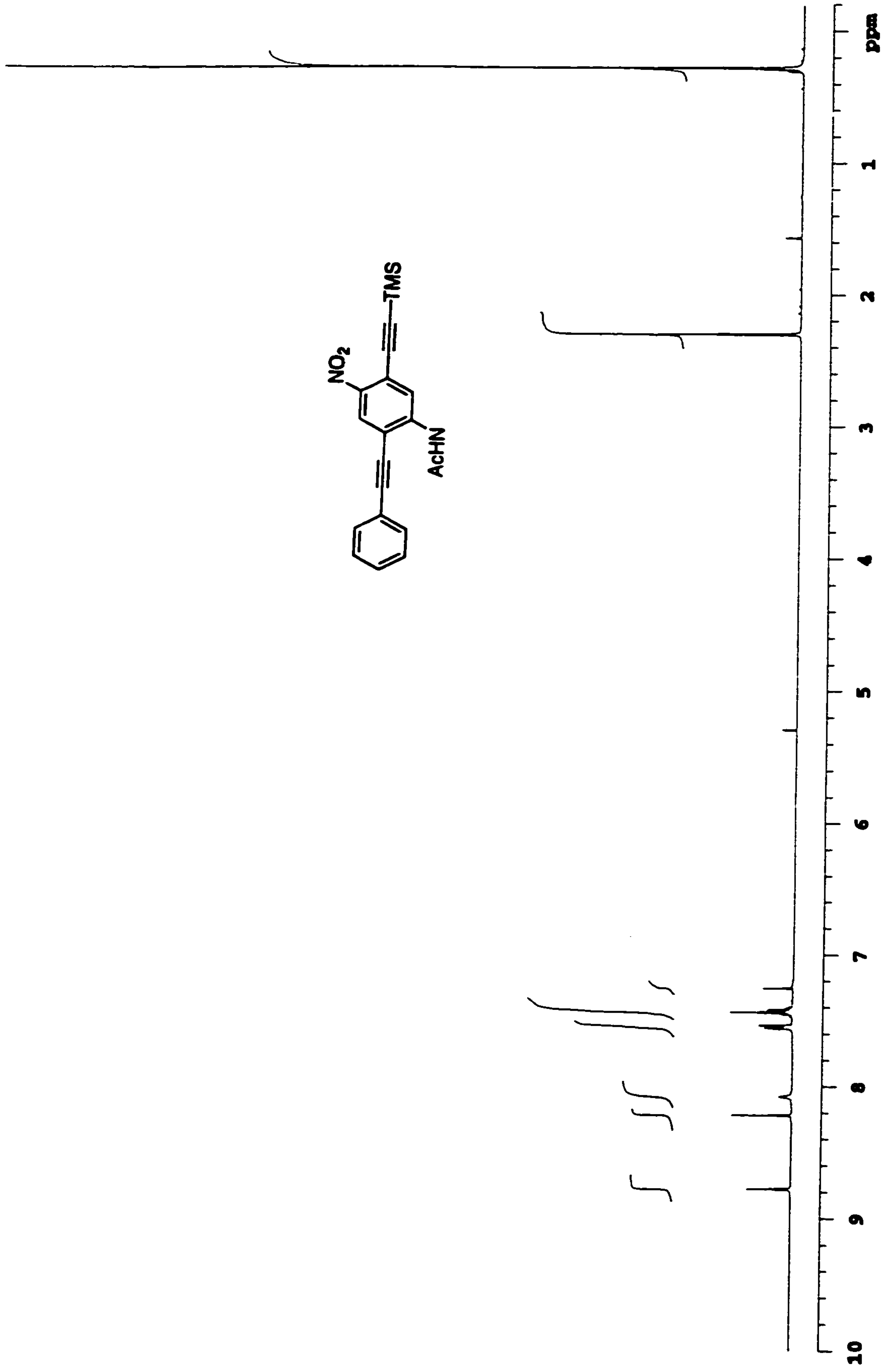
obs : 354.0034

calc = 354.0035

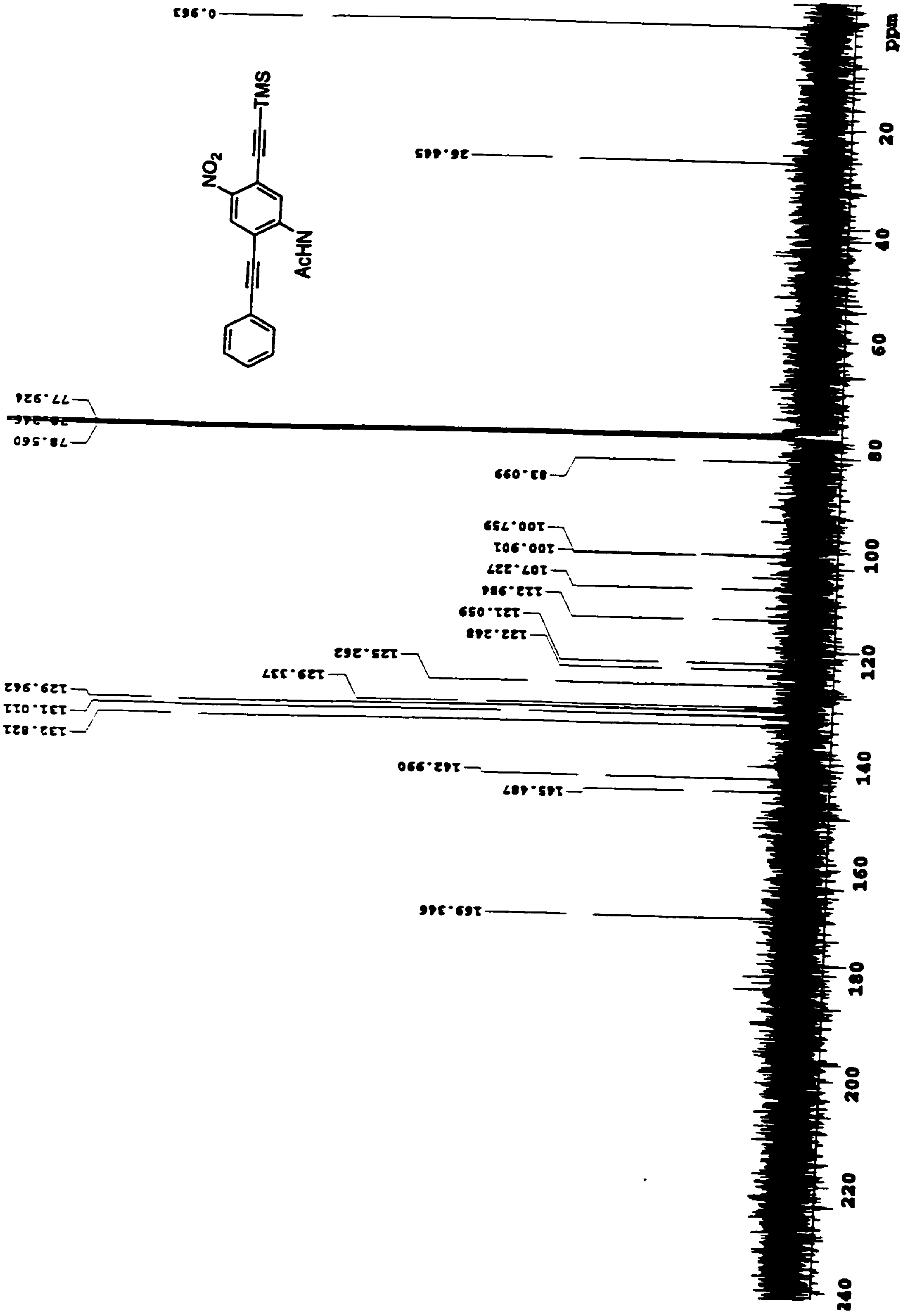
$C_{13}H_{15}N_2O_3Si^{79}Br$

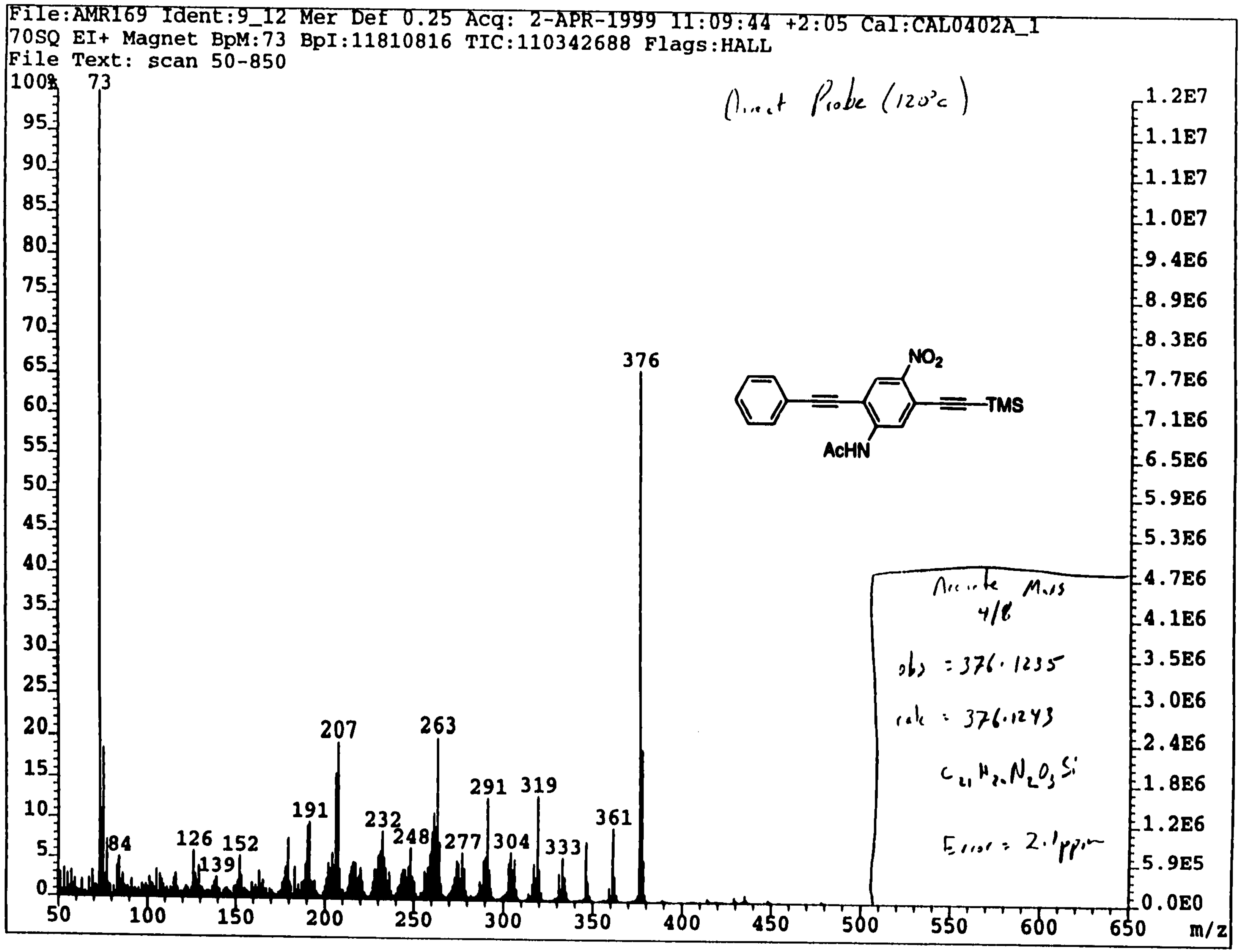
Error = 0.3ppm


PERKIN ELMER
43.81
%T
10.51
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3384.6
3128.2
2953.8
2369.2
2215.4
2153.8
1707.7
1543.6
1523
1497.4
1456.4
1384.6
1338.5
1225.6
1169.2
1112.8
1051.3
846.2
748.7
687.2
620.5
NO2
AcHN
TMS



NO$_2$
TMS
AcHN
ppm
1
2
3
4
5
6
7
8
9
10


NO$_2$
TMS
AcHN
0.963
26.445
77.924
78.246
78.560
83.099
100.759
100.901
107.227
112.984
121.059
122.248
125.262
129.337
129.962
131.011
132.821
142.990
145.487
169.346
ppm
20
40
60
80
100
120
140
160
180
200
220
240



Direct Probe (120°c)

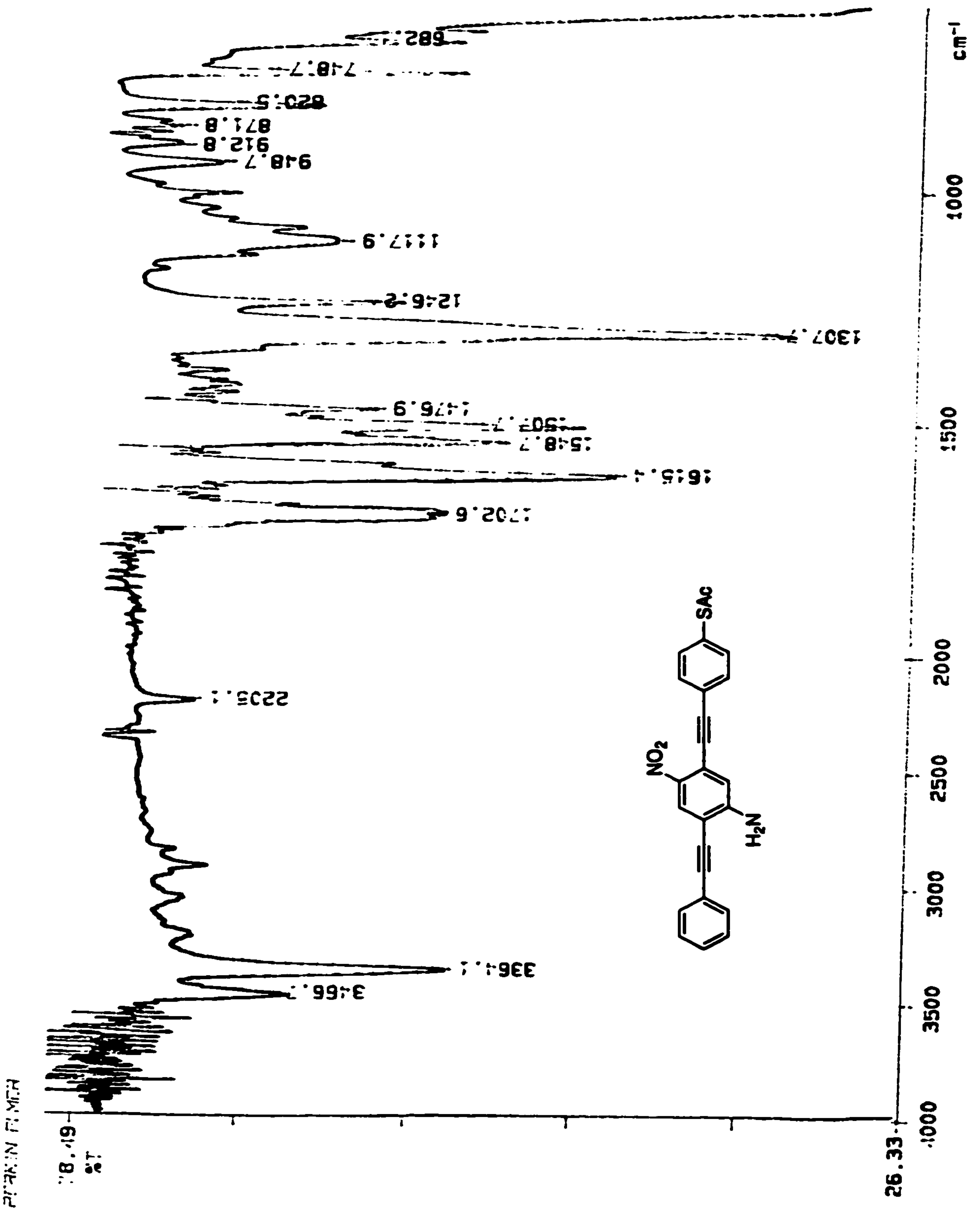
Accurate Mass
4/8

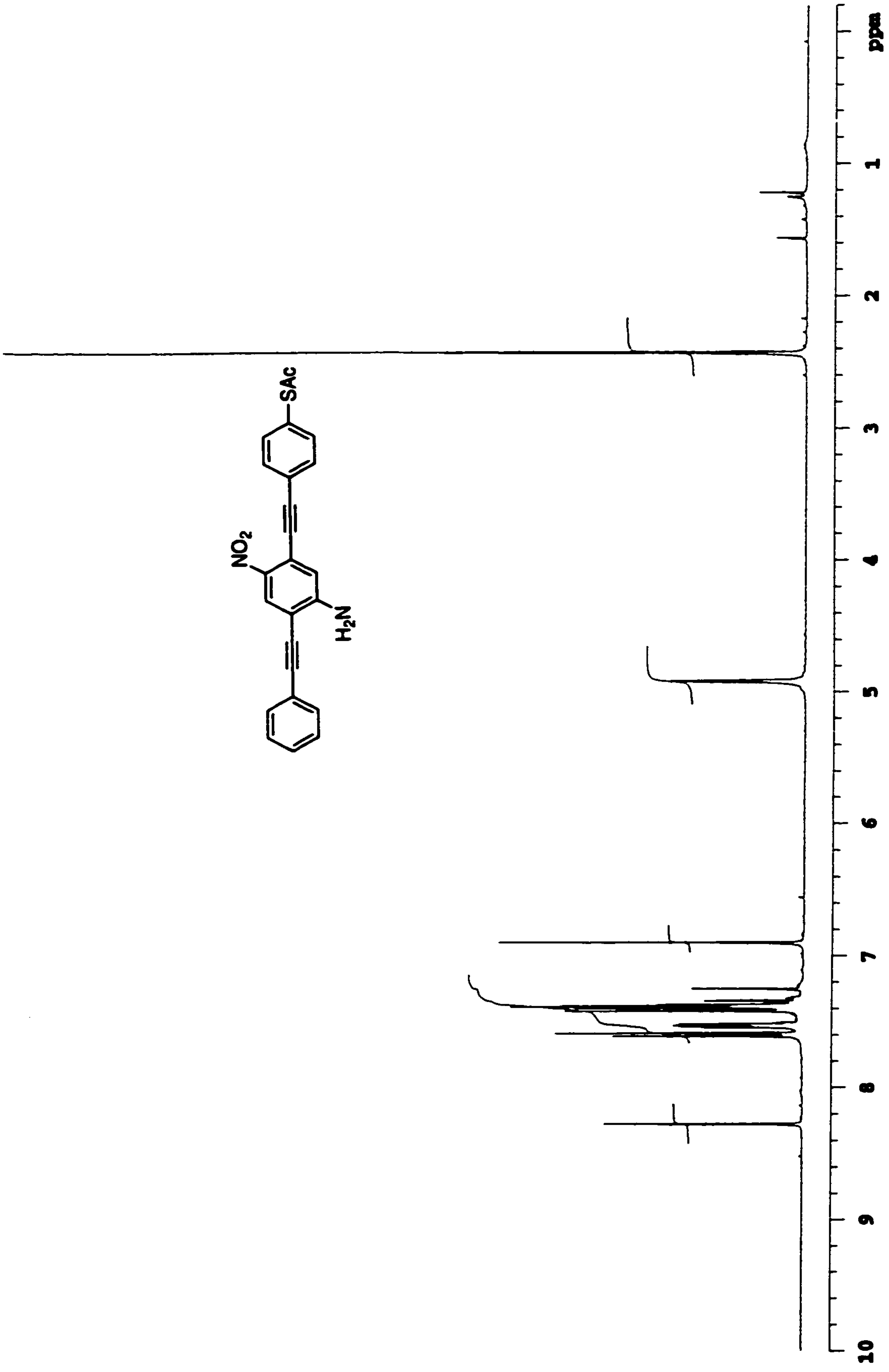
obs = 376.1235

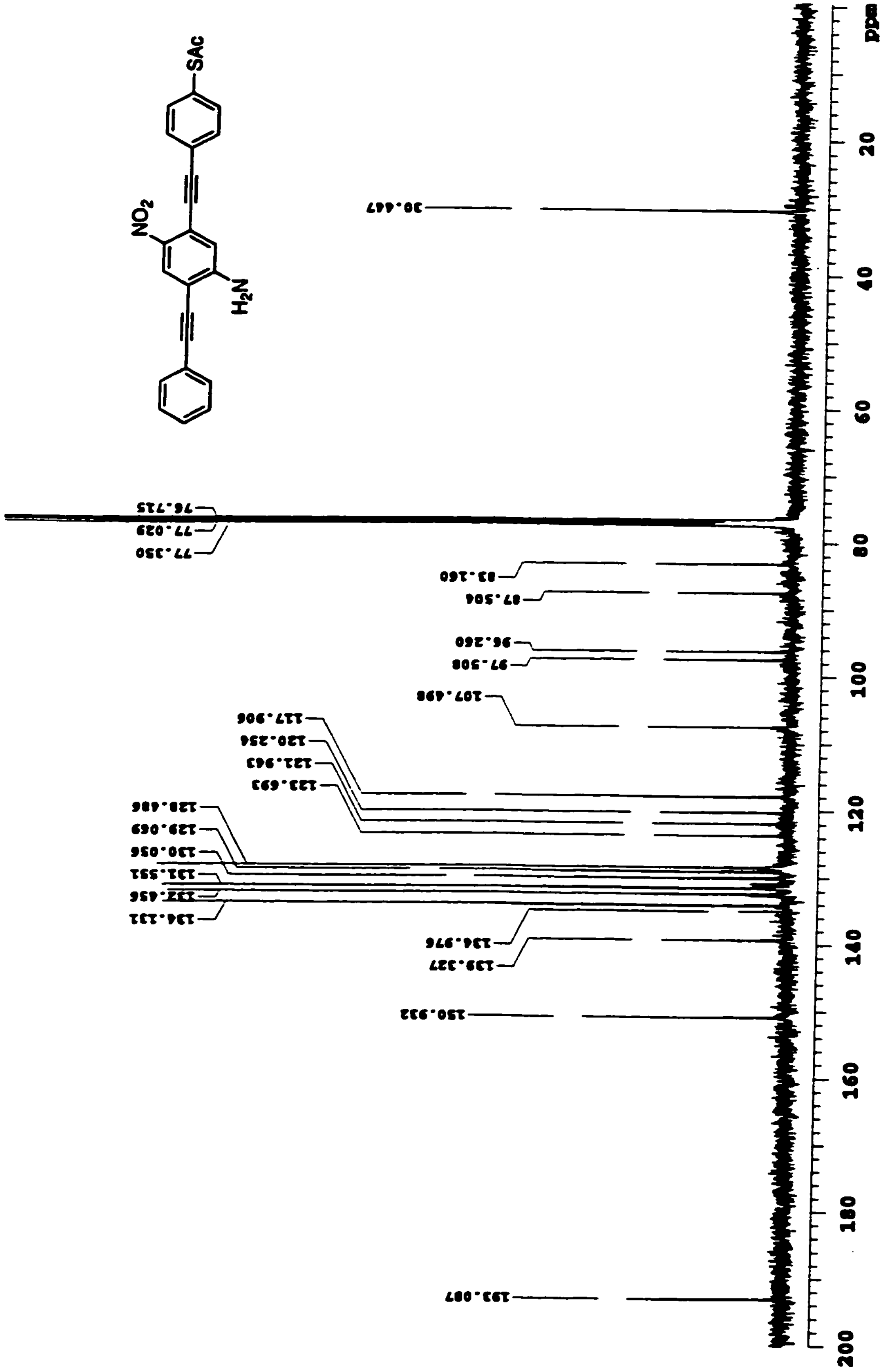
calc = 376.1243

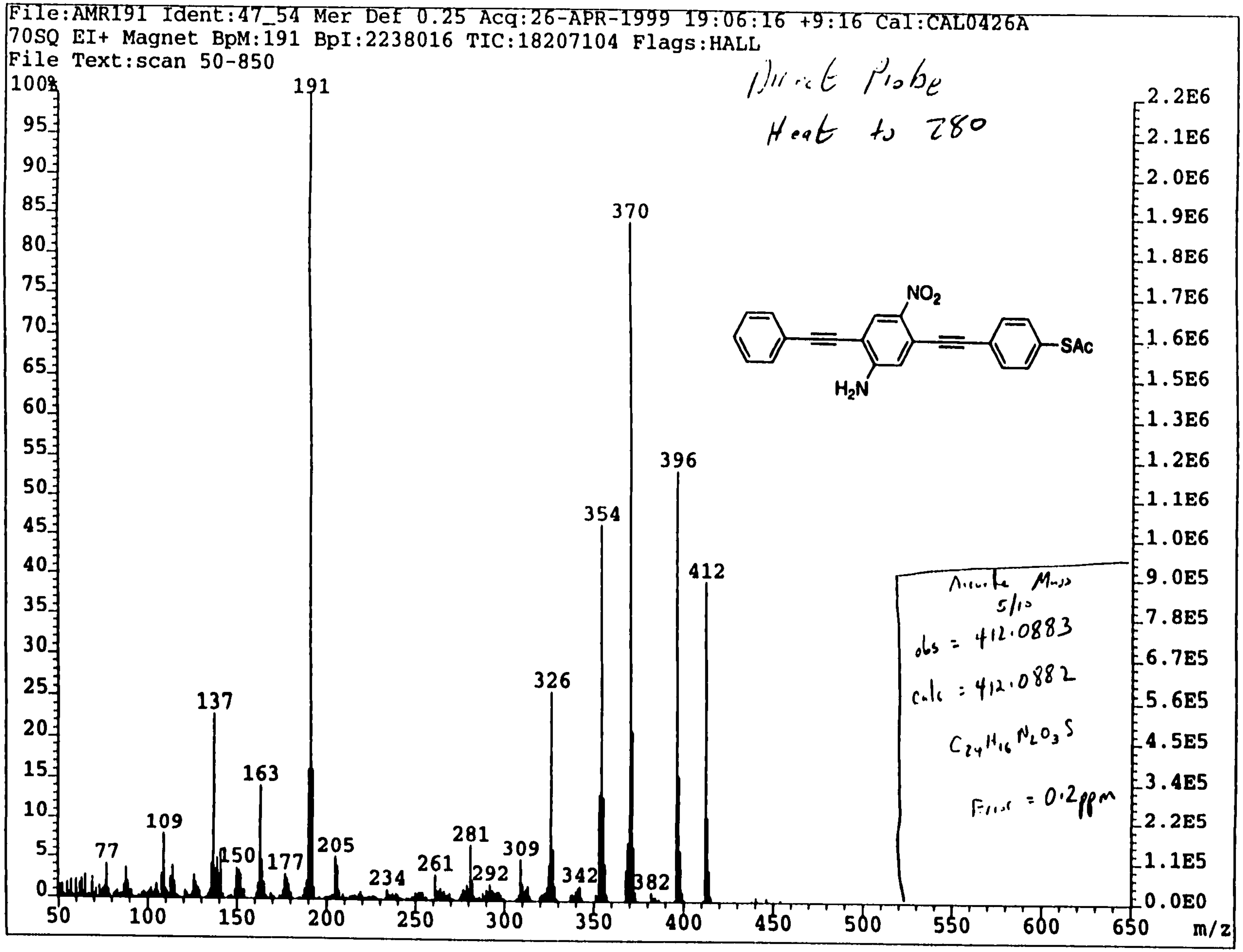
$C_{21}H_{20}N_2O_3Si$

Error = 2.1ppm


PERKIN ELMER
78.49
%T
26.33
4000
3500
3000
2500
2000
1500
1000
cm-1
3466.1
3364.1
2203.1
1702.6
1615.4
1548.7
1507.7
1476.9
1307.7
1246.2
1117.9
948.7
912.8
871.8
820.5
748.7
682
NO2
H2N
SAc


SAc
NO$_2$
H$_2$N
ppm
1
2
3
4
5
6
7
8
9
10

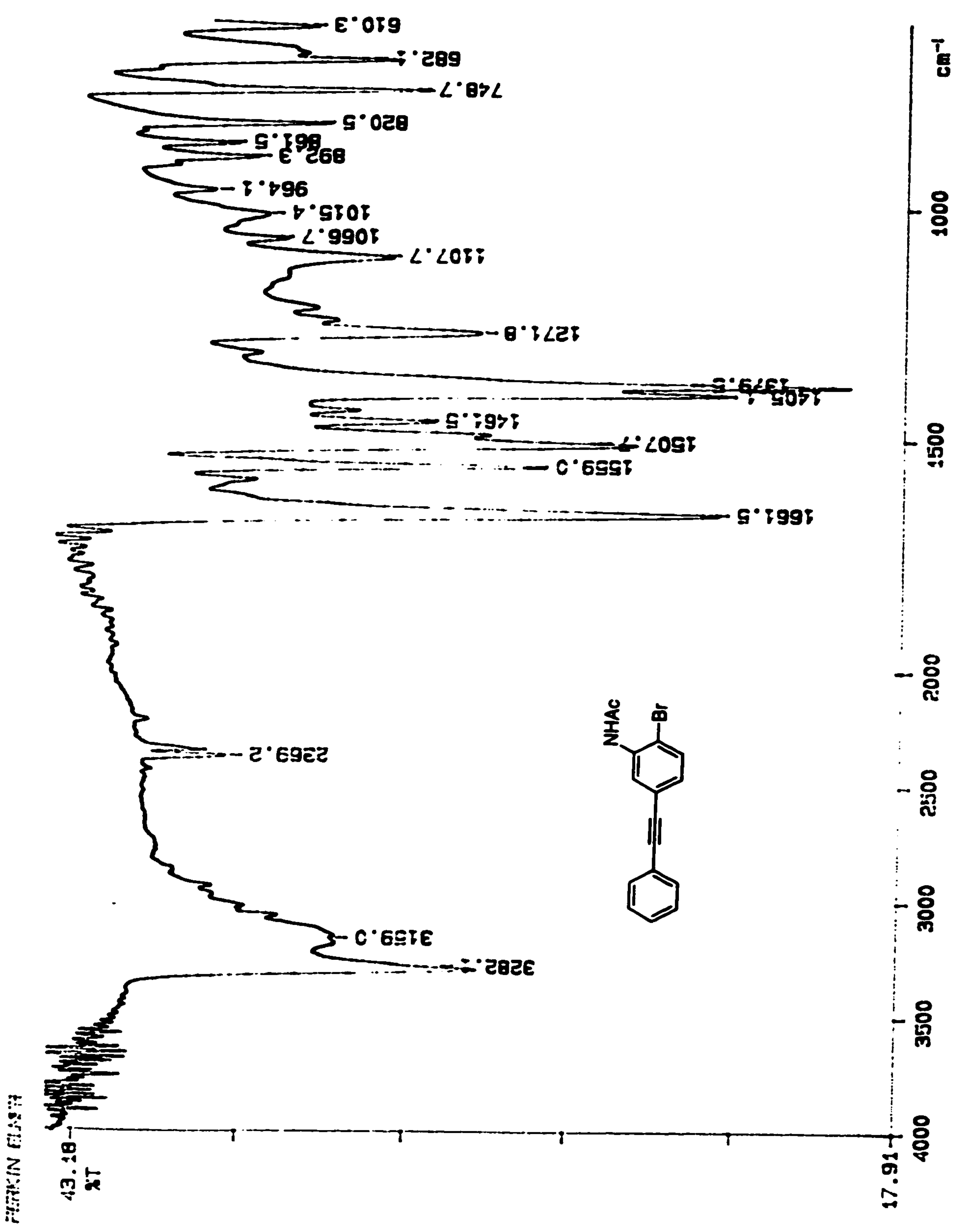

SAc
NO$_2$
H$_2$N
30.447
76.715
77.029
77.350
83.160
87.506
96.260
97.508
107.498
117.906
120.256
121.963
123.693
128.486
129.069
130.036
131.531
132.456
134.131
134.976
139.327
150.933
193.087
ppm
20
40
60
80
100
120
140
160
180
200

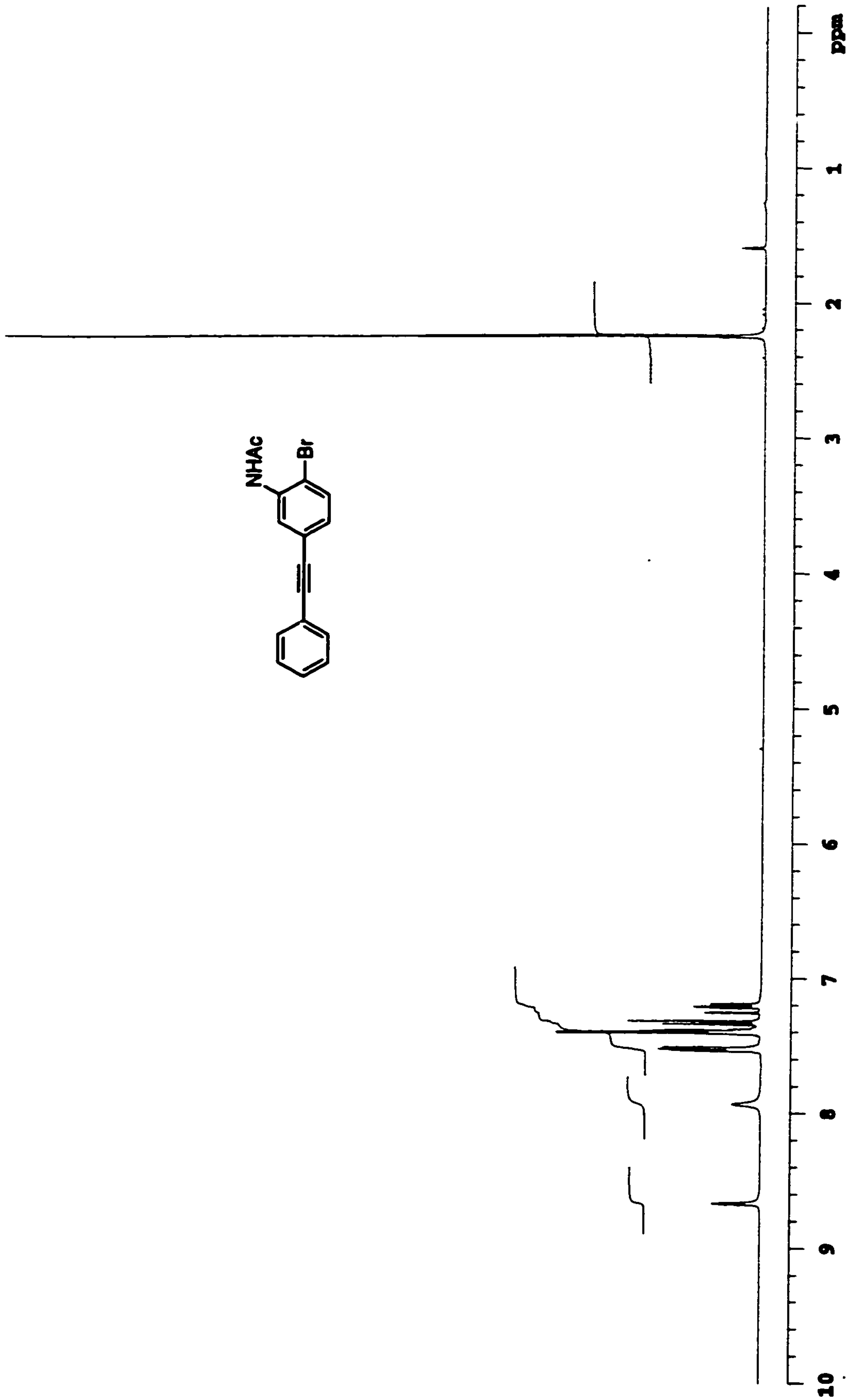


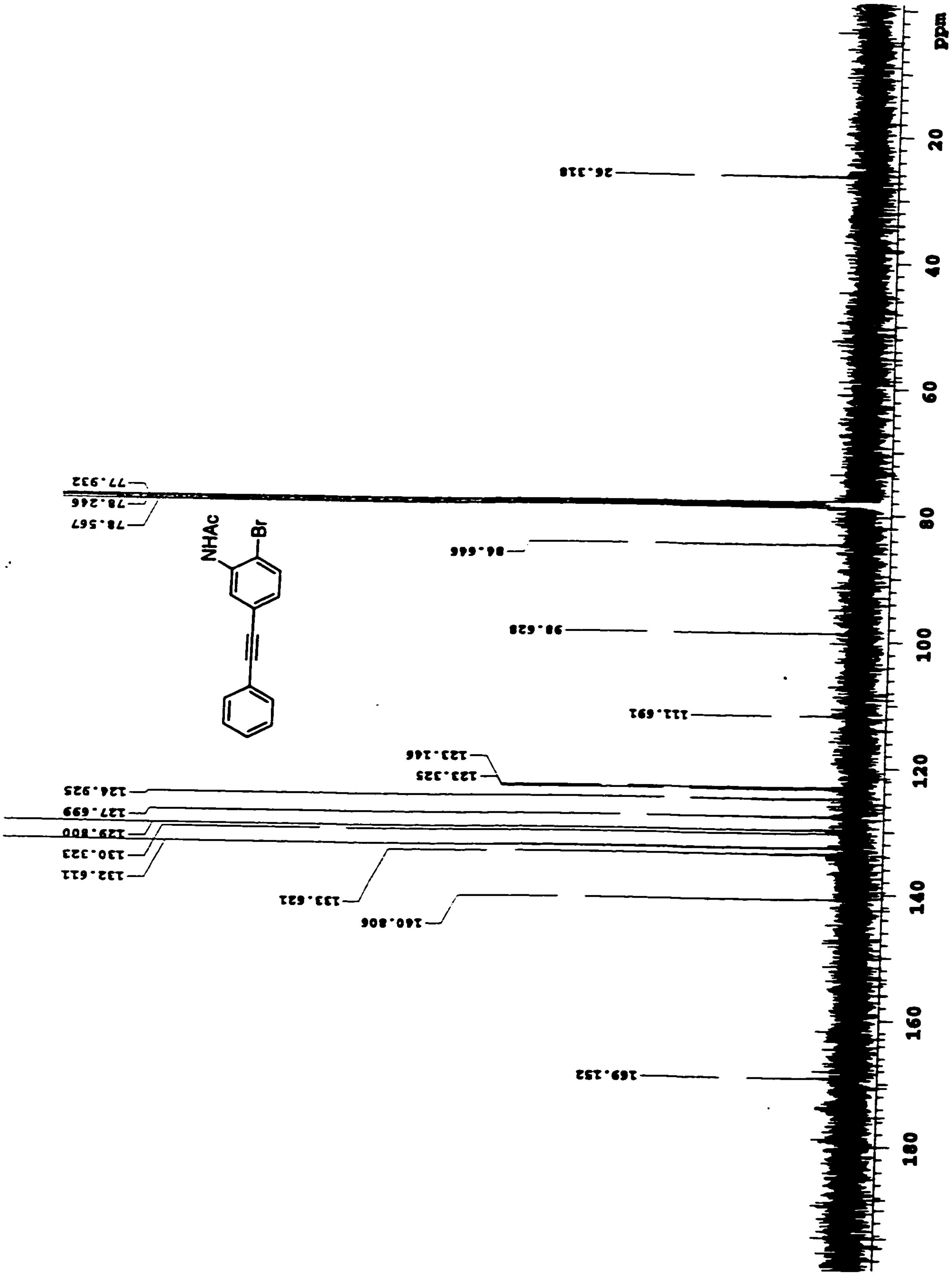
File:AMR191 Ident:47_54 Mer Def 0.25 Acq:26-APR-1999 19:06:16 +9:16 Cal:CAL0426A
70SQ EI+ Magnet BpM:191 BpI:2238016 TIC:18207104 Flags:HALL
File Text:scan 50-850

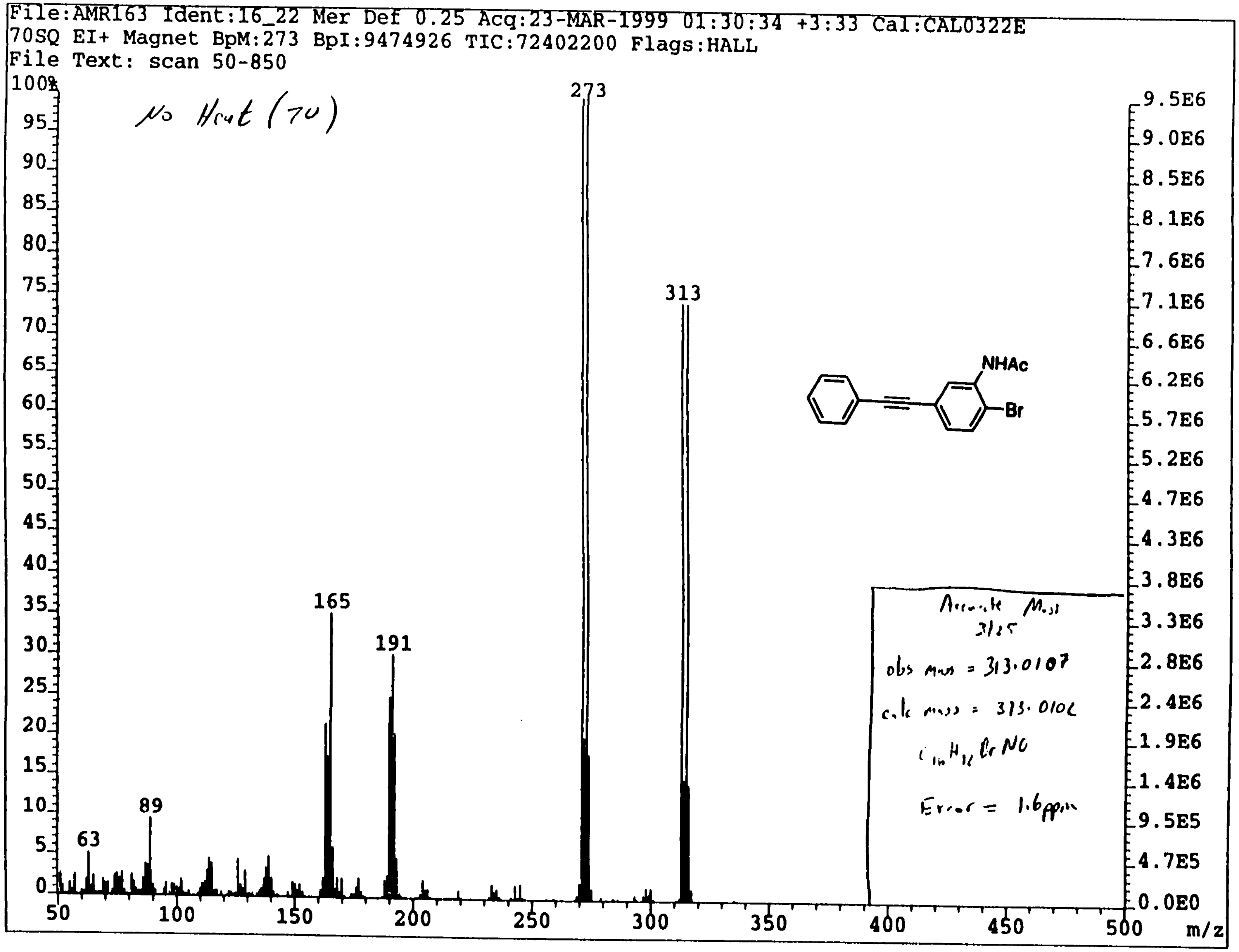
Direct Probe
Heat to 280

Accurate Mass
5/10
obs = 412.0883
calc = 412.0882
$C_{24}H_{16}N_2O_3S$
Error = 0.2ppm


PERKIN ELMER
43.18
%T
17.91
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3282.?
3159.0
2269.2
1661.5
1559.0
1507.7
1461.5
1405.?
1379.5
1271.8
1107.7
1066.7
1015.4
964.1
892.3
861.5
820.5
748.7
682.?
610.3
NHAc
Br


NHAc
Br
ppm
1
2
3
4
5
6
7
8
9
10

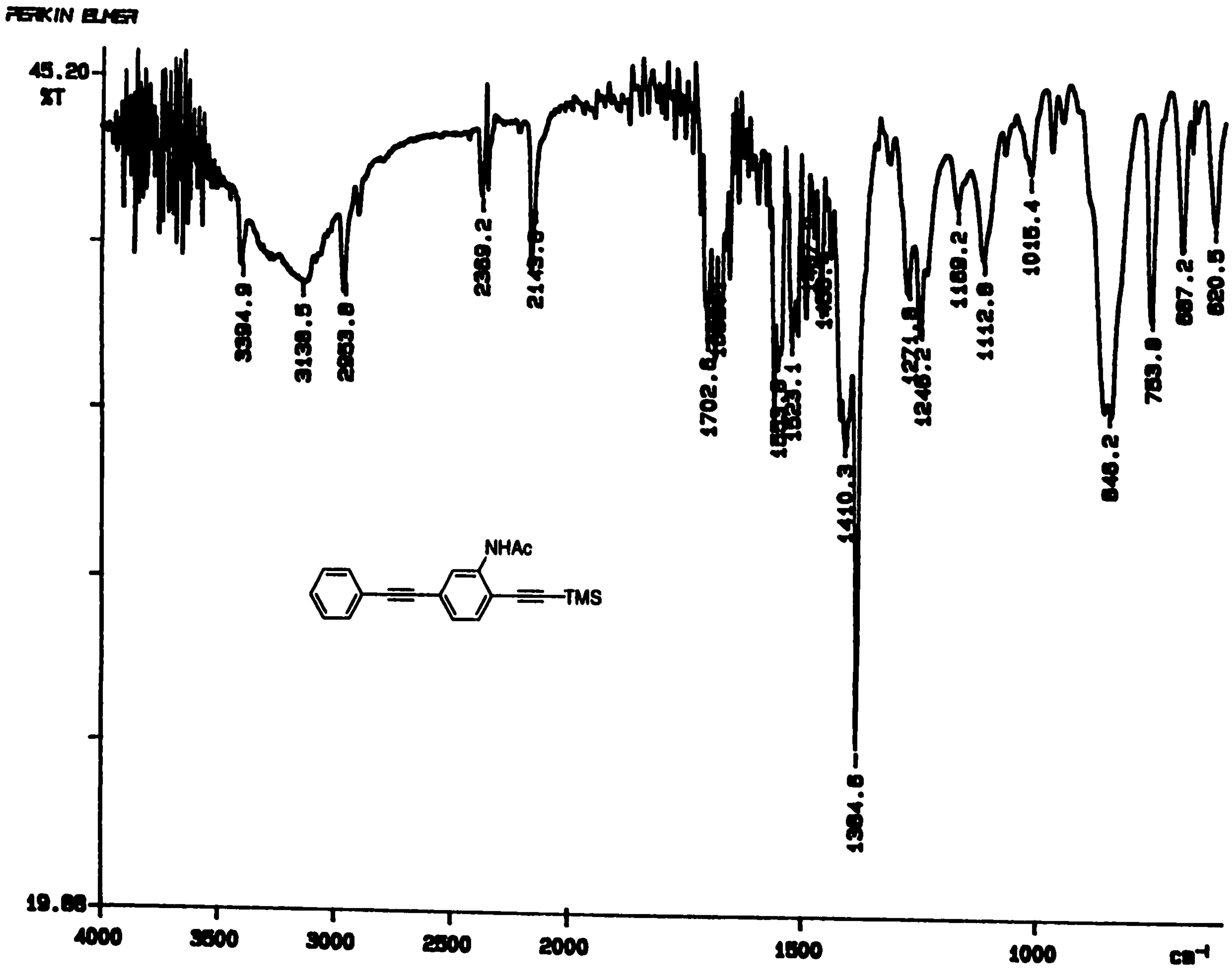

ppm
20
40
60
80
100
120
140
160
180
26.318
77.932
78.246
78.567
84.646
98.628
111.691
123.146
123.325
124.925
127.699
129.800
130.323
132.611
133.621
140.806
169.152
NHAc
Br

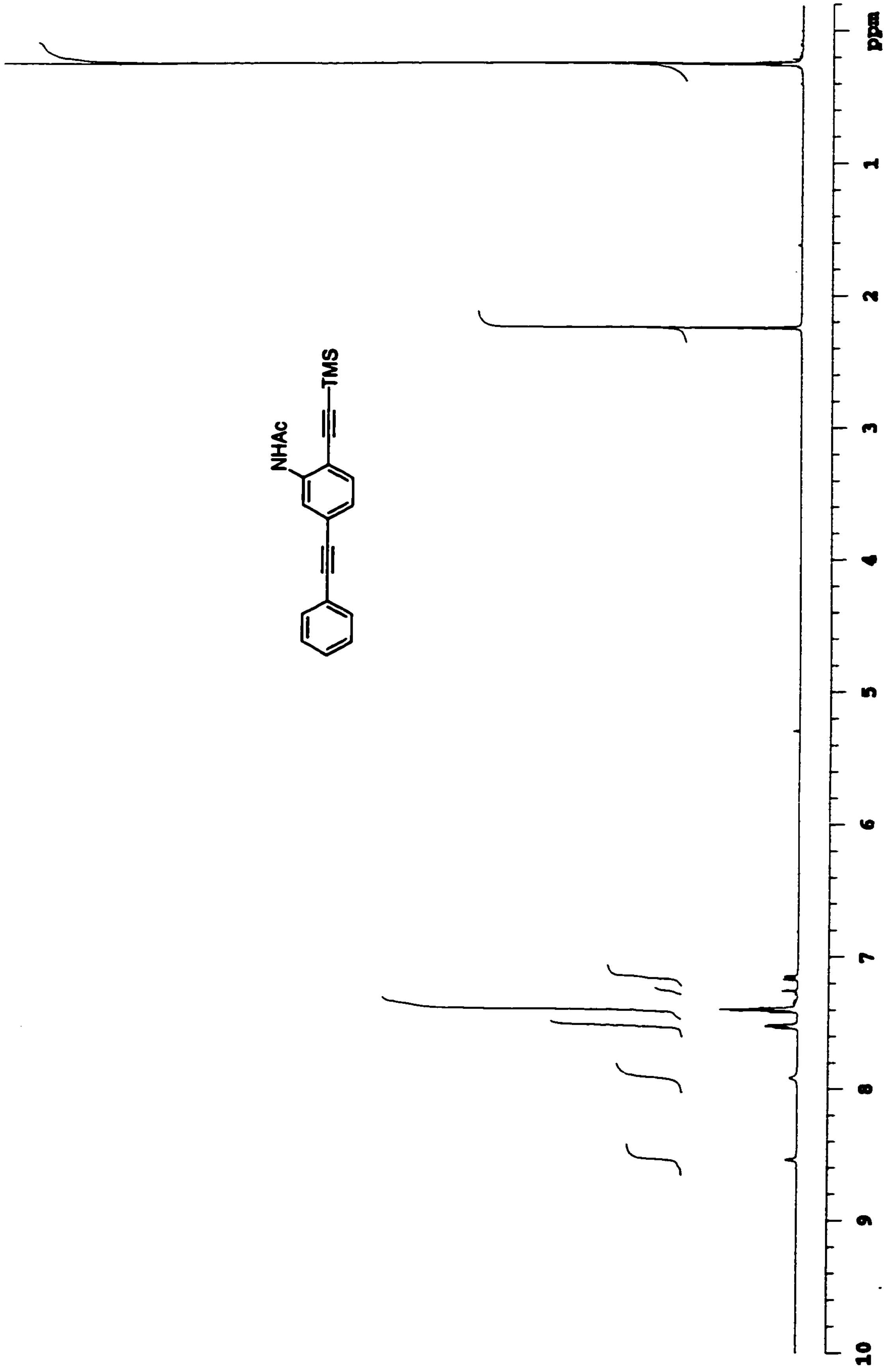


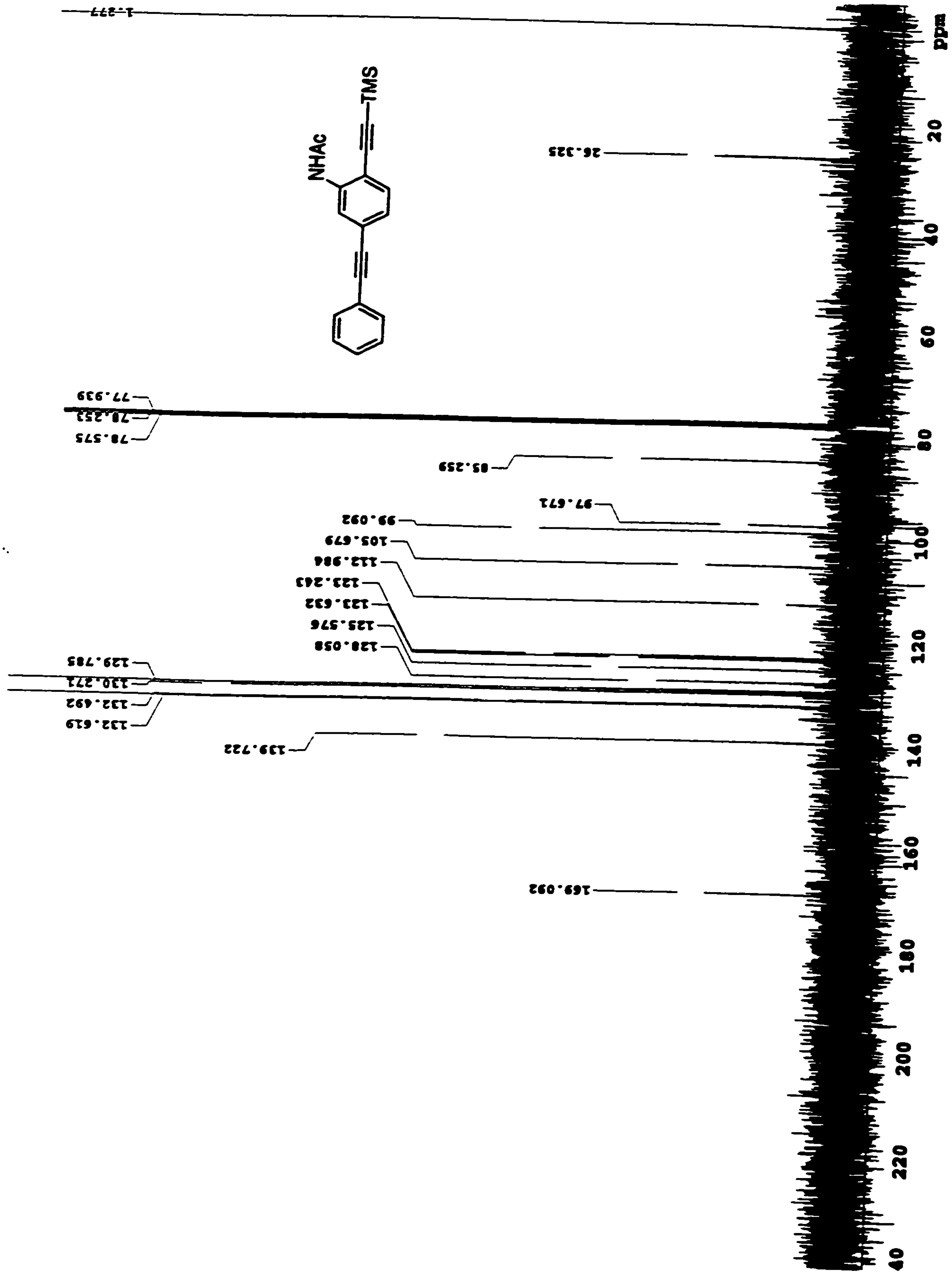
File:AMR163 Ident:16_22 Mer Def 0.25 Acq:23-MAR-1999 01:30:34 +3:33 Cal:CAL0322E
70SQ EI+ Magnet BpM:273 BpI:9474926 TIC:72402200 Flags:HALL
File Text: scan 50-850

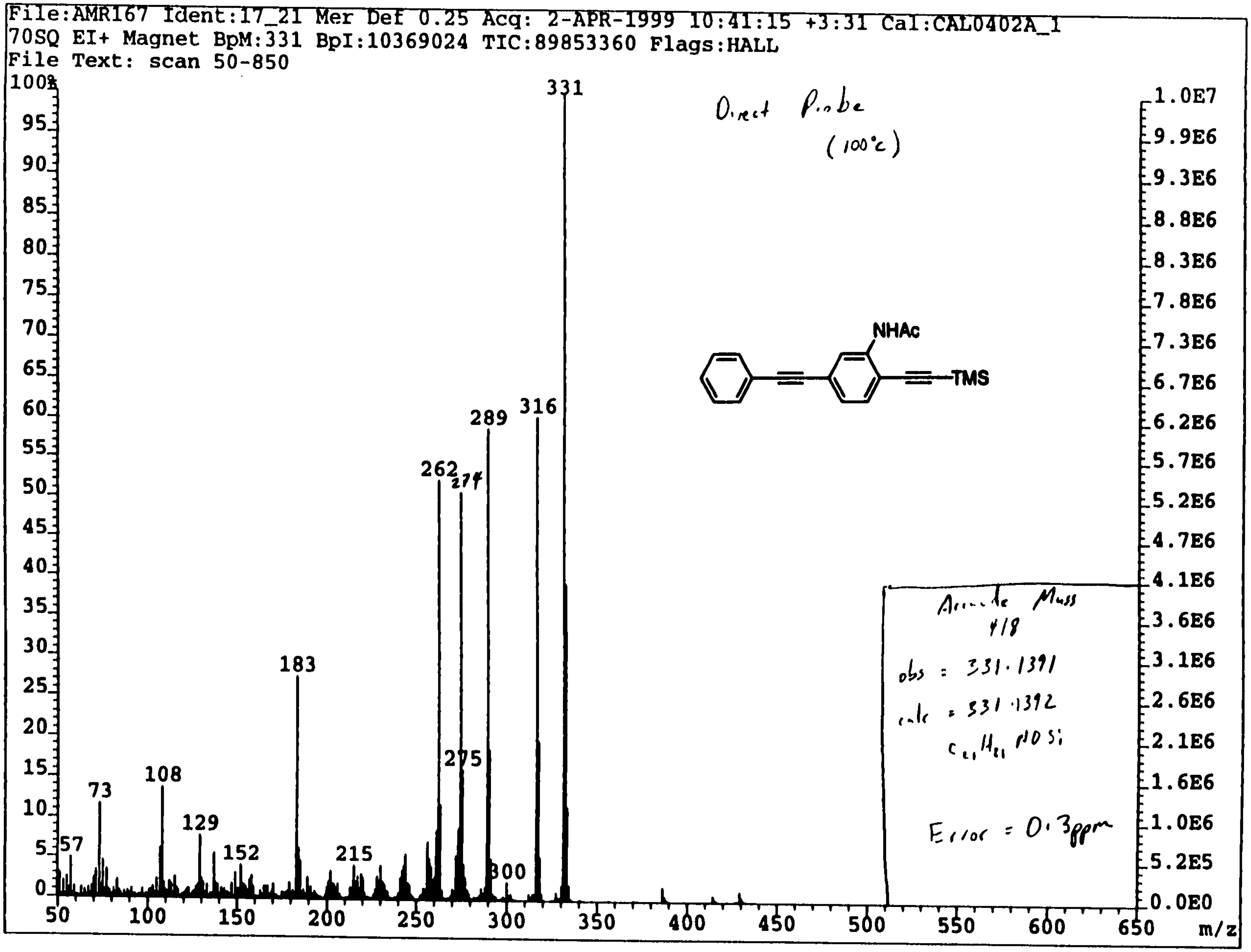
No Heat (70)

Accurate Mass
3/25
obs mass = 313.0107
calc mass = 313.0102
$C_{16}H_{12}BrNO$
Error = 1.6ppm


PERKIN ELMER
45.20
%T
19.88
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3394.9
3138.5
2953.8
2369.2
2143.8
1702.6
1523.1
1410.3
1384.6
1271.8
1246.2
1169.2
1112.8
1015.4
846.2
753.8
687.2
620.5
NHAc
TMS


NHAc
TMS
ppm
1
2
3
4
5
6
7
8
9
10


NHAc
TMS
1.277
26.325
77.939
78.253
78.575
85.259
97.671
99.092
105.679
113.984
123.243
123.633
125.576
128.058
129.785
130.271
132.492
132.619
139.722
169.092
ppm
20
40
60
80
100
120
140
160
180
200
220
40



File:AMR167 Ident:17_21 Mer Def 0.25 Acq: 2-APR-1999 10:41:15 +3:31 Cal:CAL0402A_1
70SQ EI+ Magnet BpM:331 BpI:10369024 TIC:89853360 Flags:HALL
File Text: scan 50-850

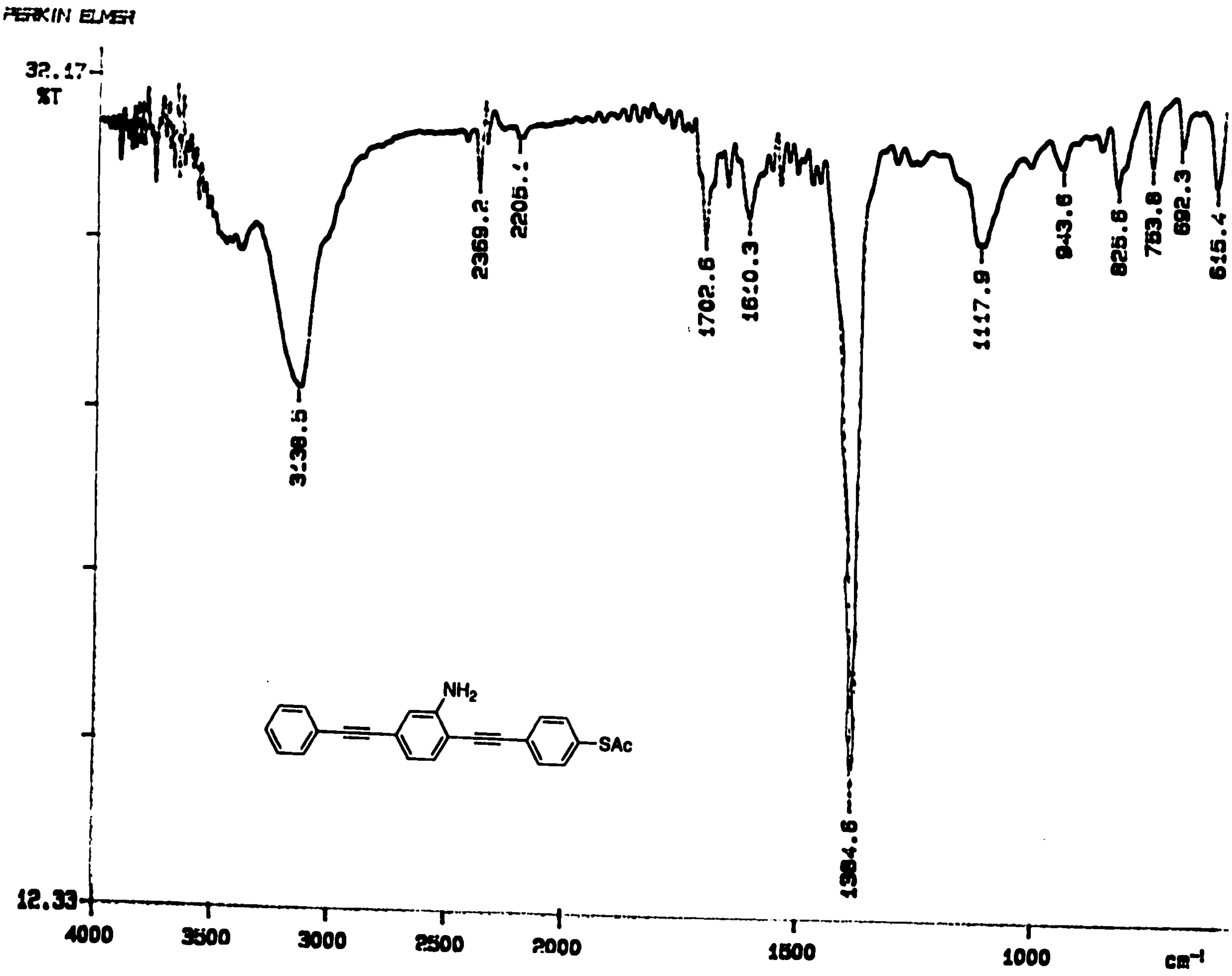
Direct Probe
(100°c)

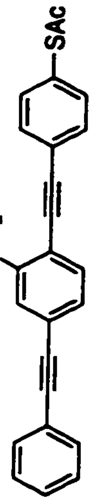
Accurate Mass
4/8

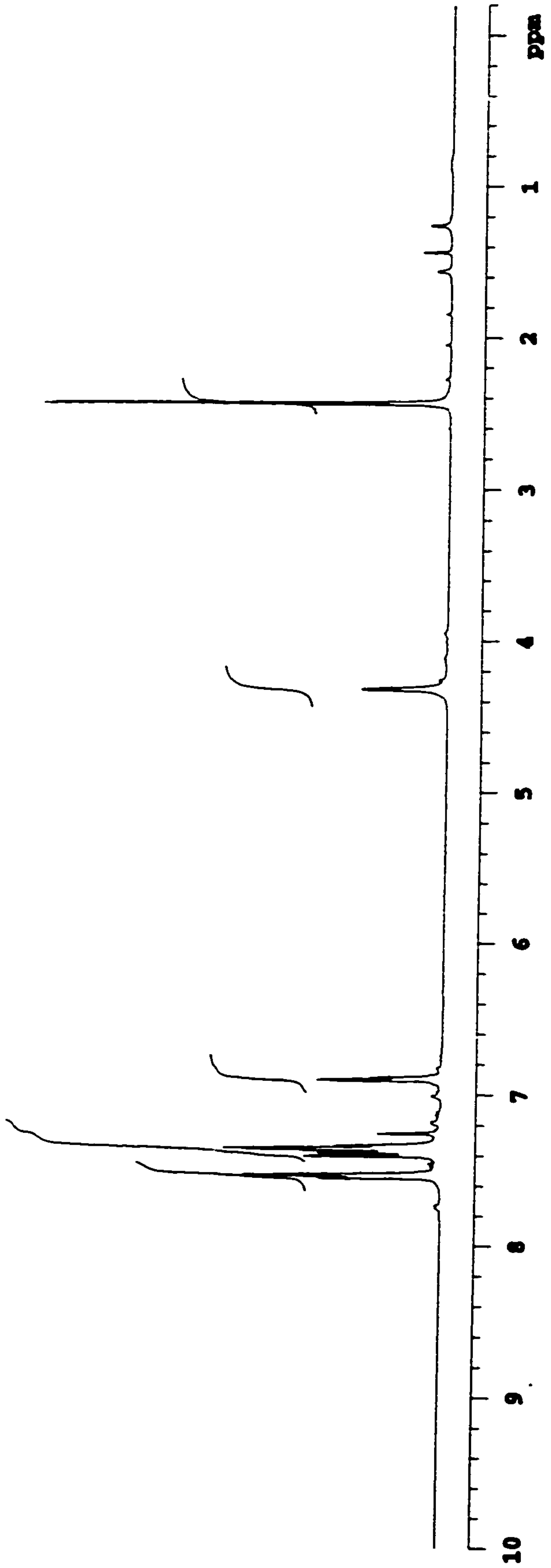
obs = 331.1391

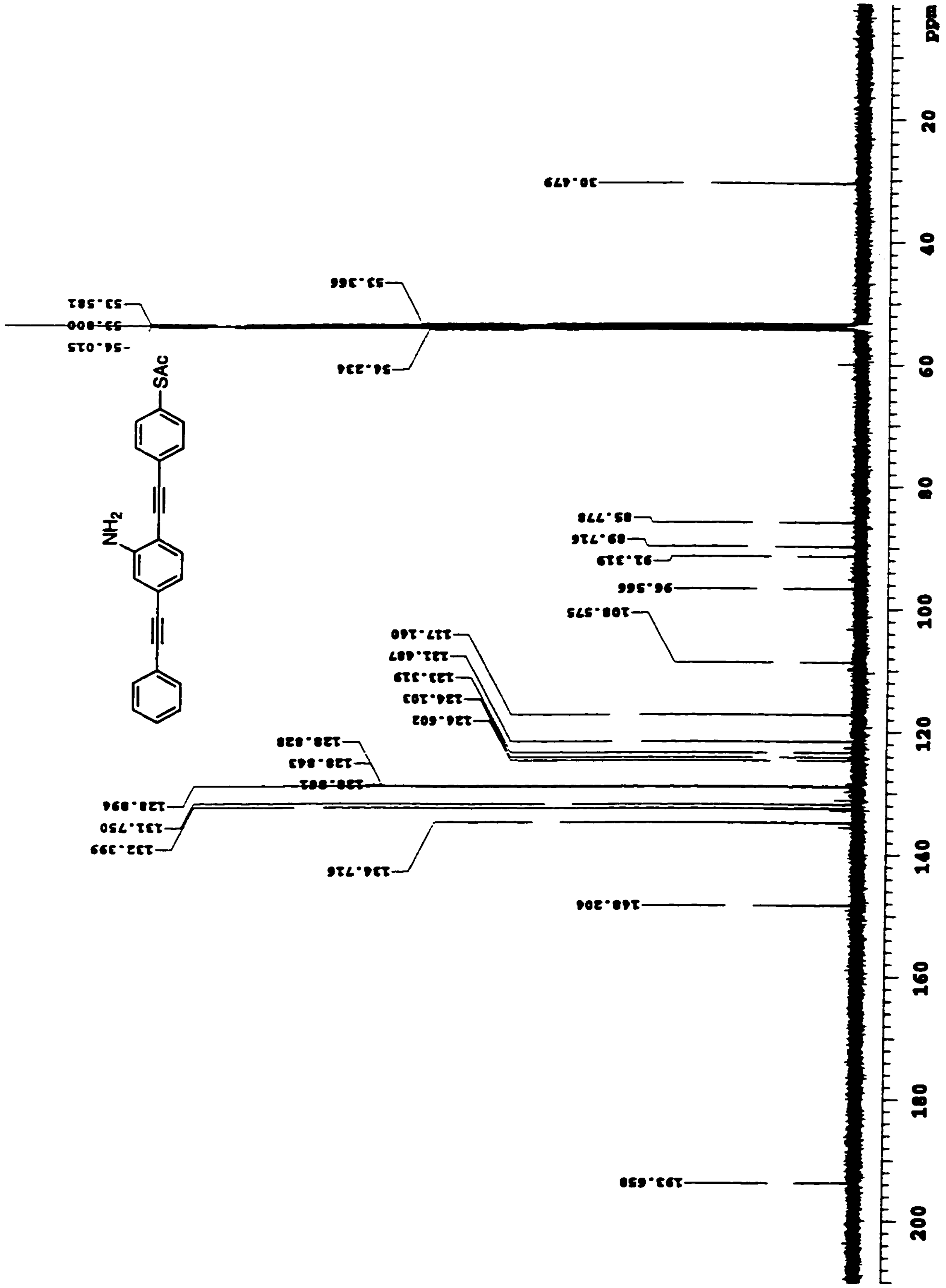
calc = 331.1392
$C_{21}H_{21}NOSi$

Error = 0.3ppm

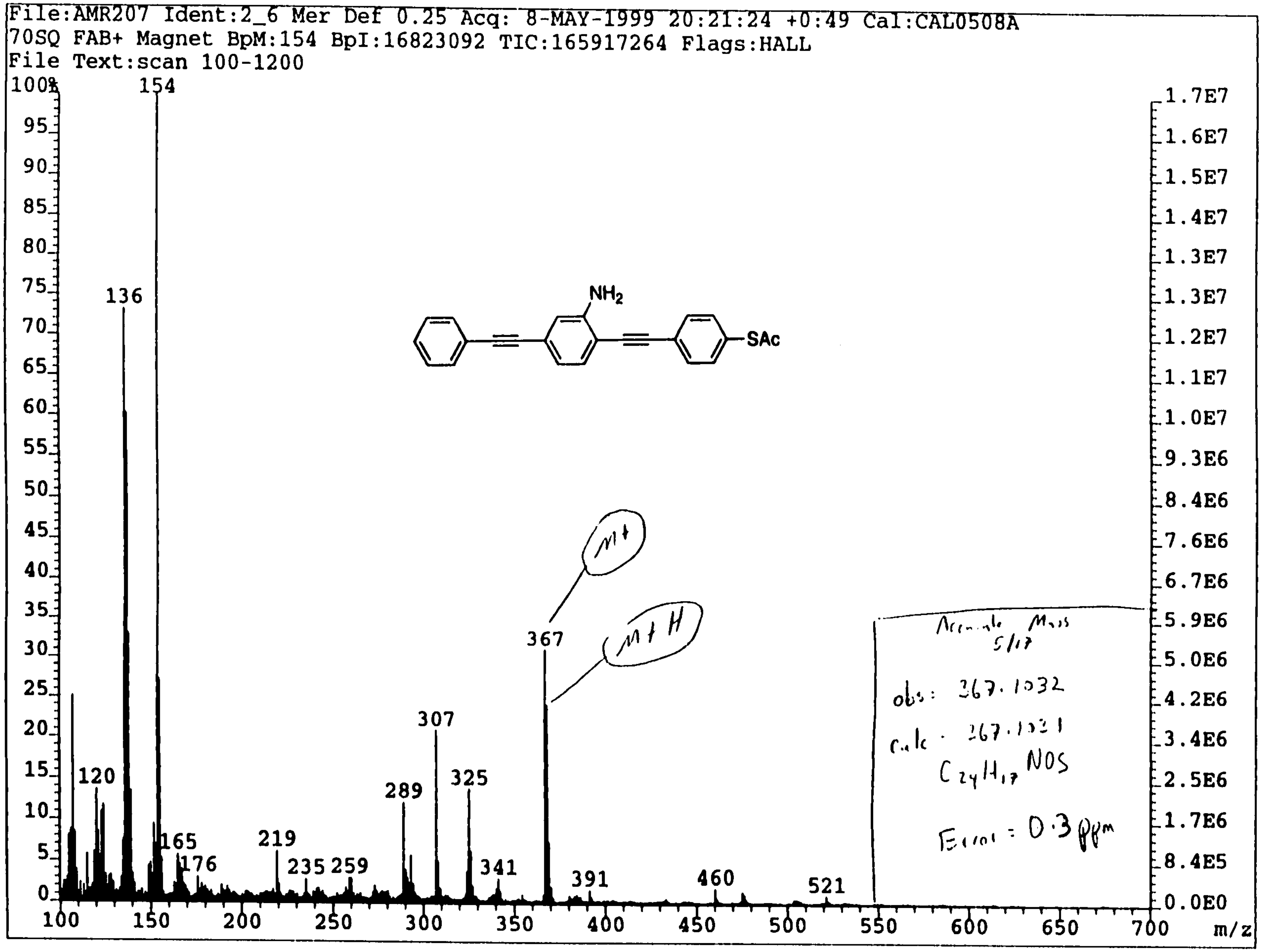

PERKIN ELMER
32.17
%T
12.33
3138.5
2369.2
2205.1
1702.6
1610.3
1384.6
1117.9
943.6
825.6
753.8
692.3
615.4
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
NH₂
SAc


SAc
NH2


ppm
1
2
3
4
5
6
7
8
9
10



ppm
20
40
60
80
100
120
140
160
180
200
30.479
53.366
53.581
53.800
54.015
54.234
85.778
89.716
91.319
96.566
108.575
117.140
121.487
123.319
124.103
124.602
128.828
128.843
128.881
128.894
131.750
132.399
134.716
148.206
193.650
NH$_2$
SAc



File:AMR207 Ident:2_6 Mer Def 0.25 Acq: 8-MAY-1999 20:21:24 +0:49 Cal:CAL0508A
70SQ FAB+ Magnet BpM:154 BpI:16823092 TIC:165917264 Flags:HALL
File Text:scan 100-1200

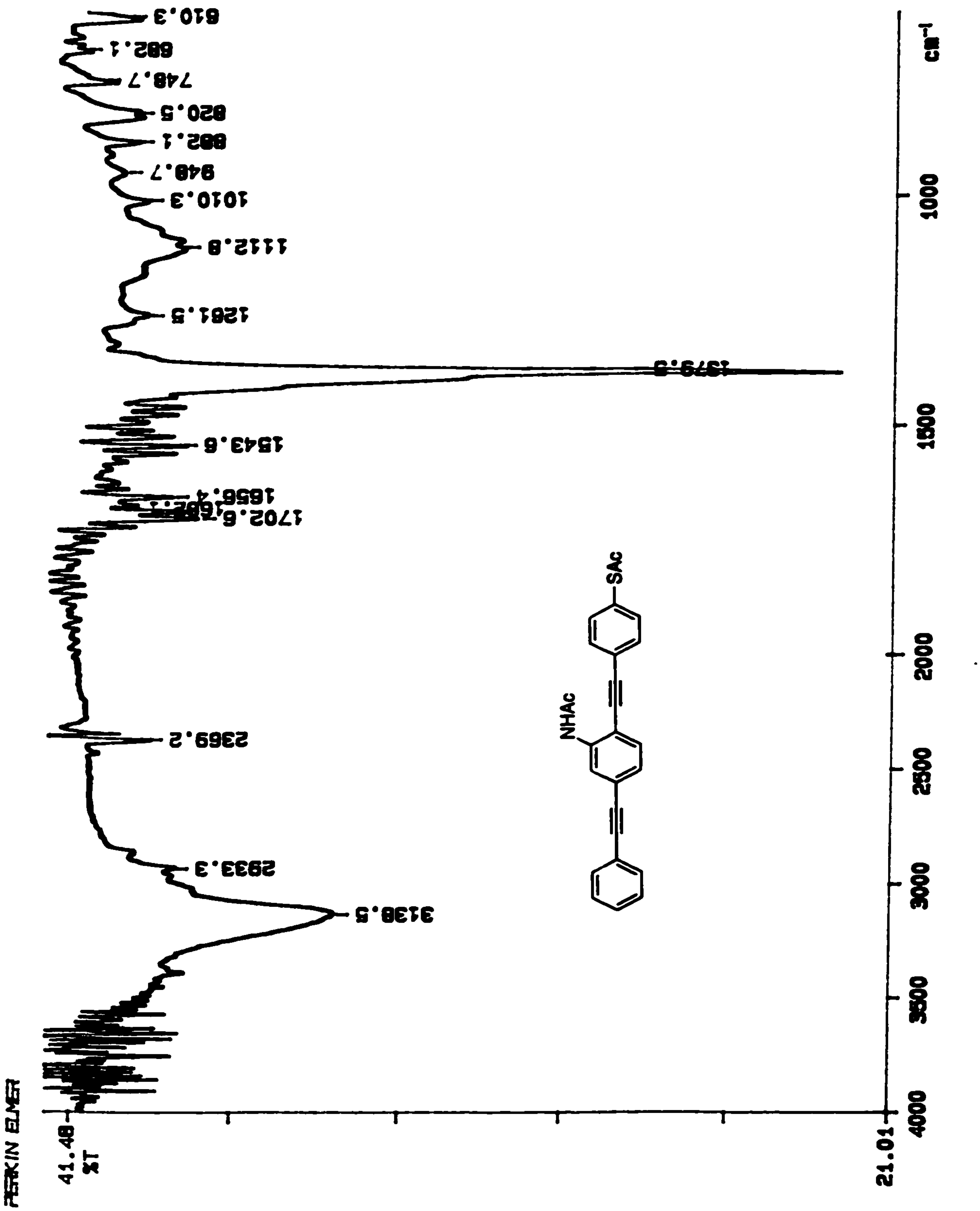
Accurate Mass 5/17

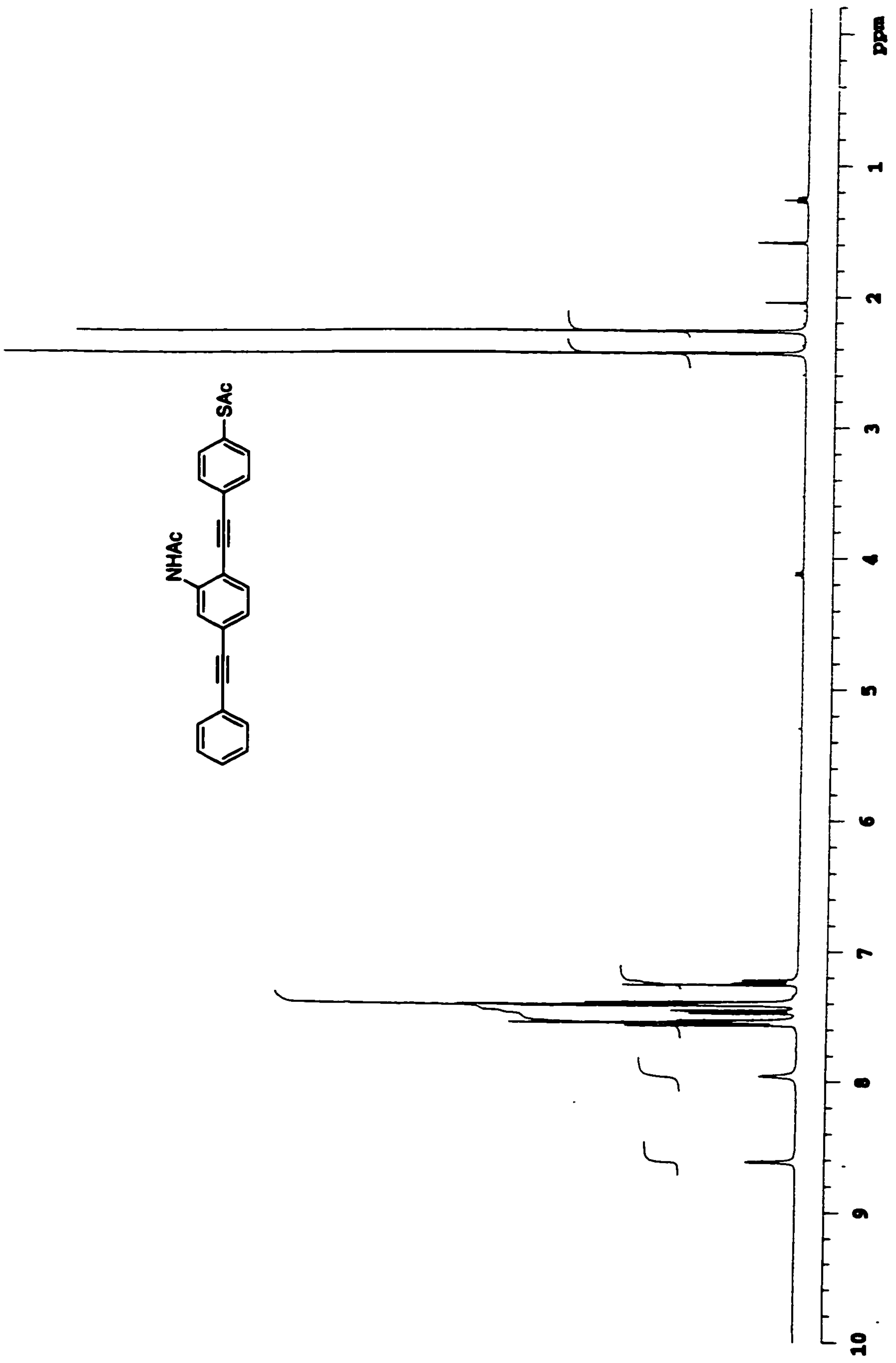
obs: 367.1032

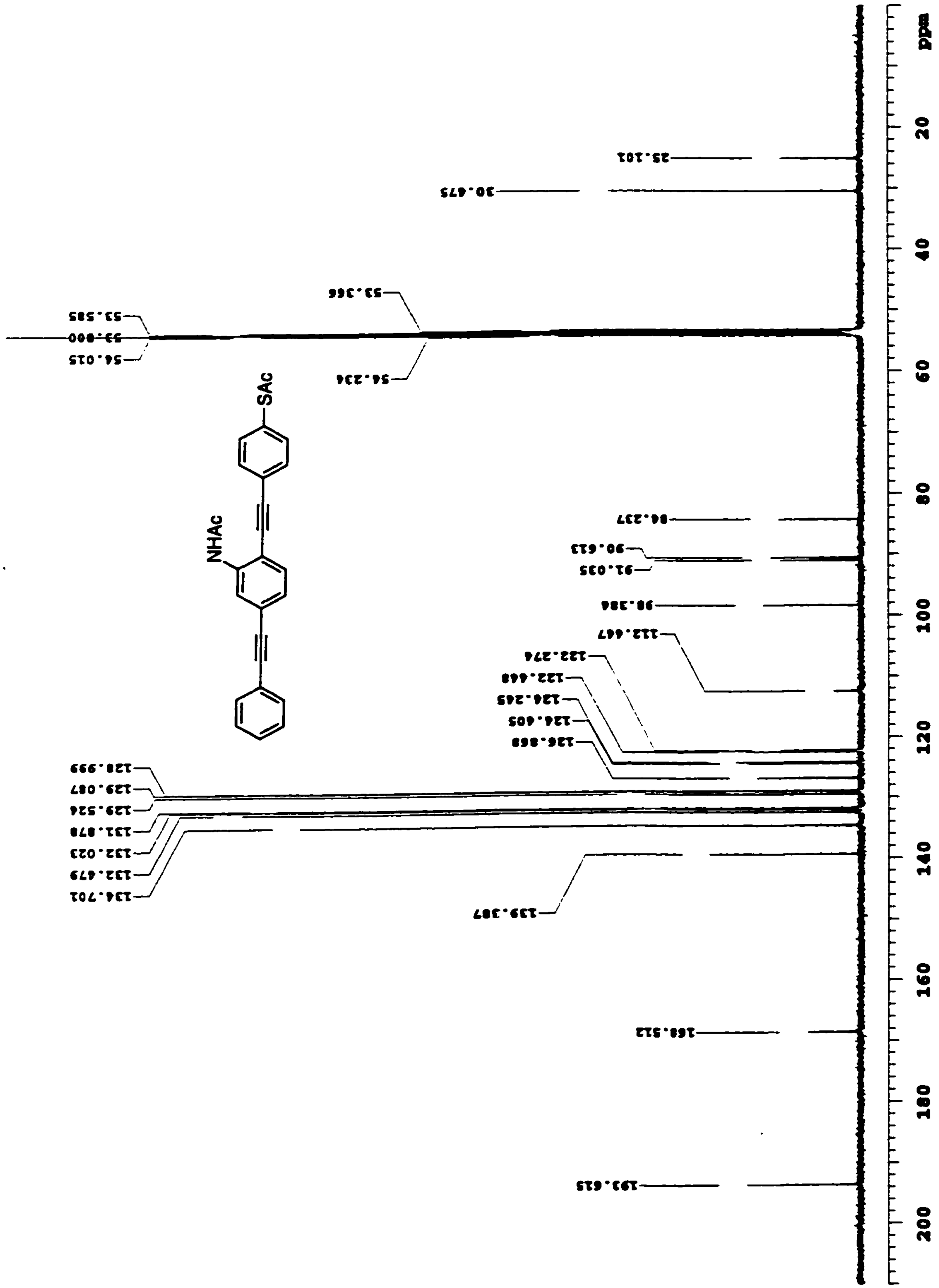
calc: 367.1031

$C_{24}H_{17}NOS$

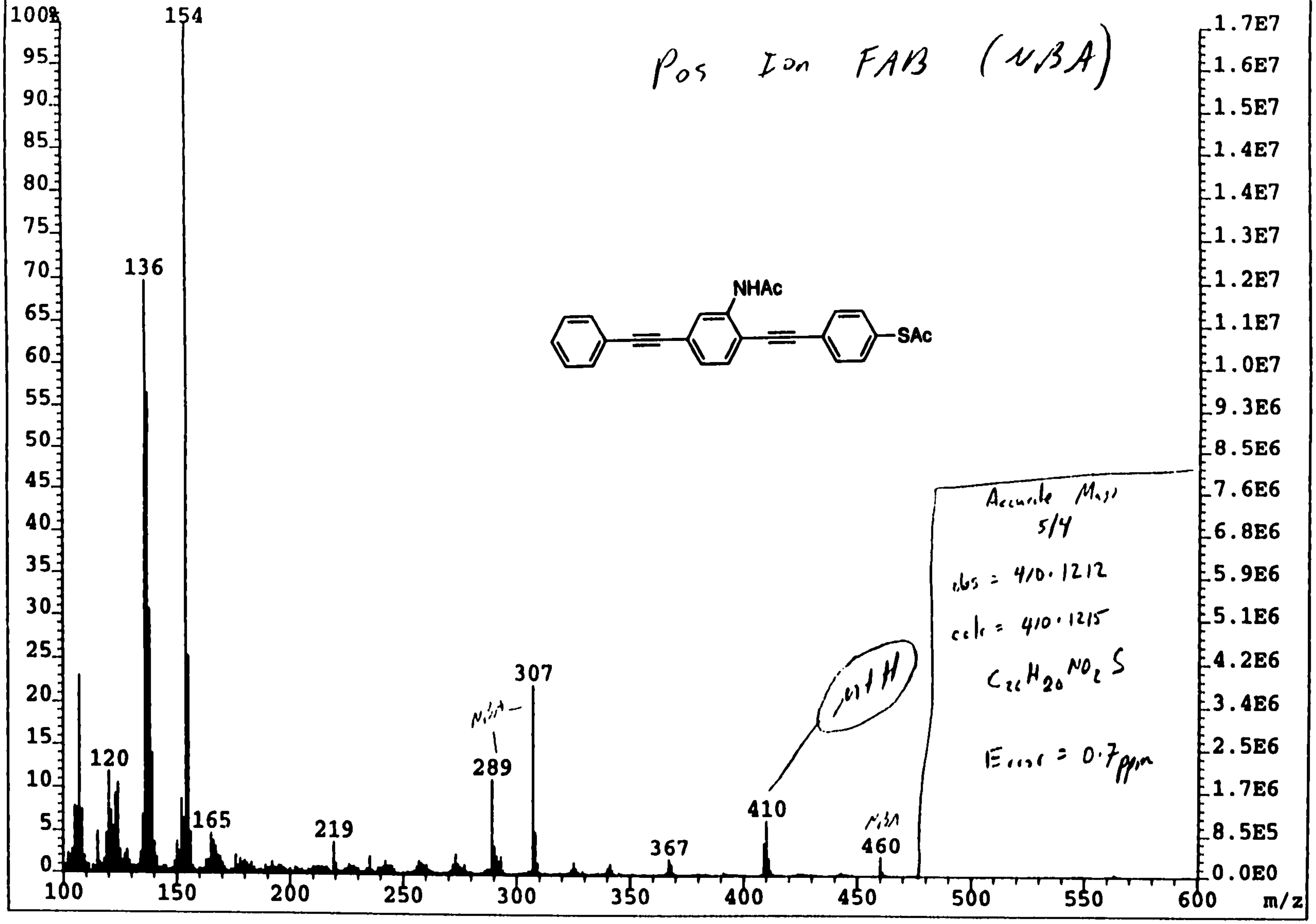
Error = 0.3 ppm


PERKIN ELMER
41.48
%T
21.01
4000
3500
3000
2500
2000
1500
1000
cm-1
3138.5
2933.3
2369.2
1702.6
1682.1
1656.4
1543.6
1379.5
1261.5
1112.8
1010.3
948.7
882.1
820.5
748.7
682.1
610.3
NHAc
SAc


NHAc
SAc
ppm
1
2
3
4
5
6
7
8
9
10

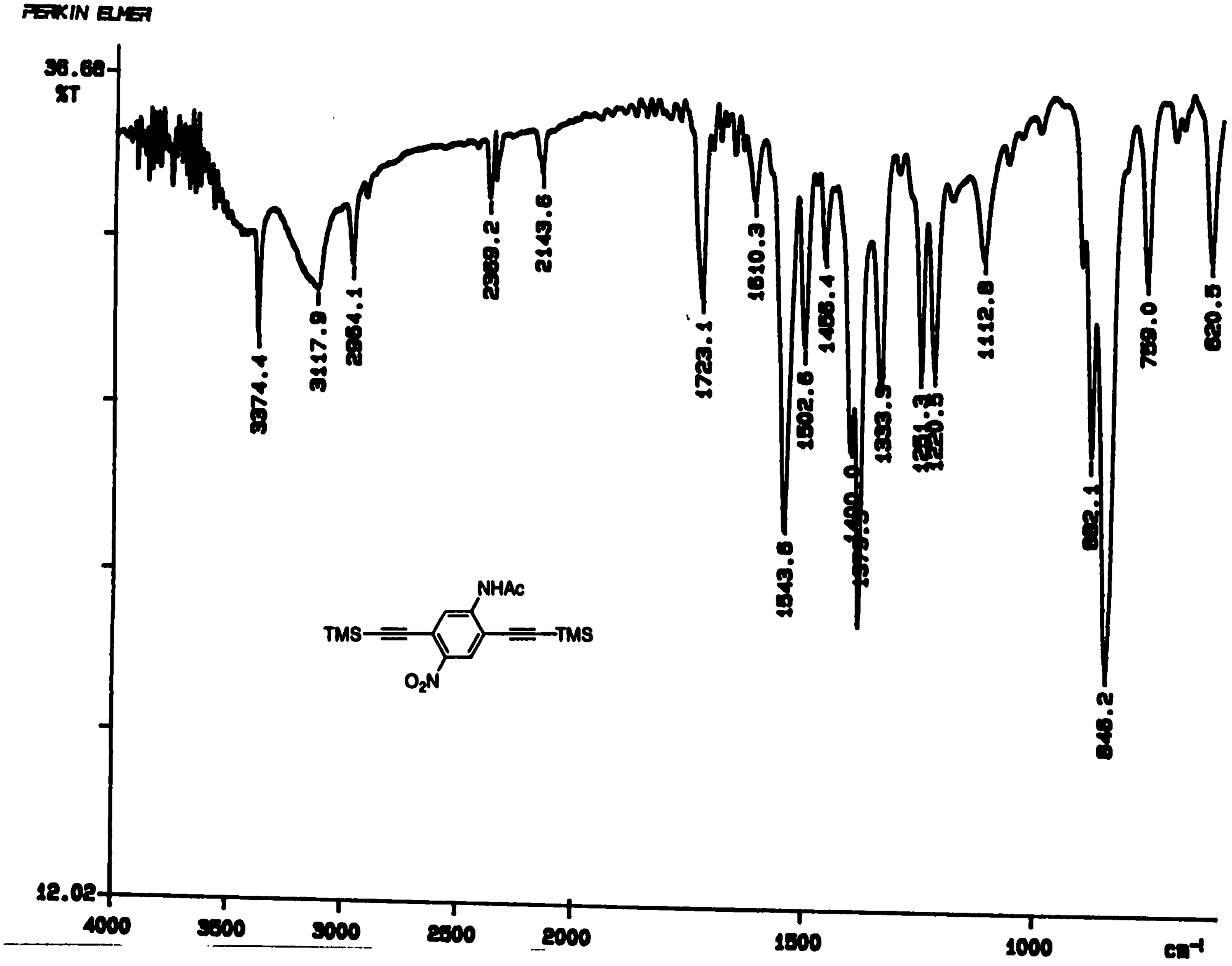

SAc
NHAc
ppm
20
40
60
80
100
120
140
160
180
200
25.101
30.475
53.366
53.585
53.800
54.015
54.234
84.237
90.613
91.035
98.384
112.467
122.274
122.448
124.245
124.405
126.868
128.999
129.087
129.524
131.878
132.023
132.479
134.701
139.387
168.512
193.615

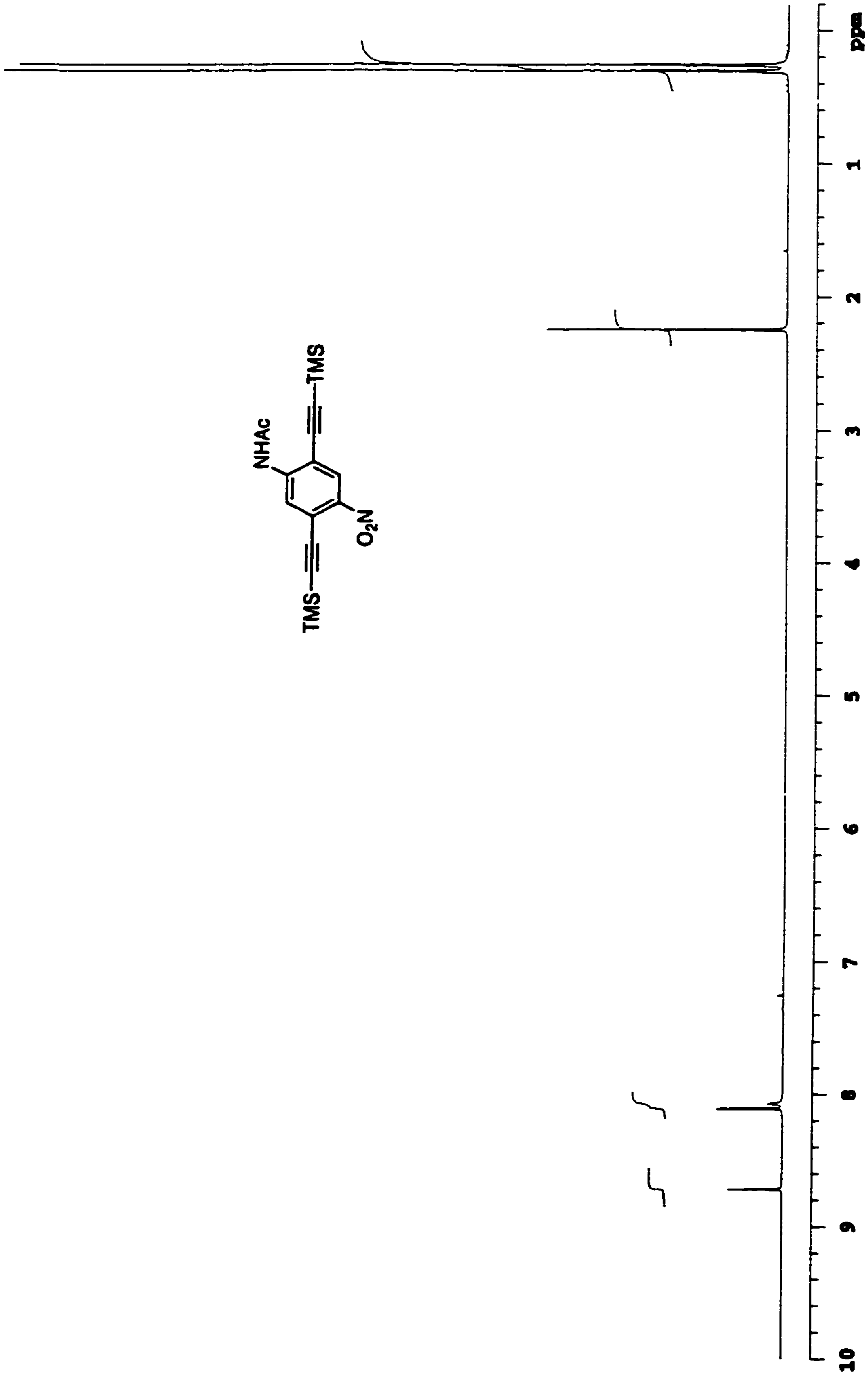
File:AMR187N Ident:3_7 Mer Def 0.25 Acq:30-APR-1999 20:13:10 +0:51 Cal:CAL0429A_1
70SQ FAB+ Magnet BpM:154 BpI:16914022 TIC:122188344 Flags:HALL
File Text: scan 100-1200

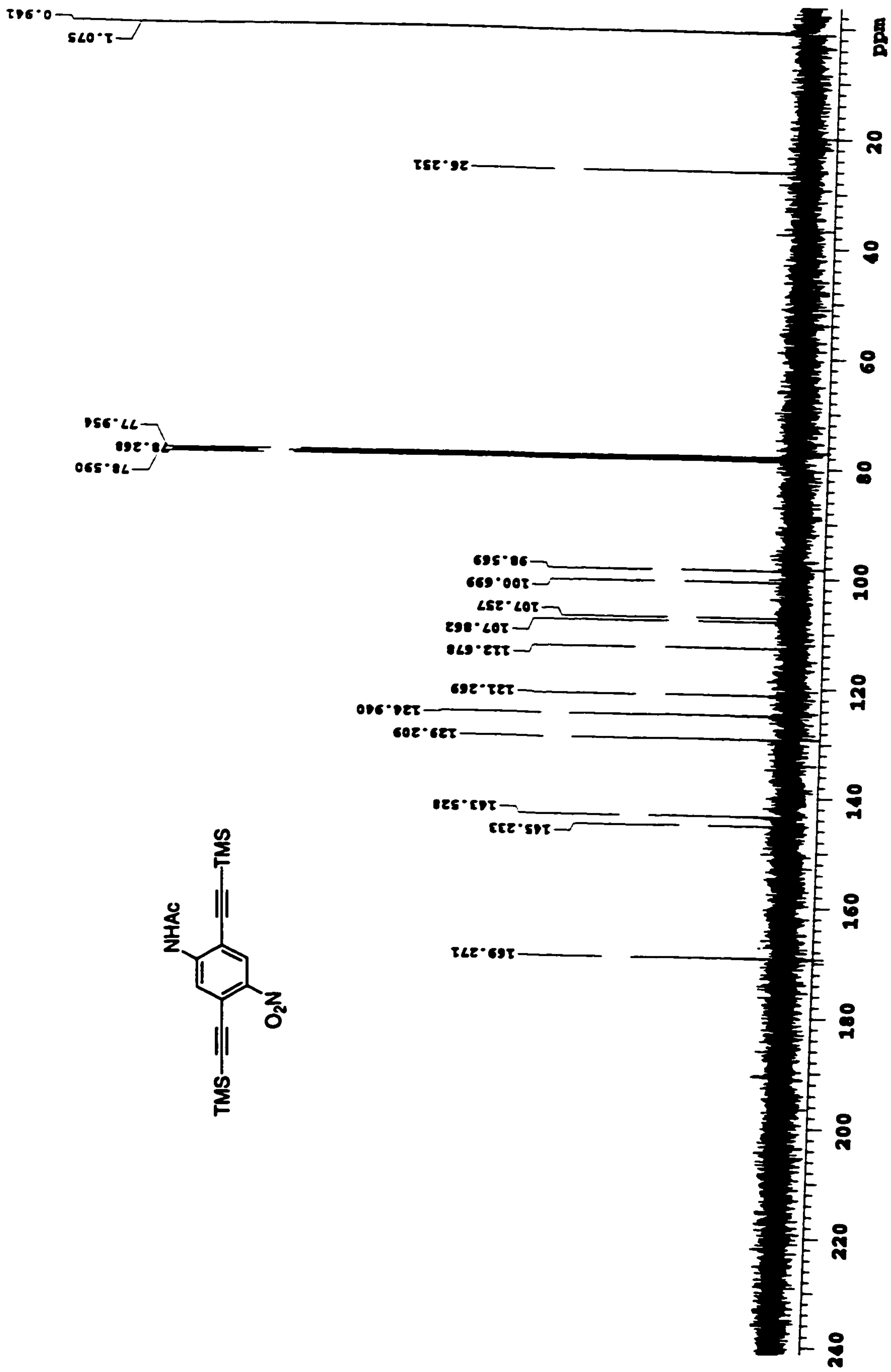


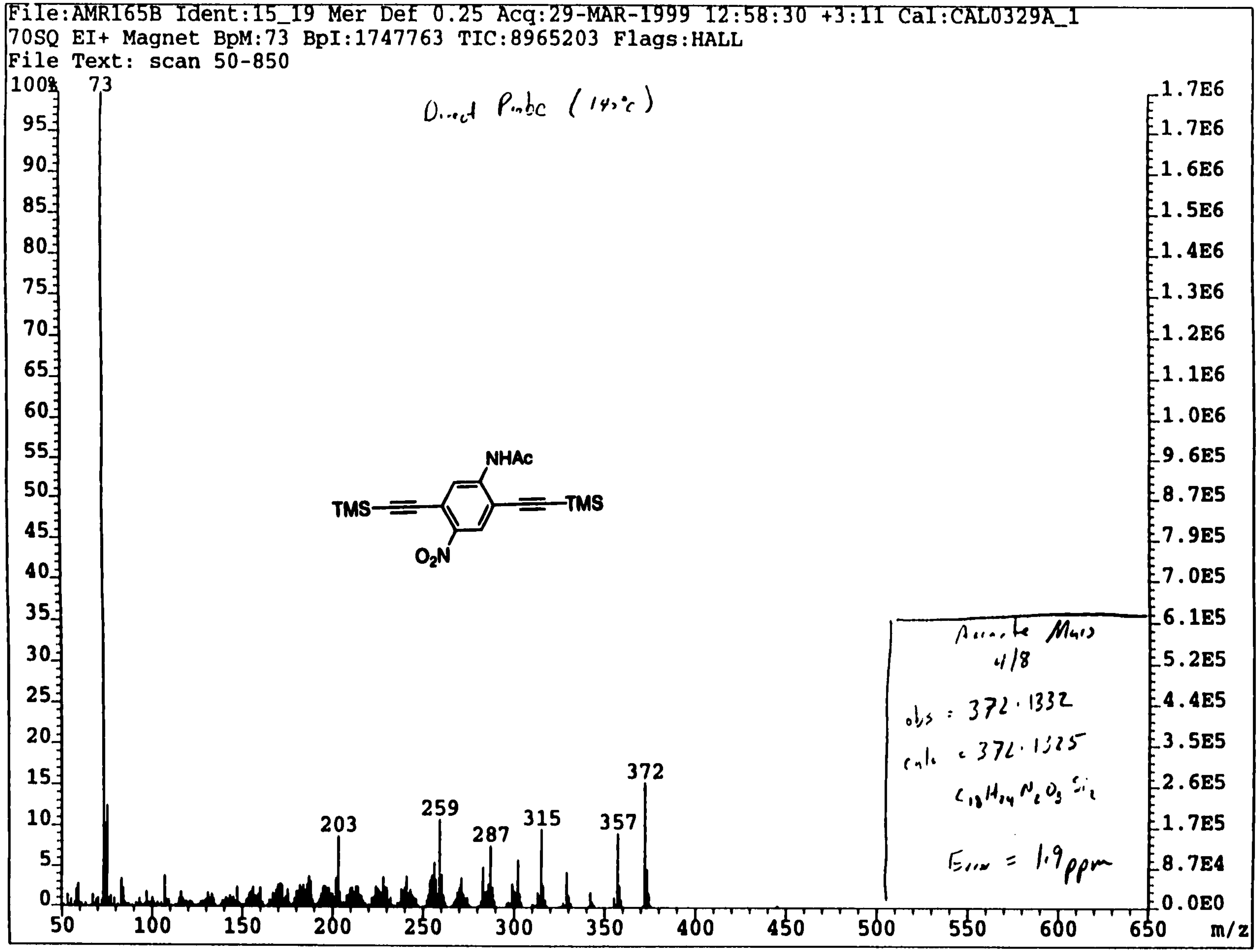
Pos Ion FAB (NBA)

Accurate Mass
5/4
obs = 410.1212
calc = 410.1215
$C_{26}H_{20}NO_2S$
Error = 0.7 ppm


PERKIN ELMER
36.68
%T
12.02
4000
3500
3000
2500
2000
1500
1000
cm-1
3374.4
3117.9
2964.1
2369.2
2143.6
1723.1
1610.3
1543.6
1502.6
1458.4
1400.0
1378.5
1333.5
1251.3
1220.5
1112.8
882.1
846.2
759.0
620.5
NHAc
TMS
TMS
O2N


NHAc
TMS
TMS
O₂N
ppm
1
2
3
4
5
6
7
8
9
10


0.941
1.075
26.251
77.954
78.268
78.590
98.569
100.699
107.257
107.862
112.678
121.269
124.940
129.209
143.528
145.233
169.271
ppm
20
40
60
80
100
120
140
160
180
200
220
240
NHAc
TMS
TMS
O_2N

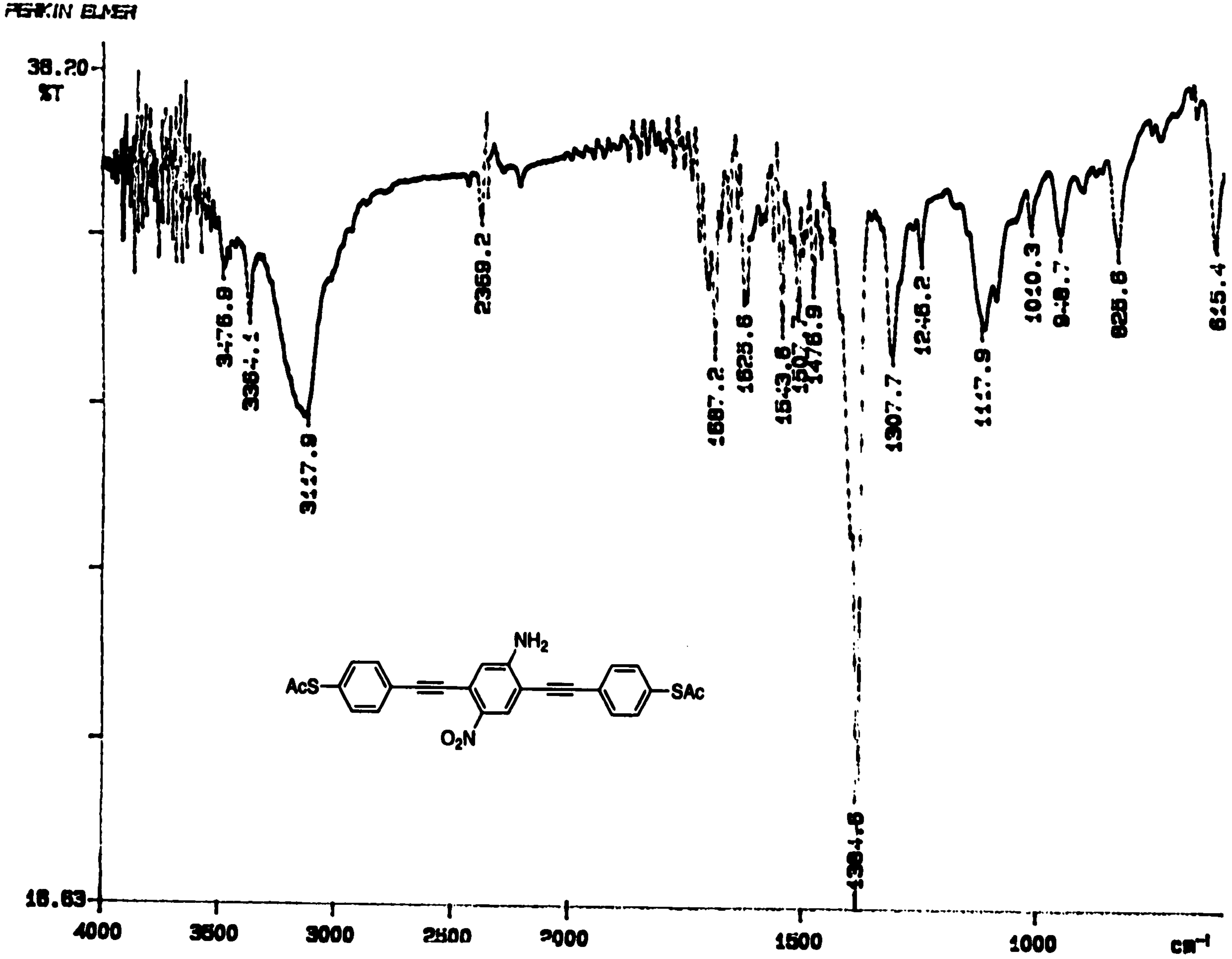


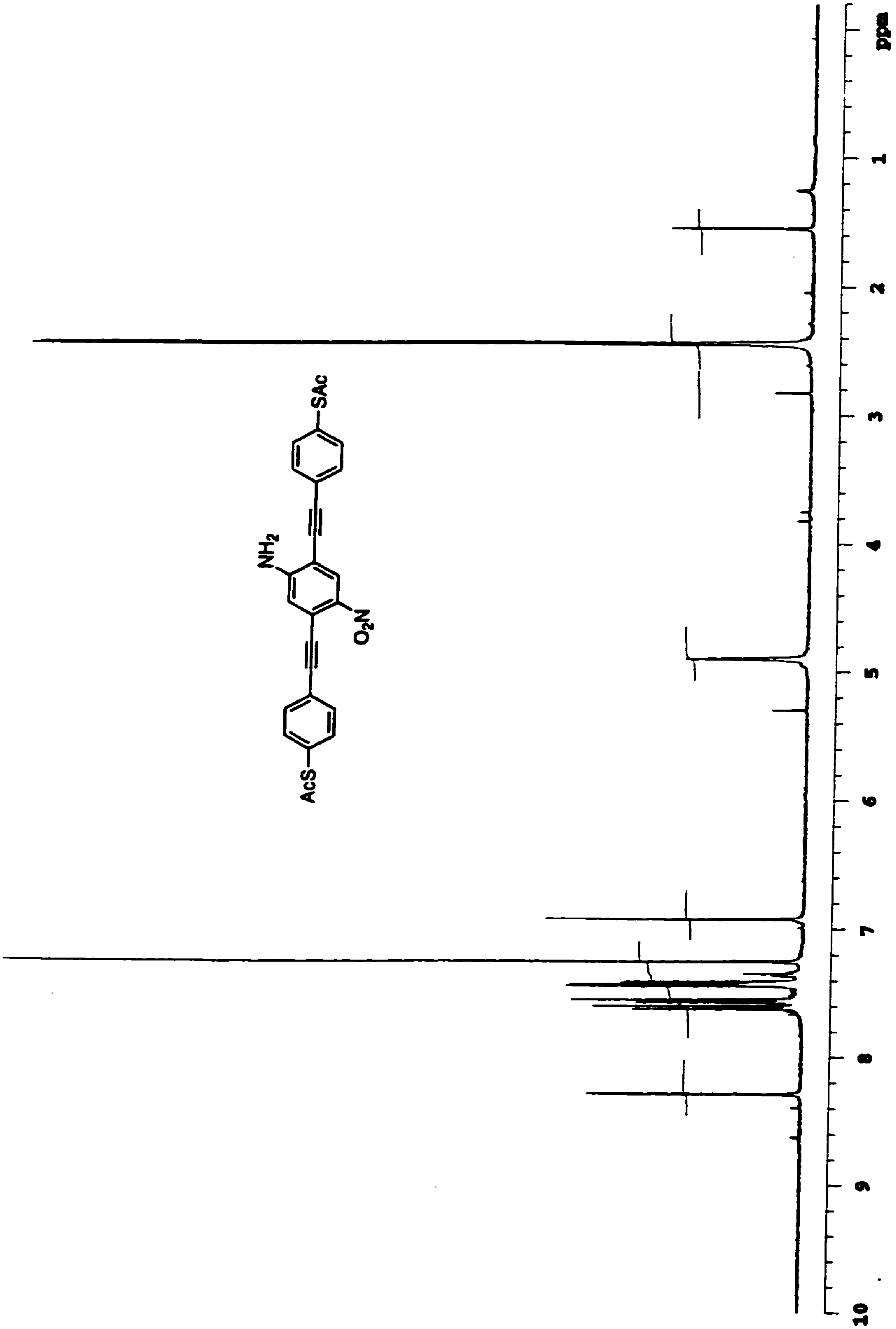
Direct Probe (145°C)

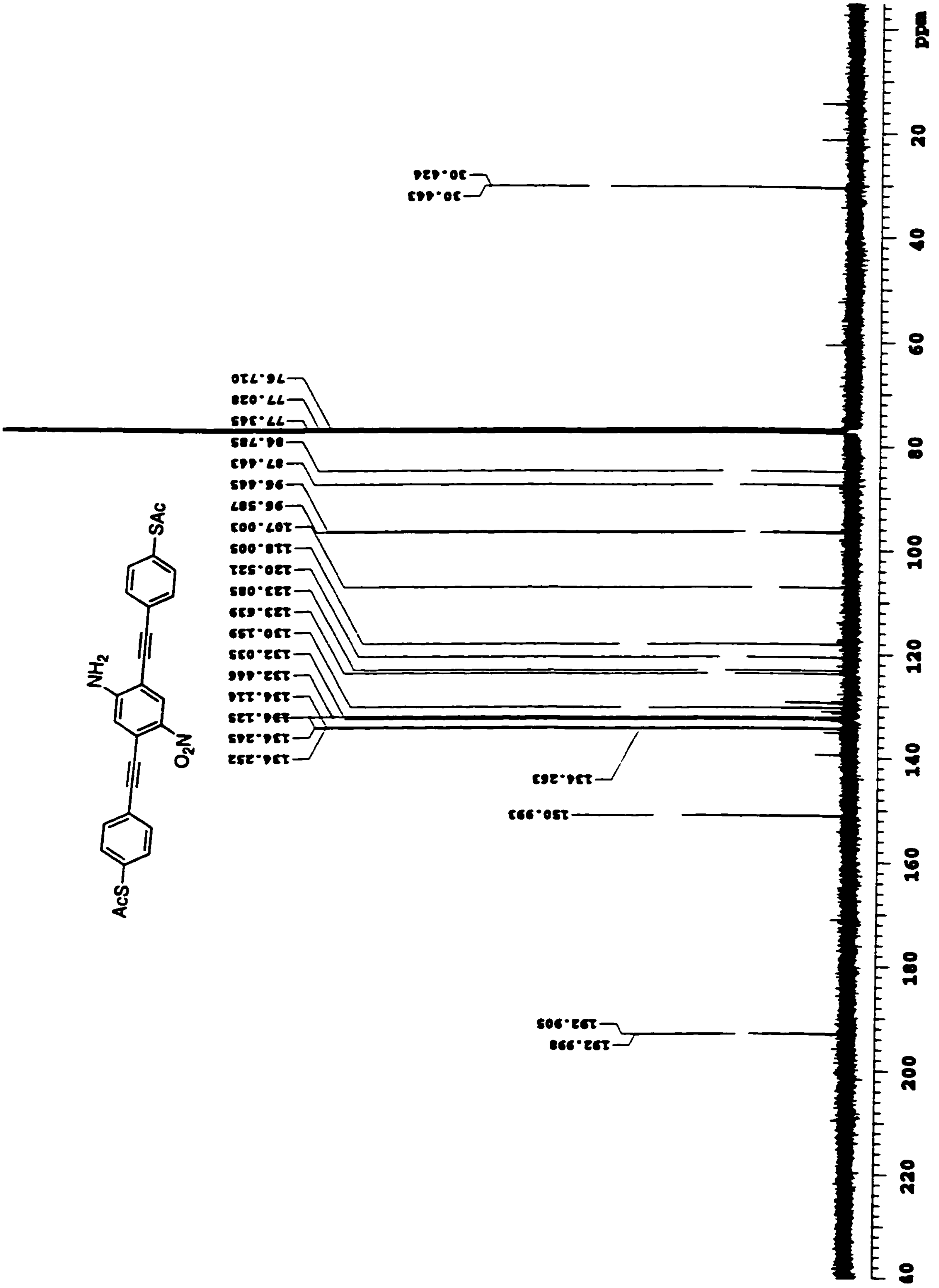
Accurate Mass
4/8

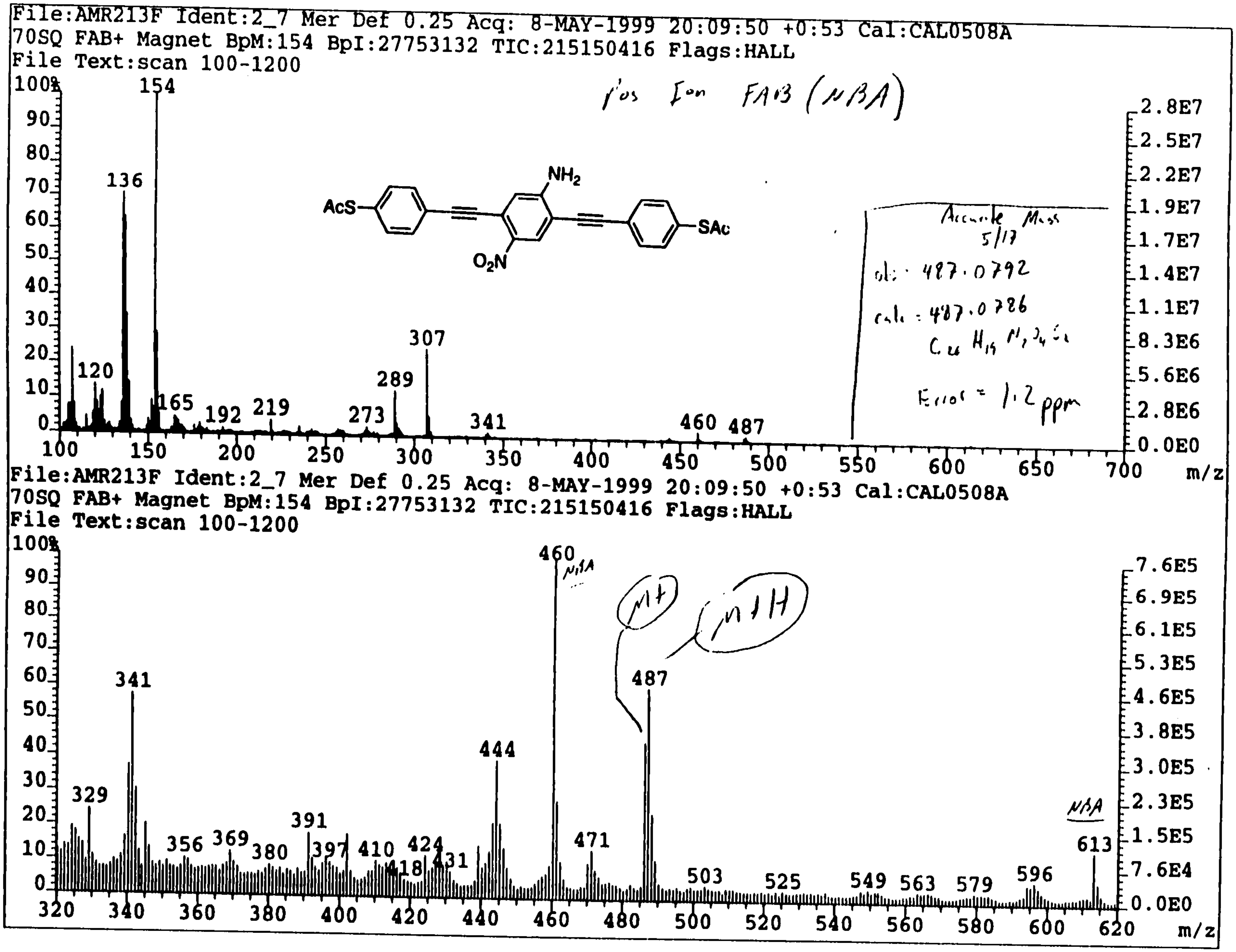
obs = 372.1332
calc = 372.1325
$C_{18}H_{24}N_2O_3Si_2$

Error = 1.9 ppm


PERKIN ELMER
38.20
%T
16.63
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3476.9
3364.1
3117.9
2369.2
1687.2
1625.6
1543.6
1507.7
1476.9
1384.6
1307.7
1246.2
1117.9
1020.3
948.7
828.6
625.4
AcS
NH2
O2N
SAc

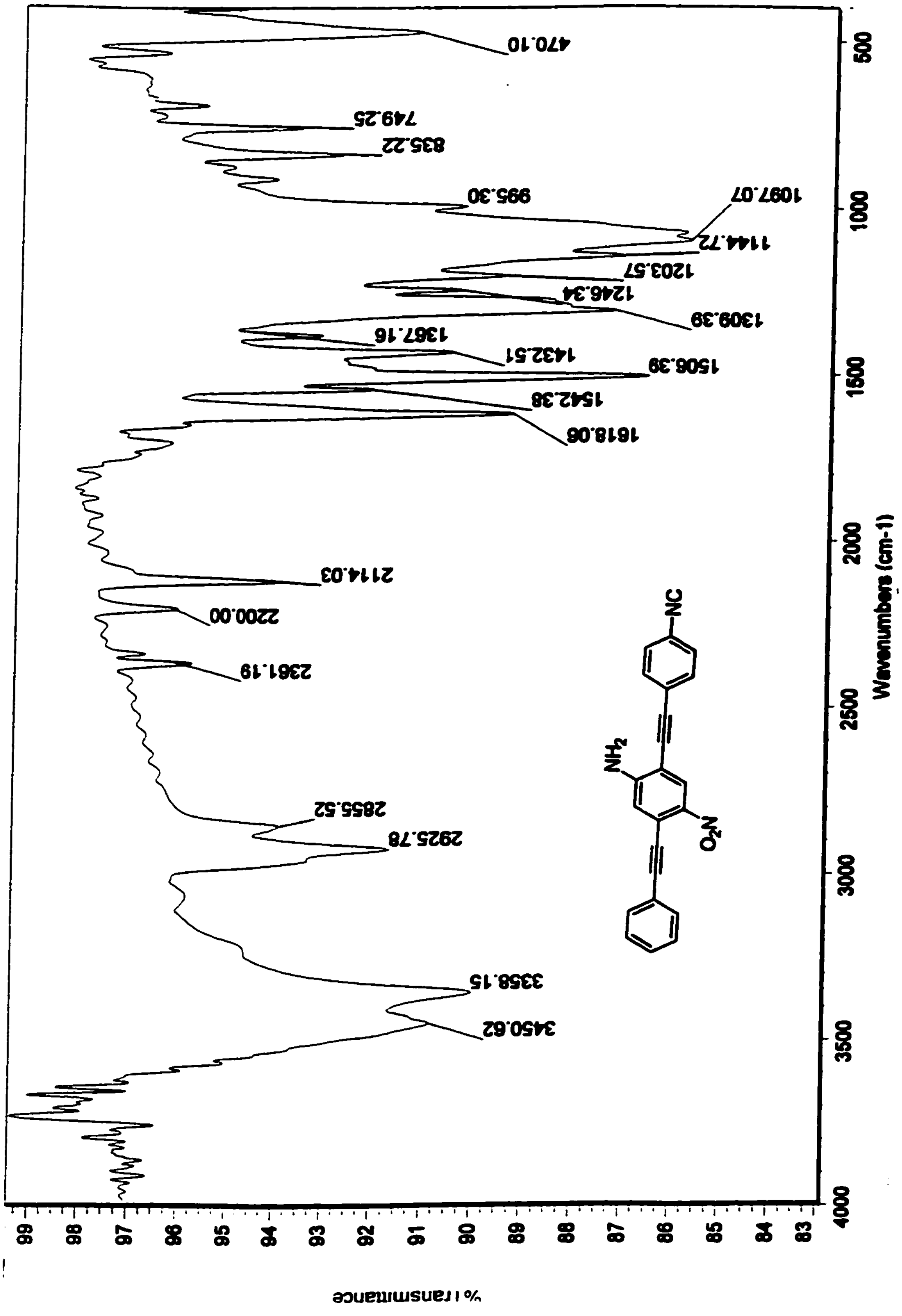

ppm
1
2
3
4
5
6
7
8
9
10
AcS
SAc
NH$_2$
O$_2$N

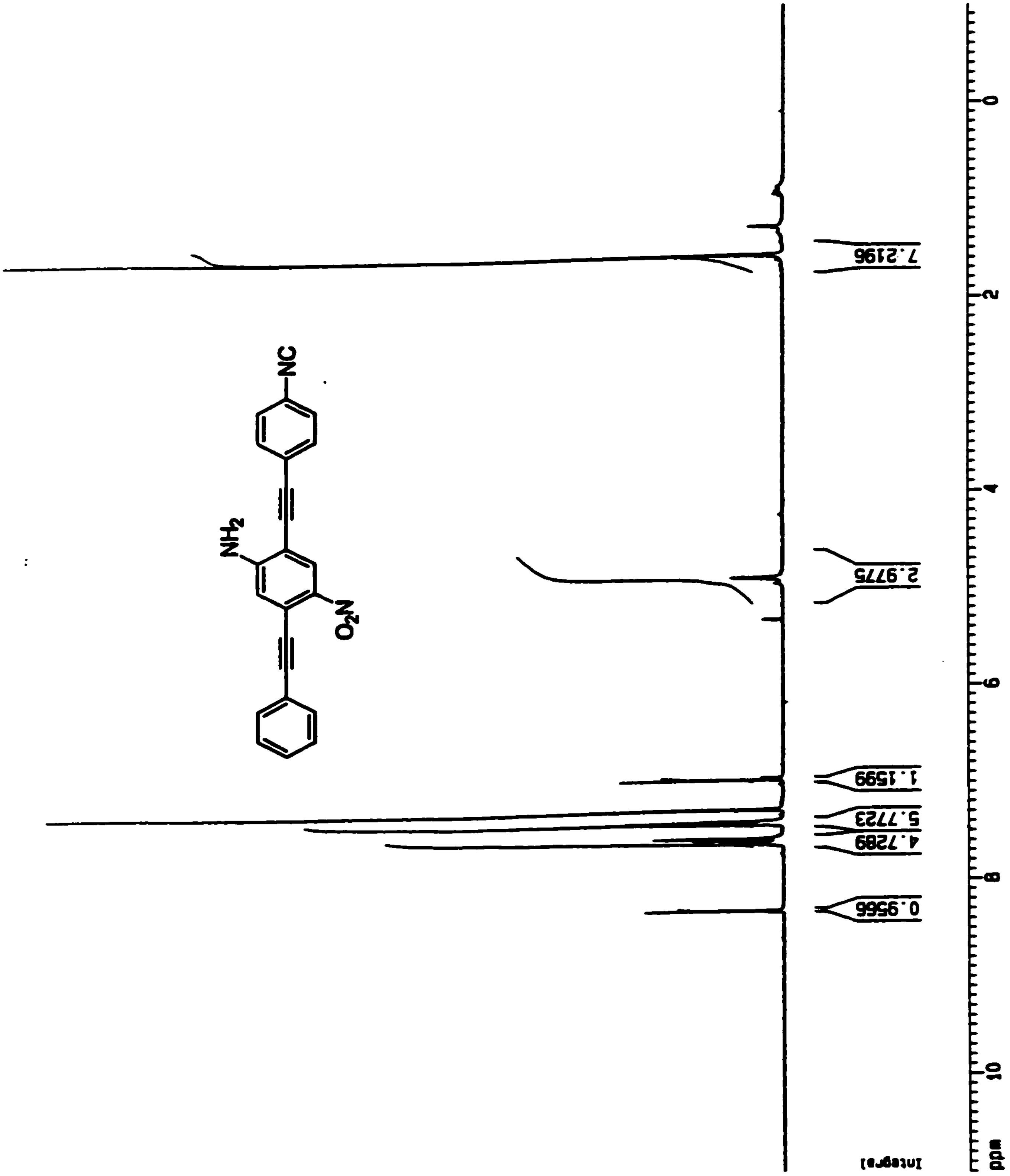

30.434
30.463
76.710
77.028
77.345
84.785
87.443
96.445
96.587
107.003
118.005
120.521
123.085
123.639
130.159
132.035
133.446
134.114
134.125
134.245
134.252
134.263
150.993
192.905
192.998
SAc
NH2
O2N
AcS
ppm
20
40
60
80
100
120
140
160
180
200
220
40

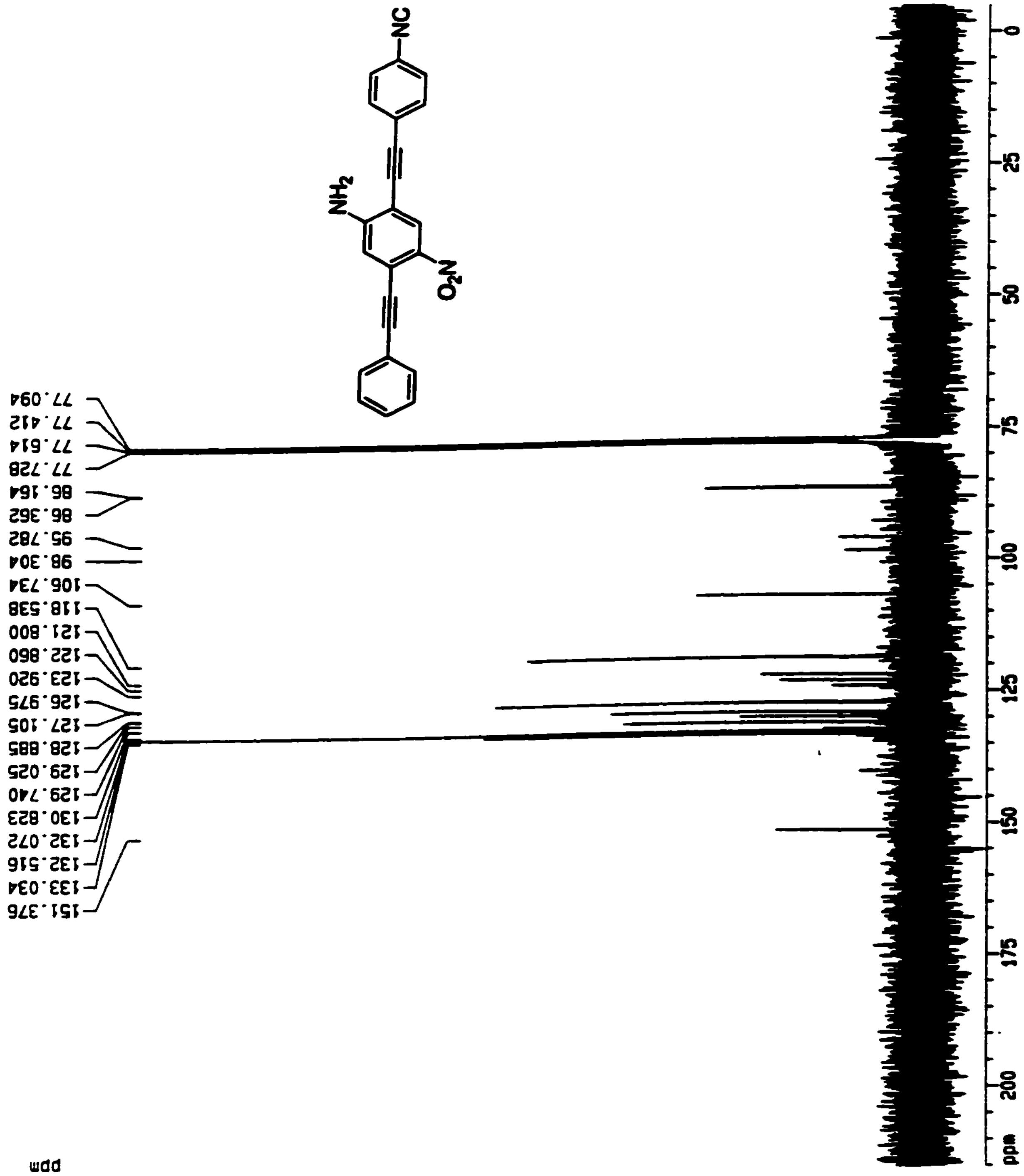


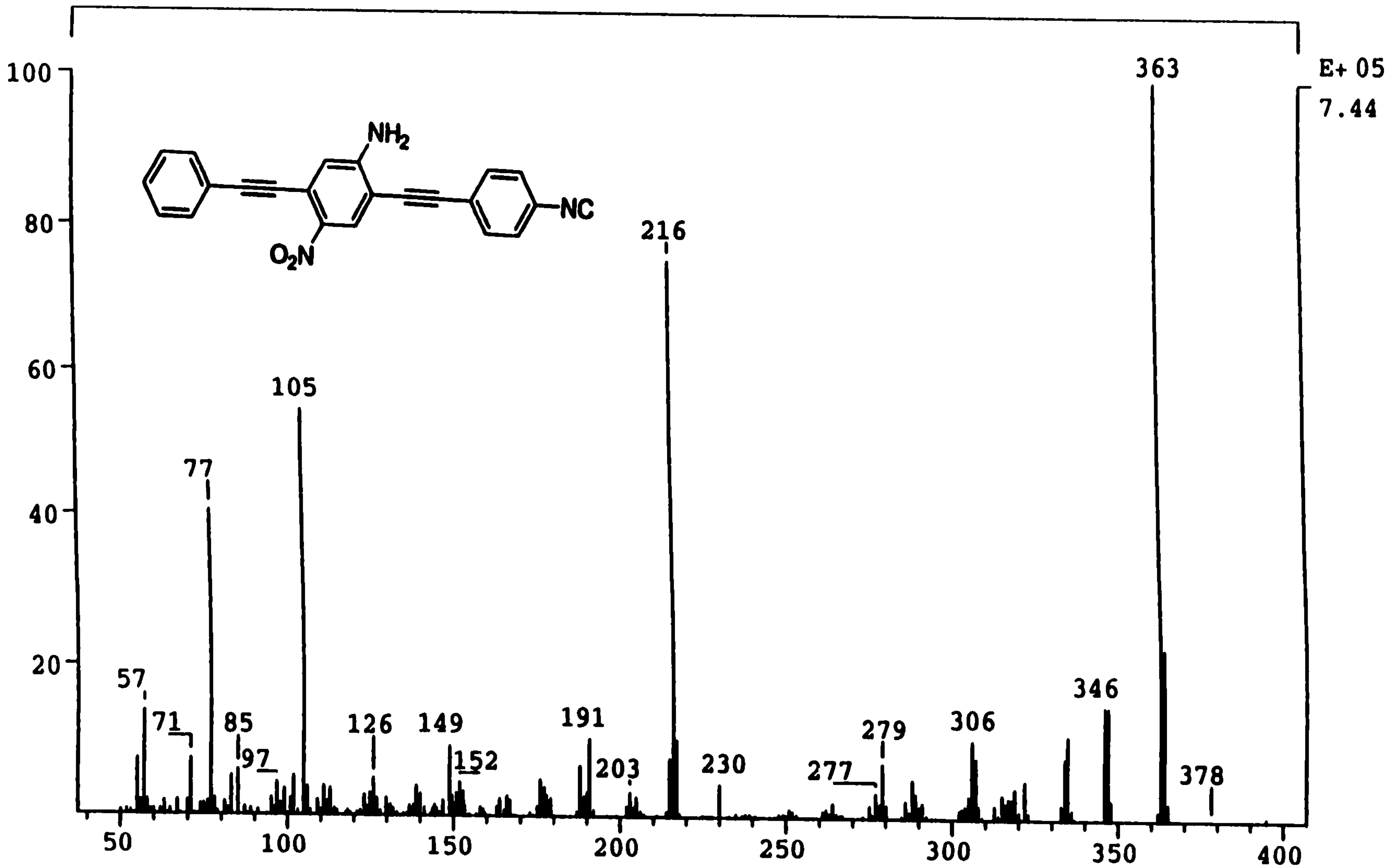
Pos Ion FAB (NBA)

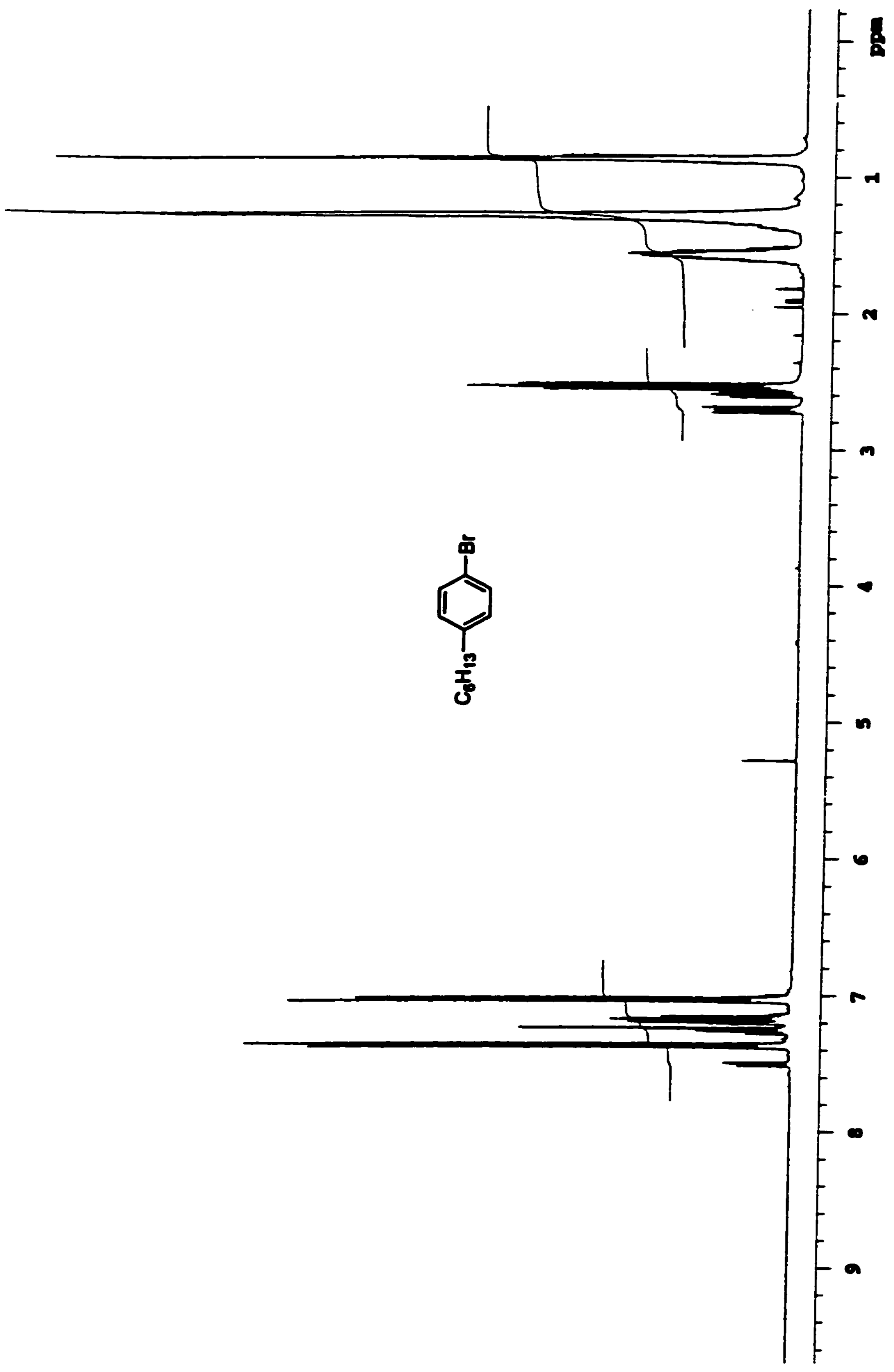
Accurate Mass
5/17
obs: 487.0792
calc: 487.0786
$C_{26}H_{19}N_2O_4S_2$
Error = 1.2 ppm


% Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
83
470.10
749.25
835.22
995.30
1097.07
1144.72
1203.57
1246.34
1309.39
1367.16
1432.51
1506.39
1542.38
1618.06
2114.03
2200.00
2361.19
2855.52
2925.78
3358.15
3450.62
NH2
O2N
NC

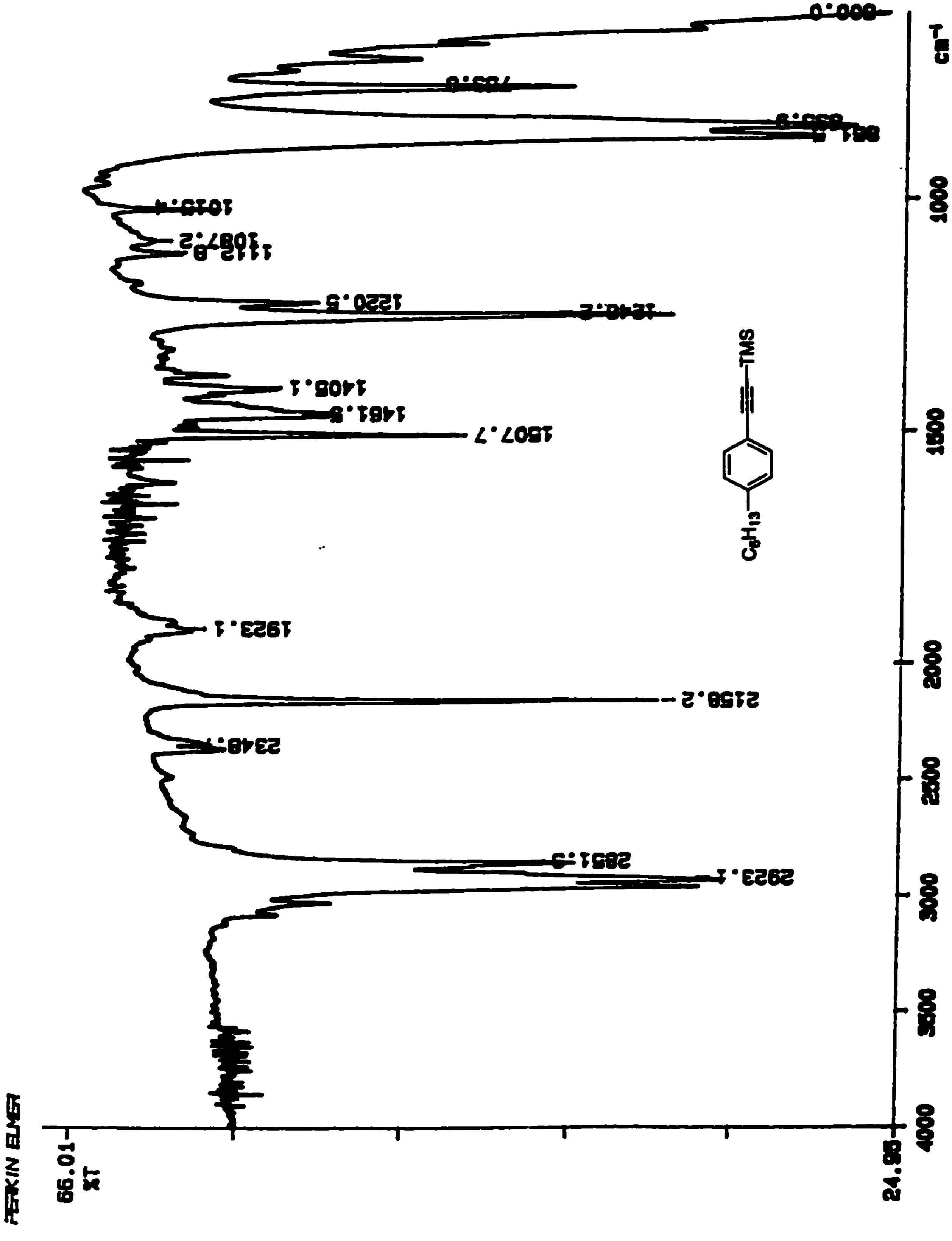

NC
NH2
O2N
7.2196
2.9775
1.1599
5.7723
4.7289
0.9566
Integral
0
2
4
6
8
10
ppm

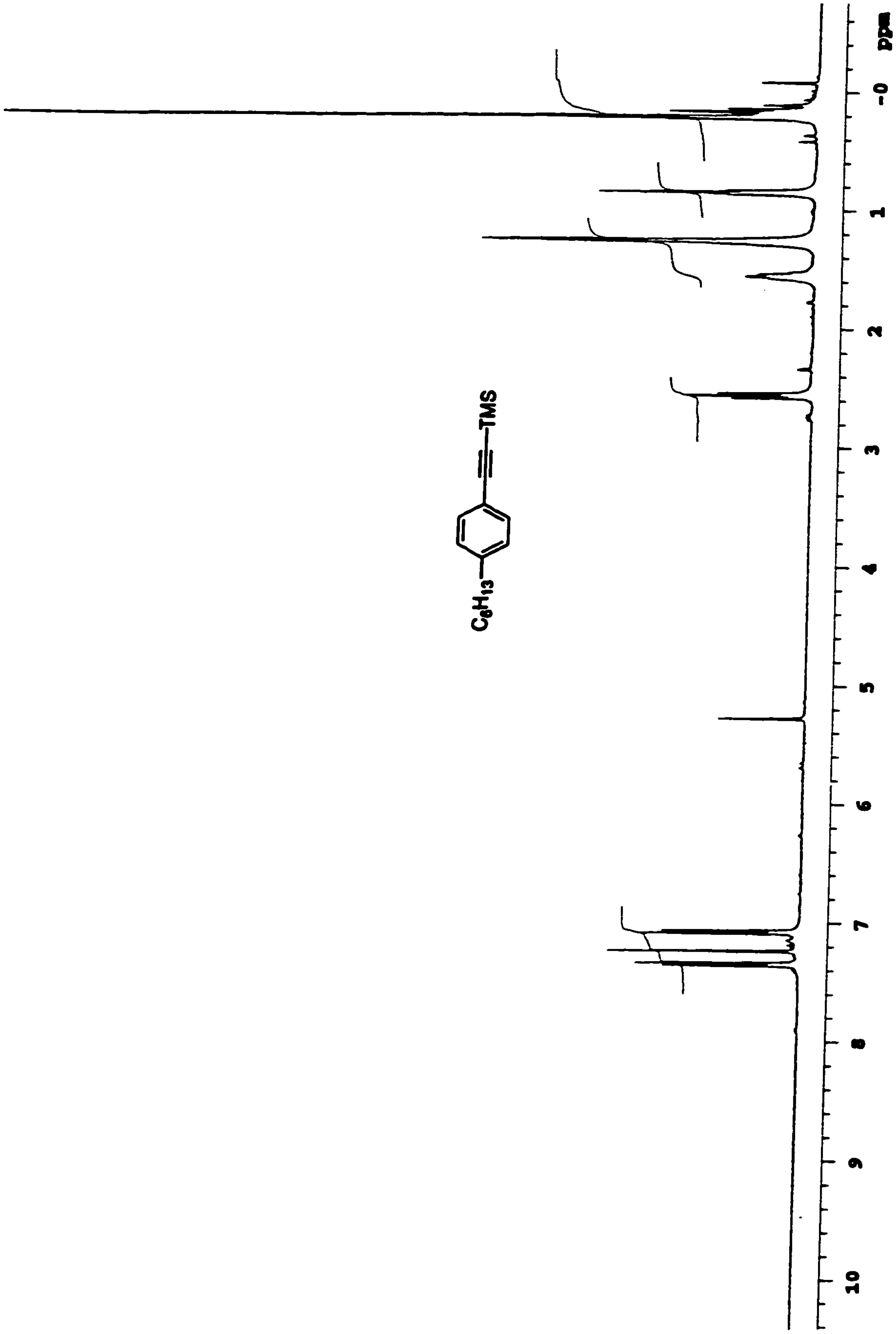

NC
NH₂
O₂N
77.094
77.412
77.614
77.728
86.164
86.362
95.782
98.304
106.734
118.538
121.800
122.860
123.920
126.975
127.105
128.885
129.025
129.740
130.823
132.072
132.516
133.034
151.376
ppm
0
25
50
75
100
125
150
175
200
ppm

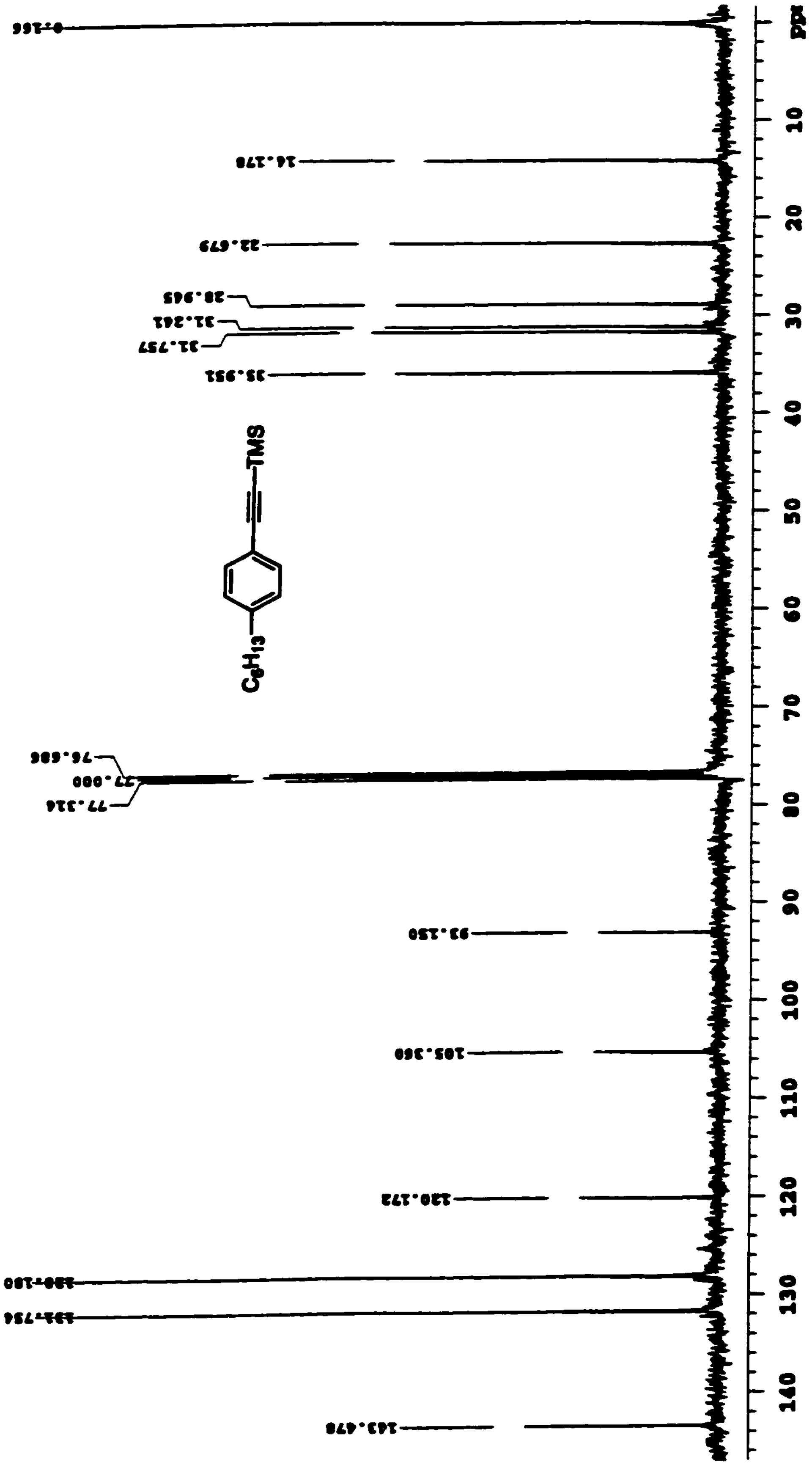

100
80
60
40
20
50
100
150
200
250
300
350
400
E+ 05
7.44
363
216
105
77
57
71
85
97
126
149
152
191
203
230
277
279
306
346
378
NH2
O2N
NC

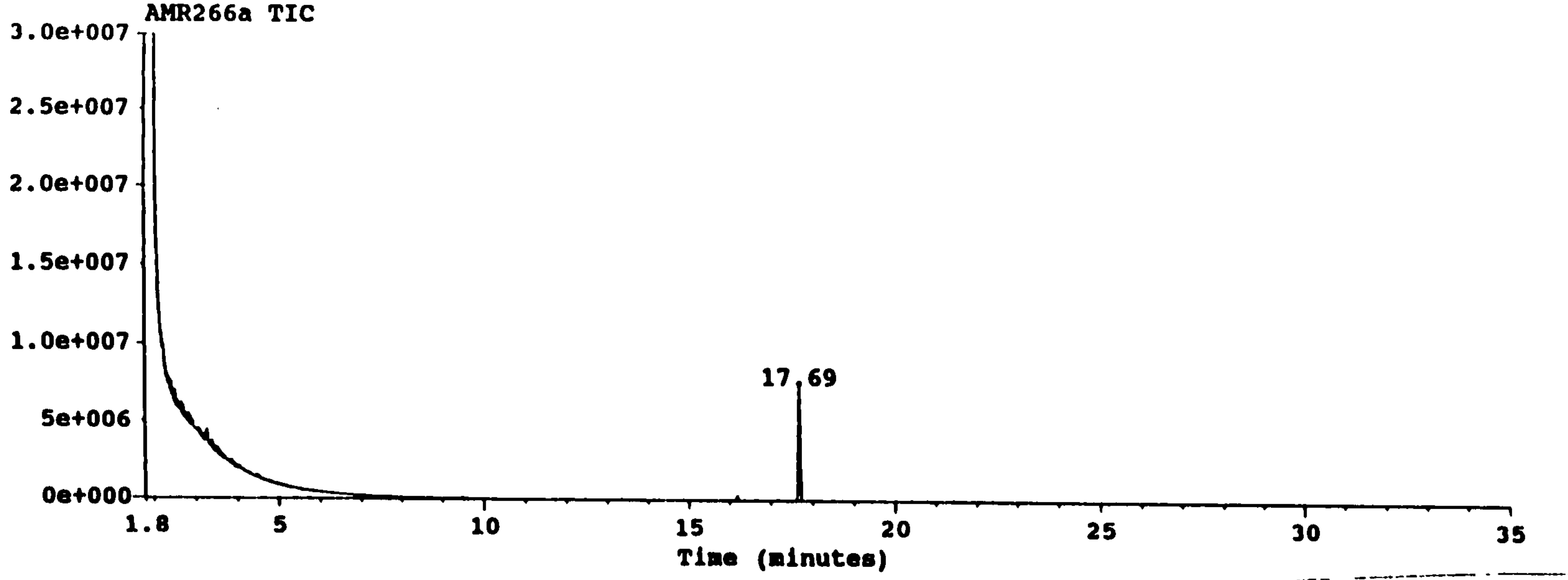


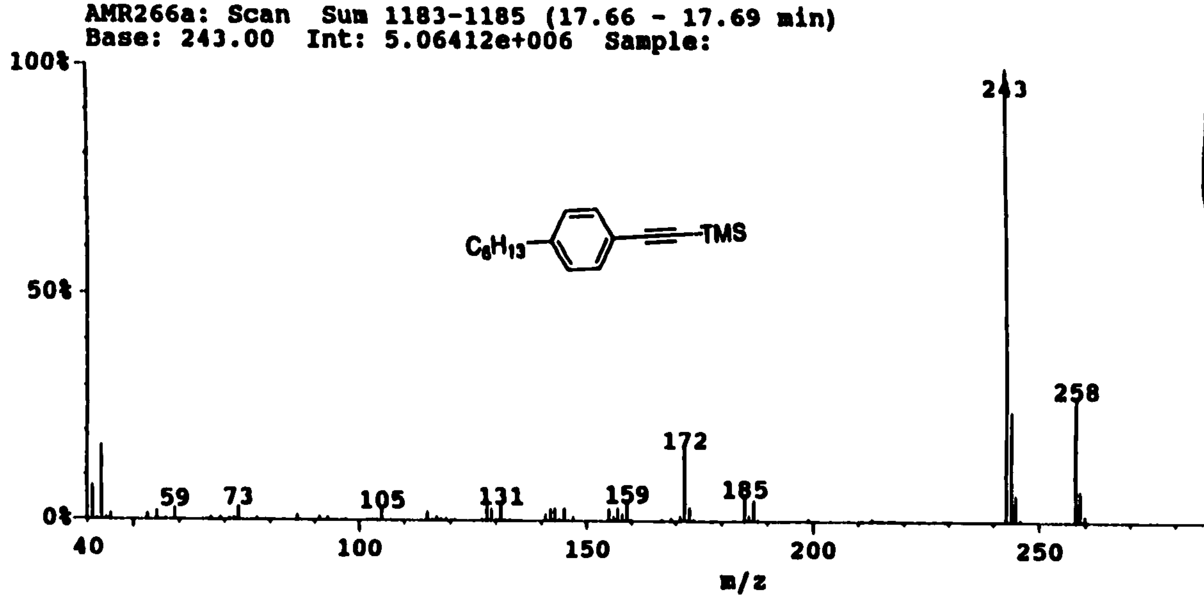
C$_6$H$_{13}$
Br
ppm
1
2
3
4
5
6
7
8
9


PERKIN ELMER
66.01
%T
24.96
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
2923.1
2851.9
2348
2158.2
1923.1
1507.7
1481.8
1405.1
1248.2
1220.5
1112.8
1087.2
1013.4
703.8
600.0
C6H13
TMS


C6H13
TMS
ppm
-0
1
2
3
4
5
6
7
8
9
10


0.166
14.178
22.679
28.945
31.241
31.757
35.951
76.686
77.000
77.316
93.150
105.360
120.173
128.180
131.754
143.478
C_6H_{13}
TMS
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

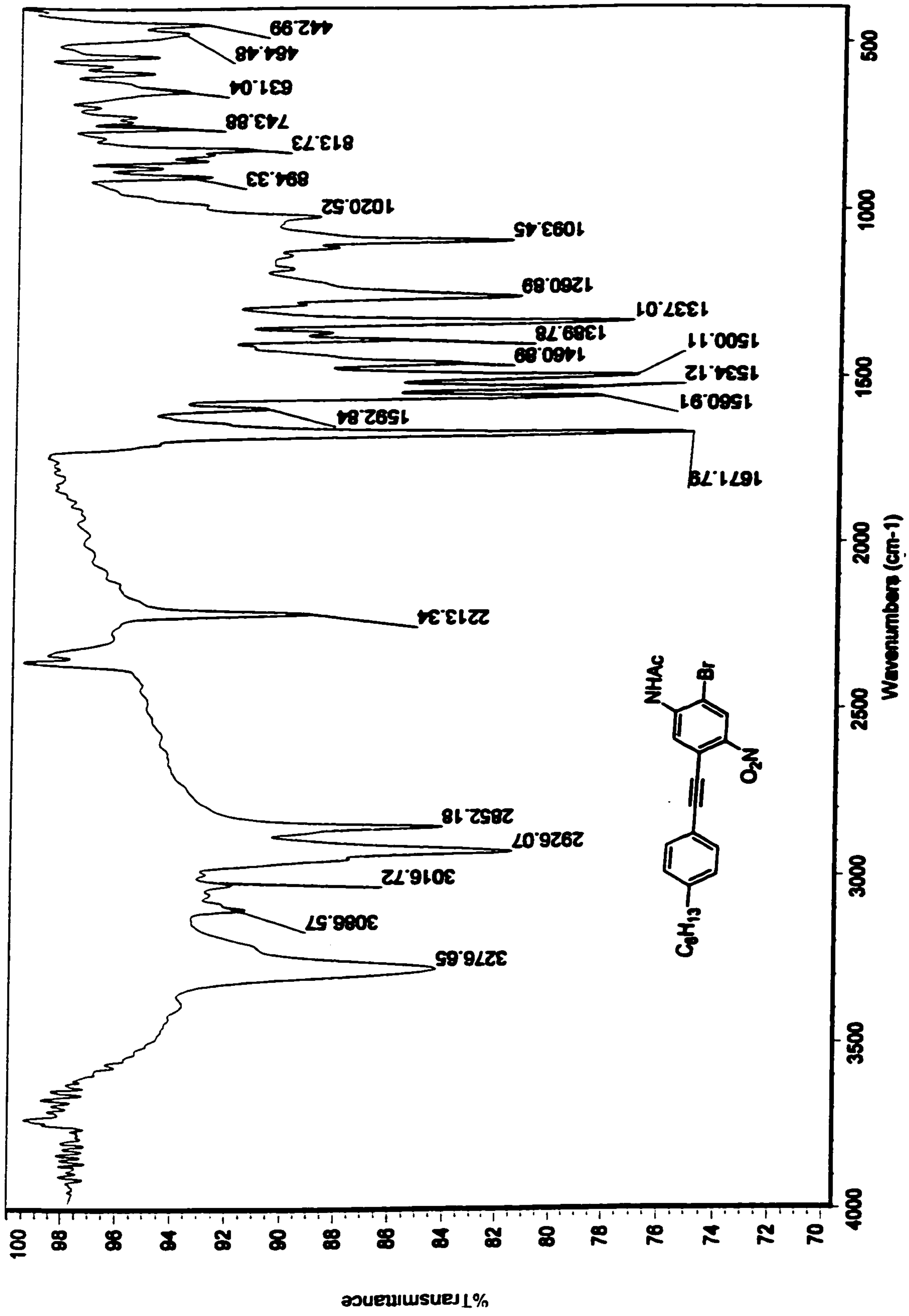


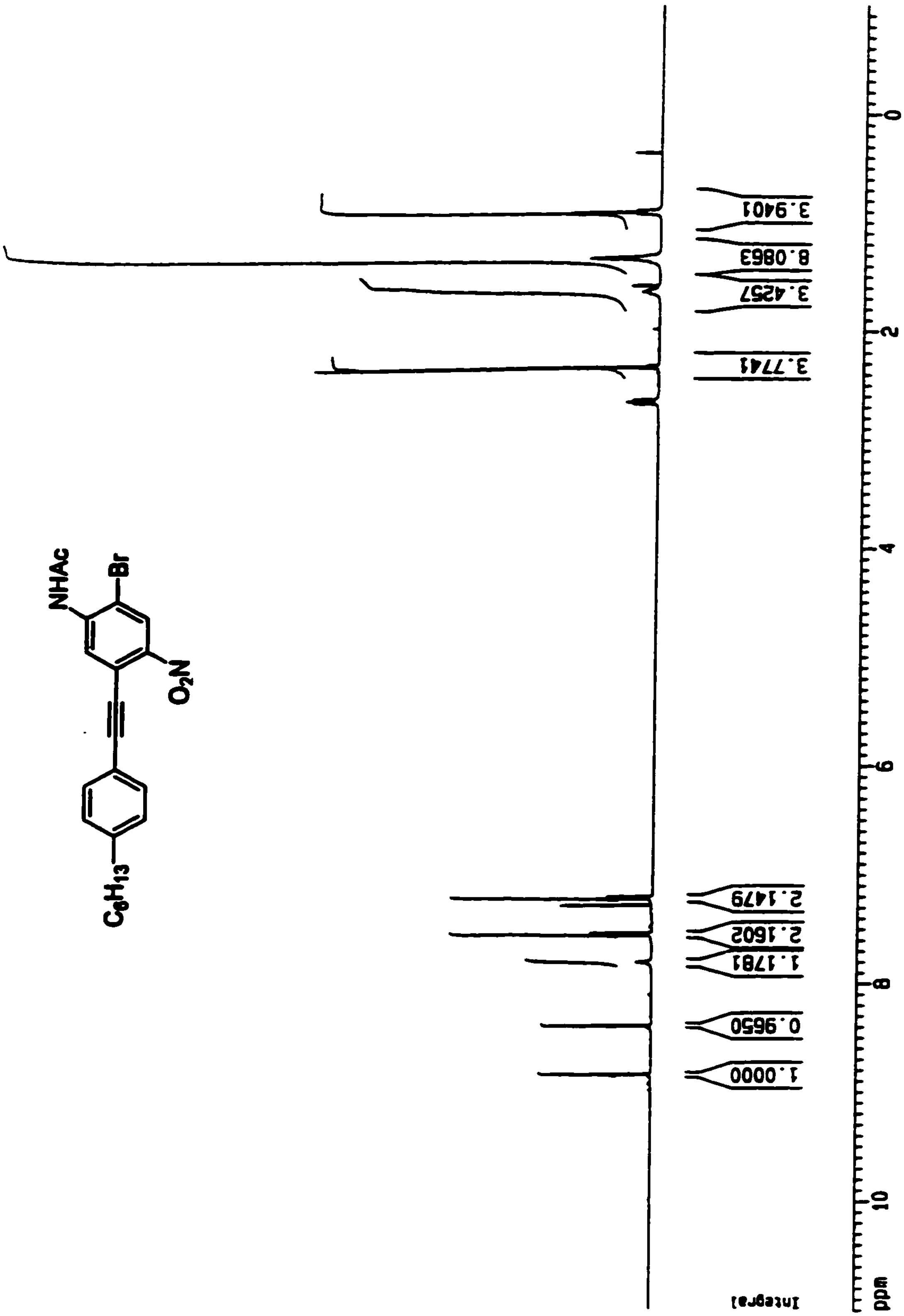


Acc. Mass
2/18

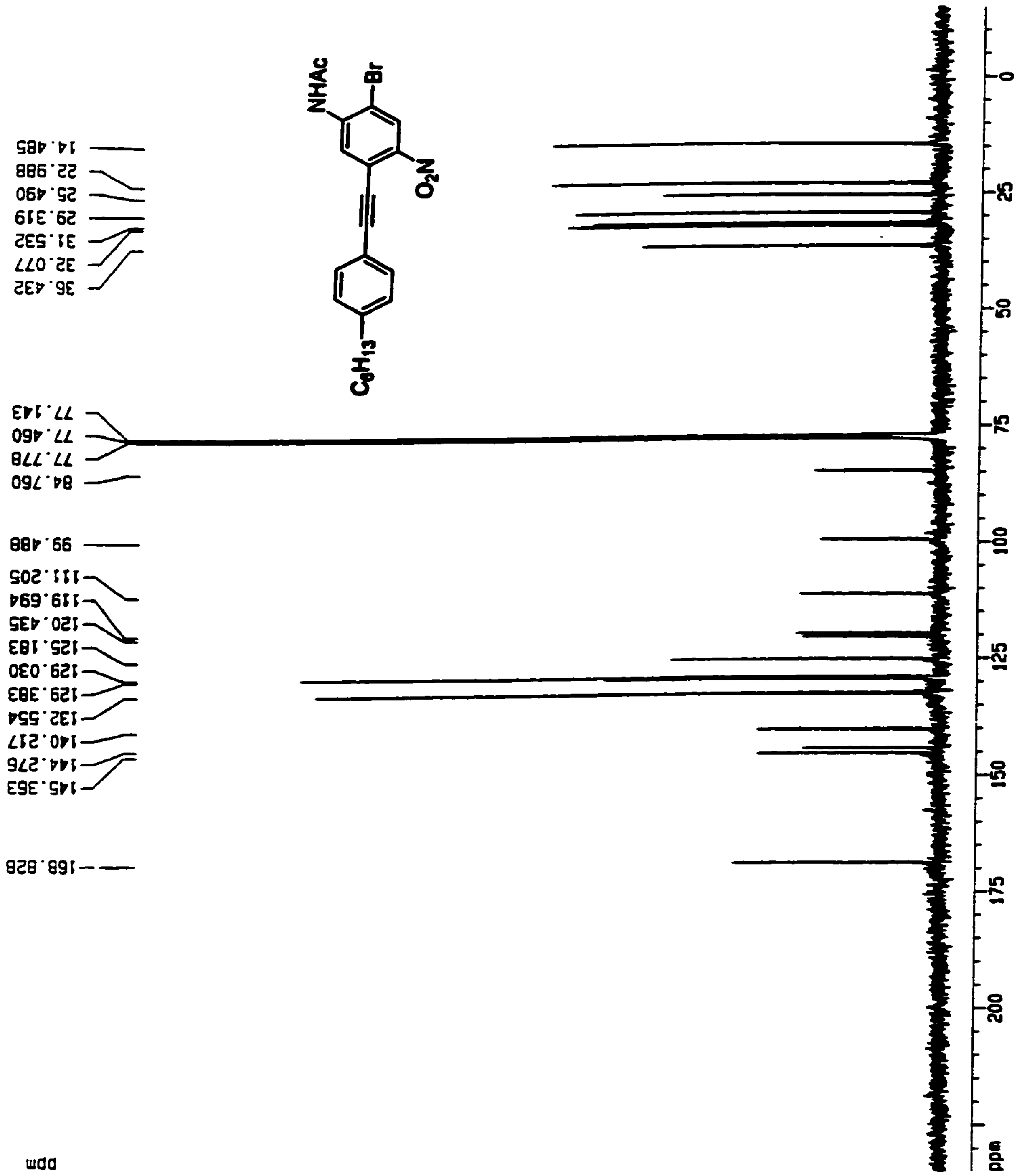
observ mass = 258.1793
calc mass = 258.1804
$C_{17}H_{26}Si$

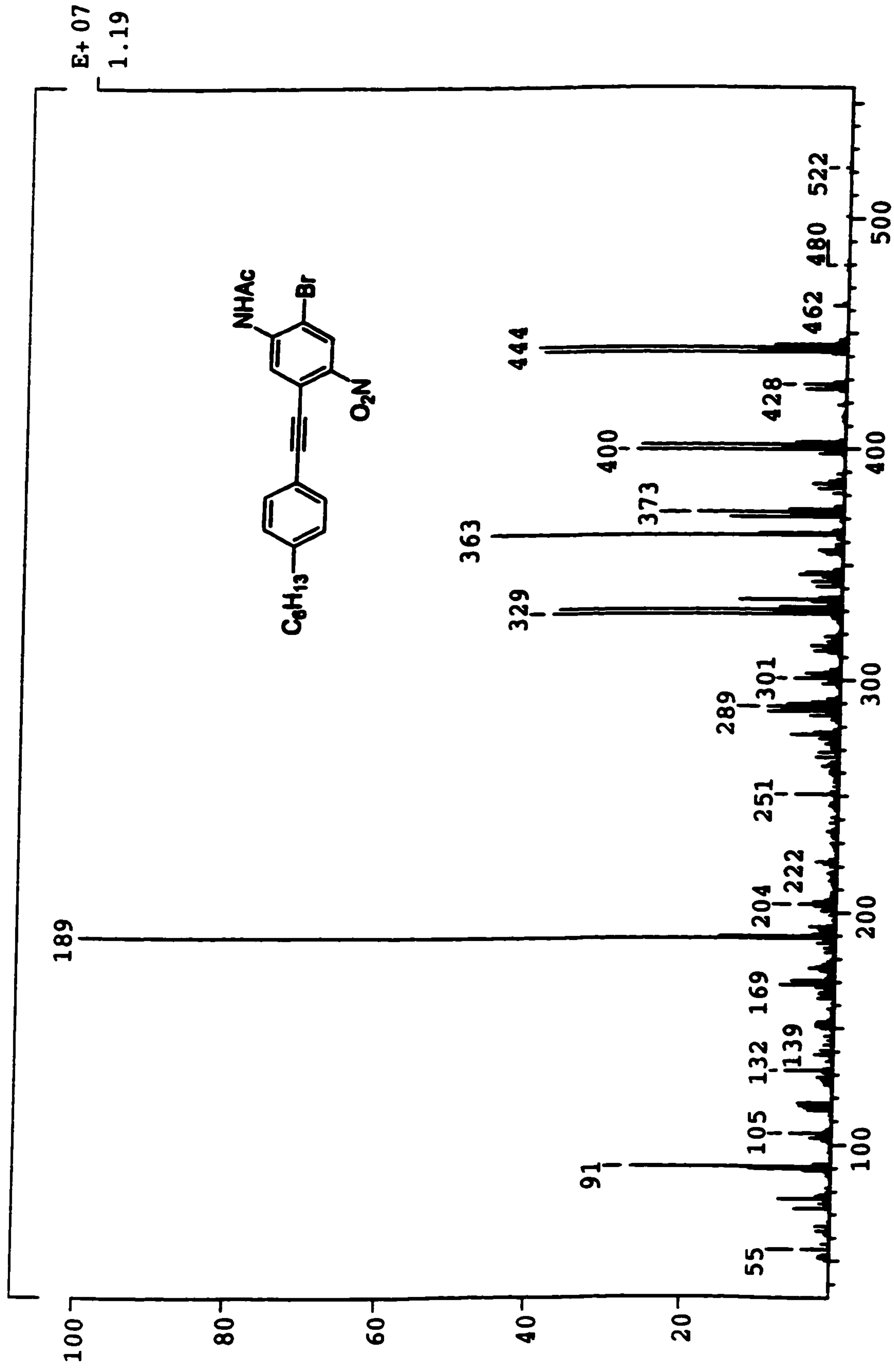
Error = 4.3 ppm

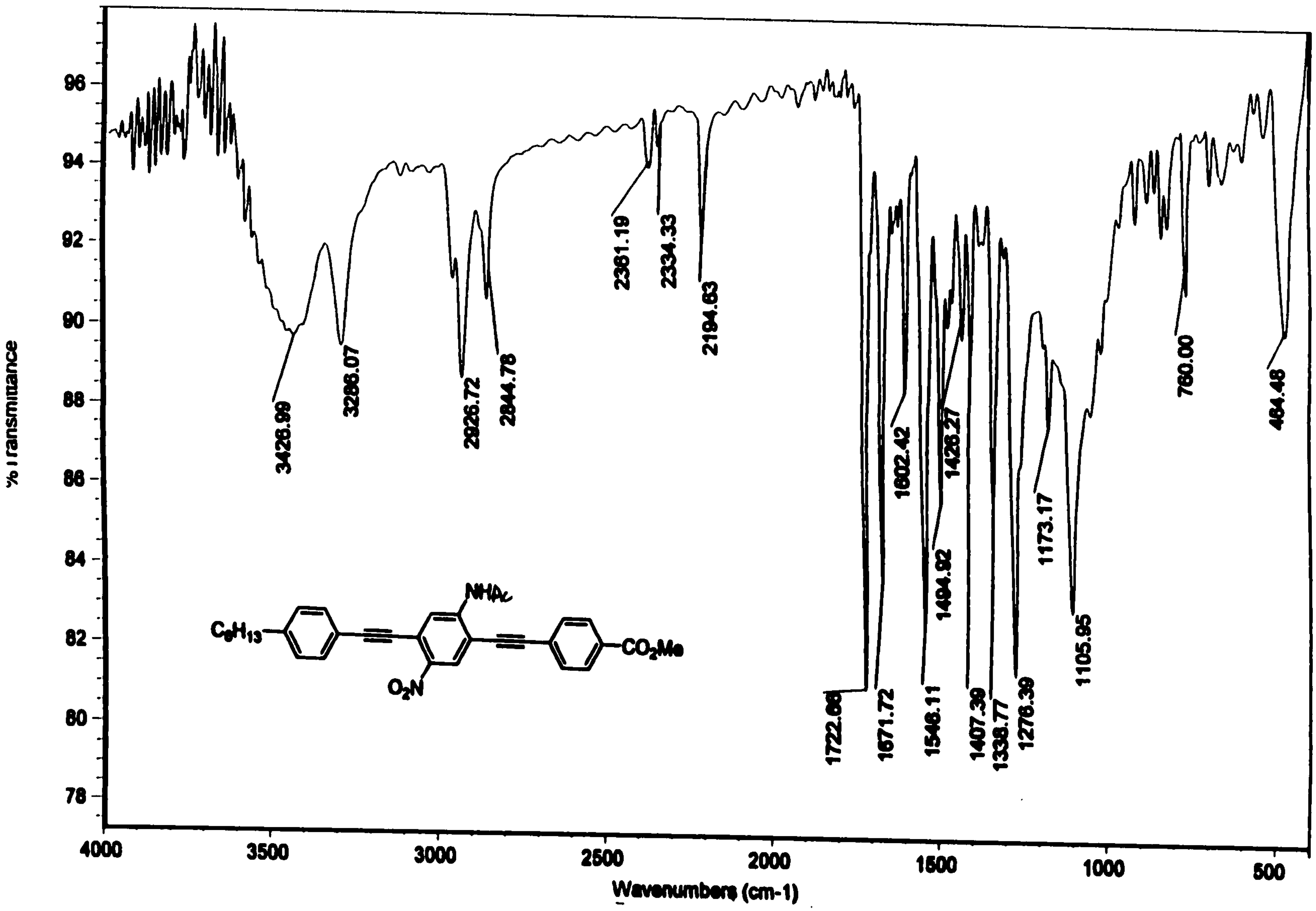

3276.65
3086.57
3016.72
2926.07
2852.18
2213.34
1671.79
1592.84
1560.91
1534.12
1500.11
1460.89
1389.78
1337.01
1260.89
1093.45
1020.52
894.33
813.73
743.88
631.04
484.48
442.99
C_6H_{13}
NHAc
Br
O_2N
Wavenumbers (cm-1)
%Transmittance
4000
3500
3000
2500
2000
1500
1000
500
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70

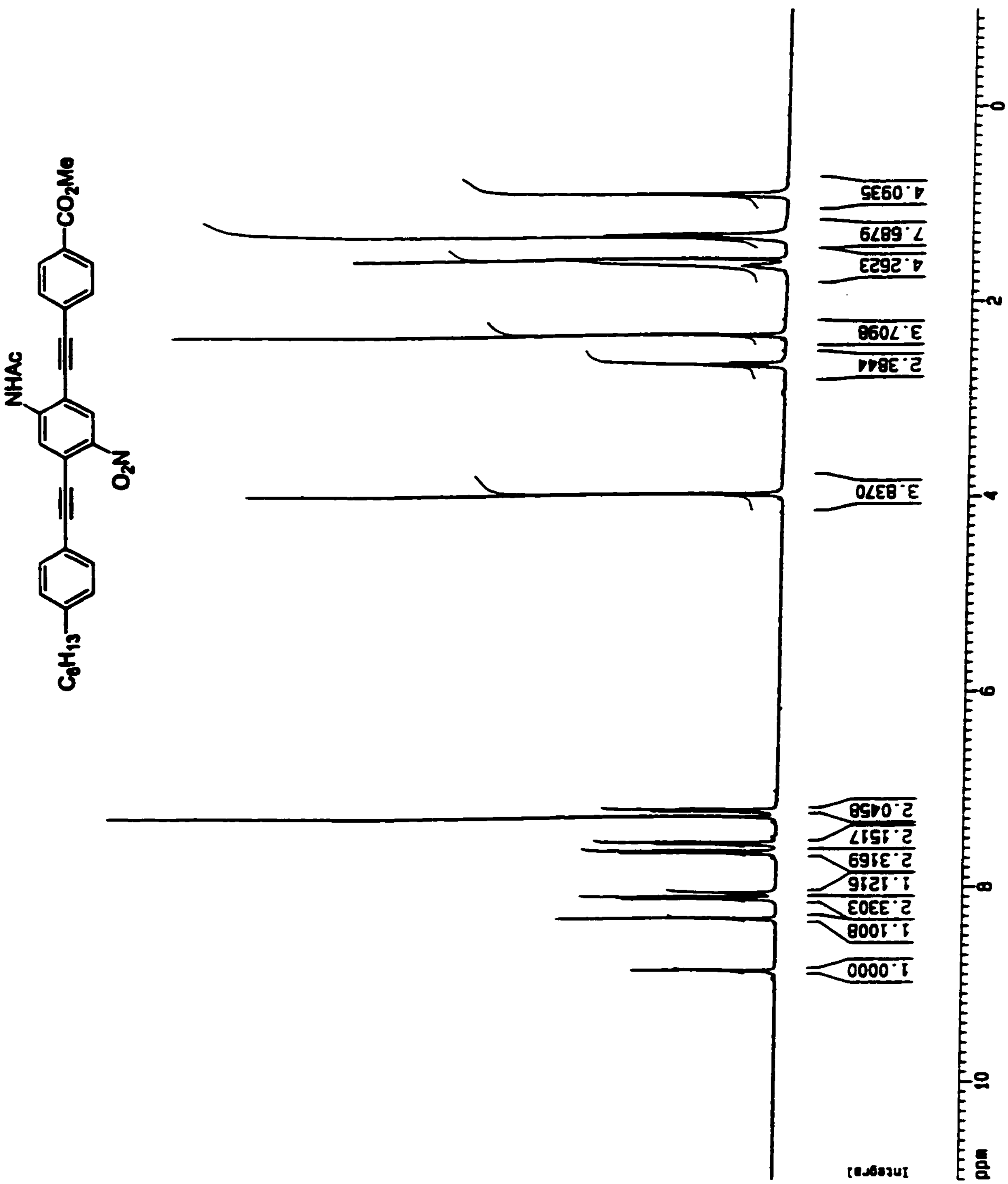


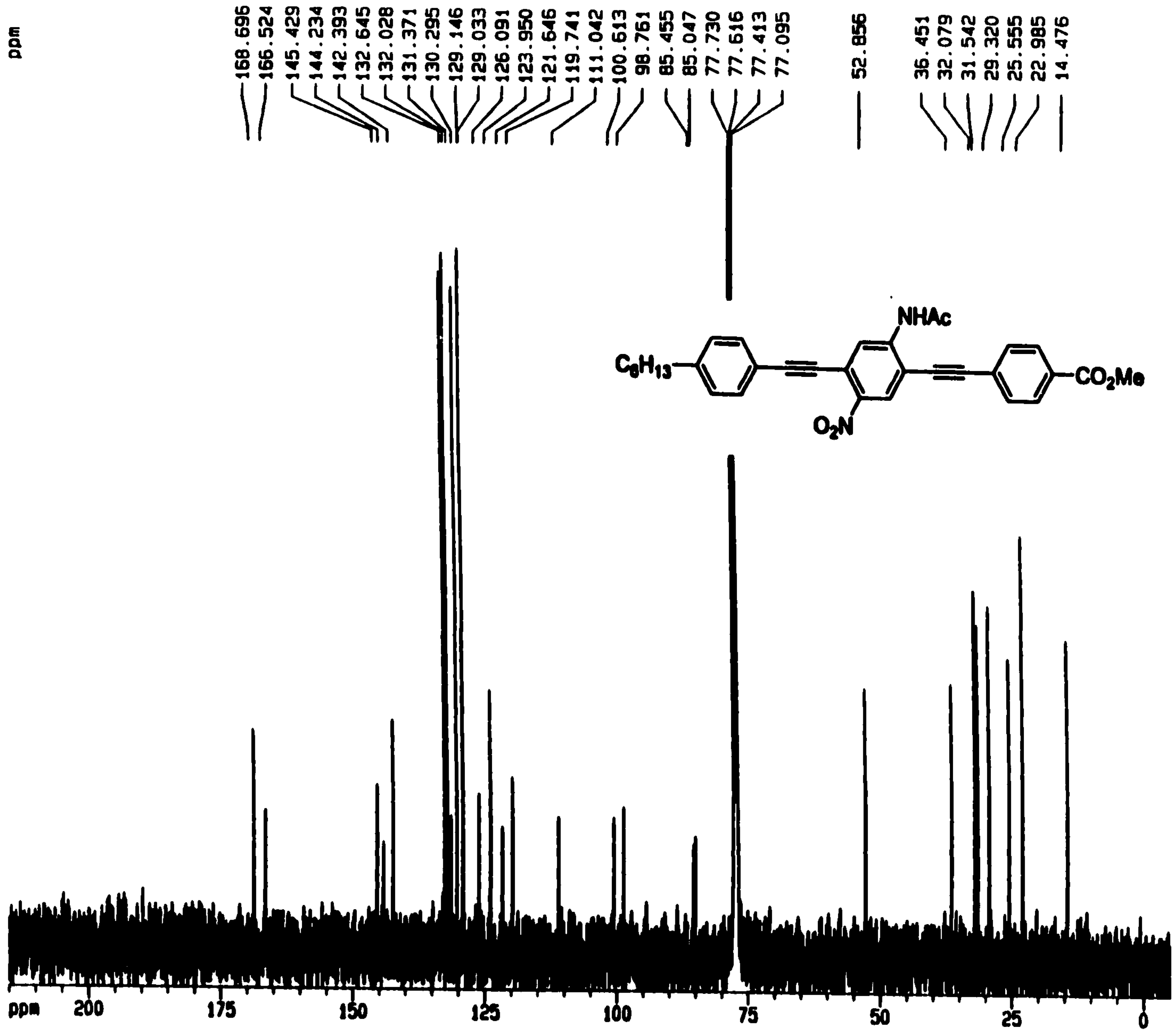
NHAc
Br
O_2N
C_6H_{13}
3.9401
8.0863
3.4257
3.7741
2.1479
2.1602
1.1781
0.9650
1.0000
Integral
ppm
0
2
4
6
8
10

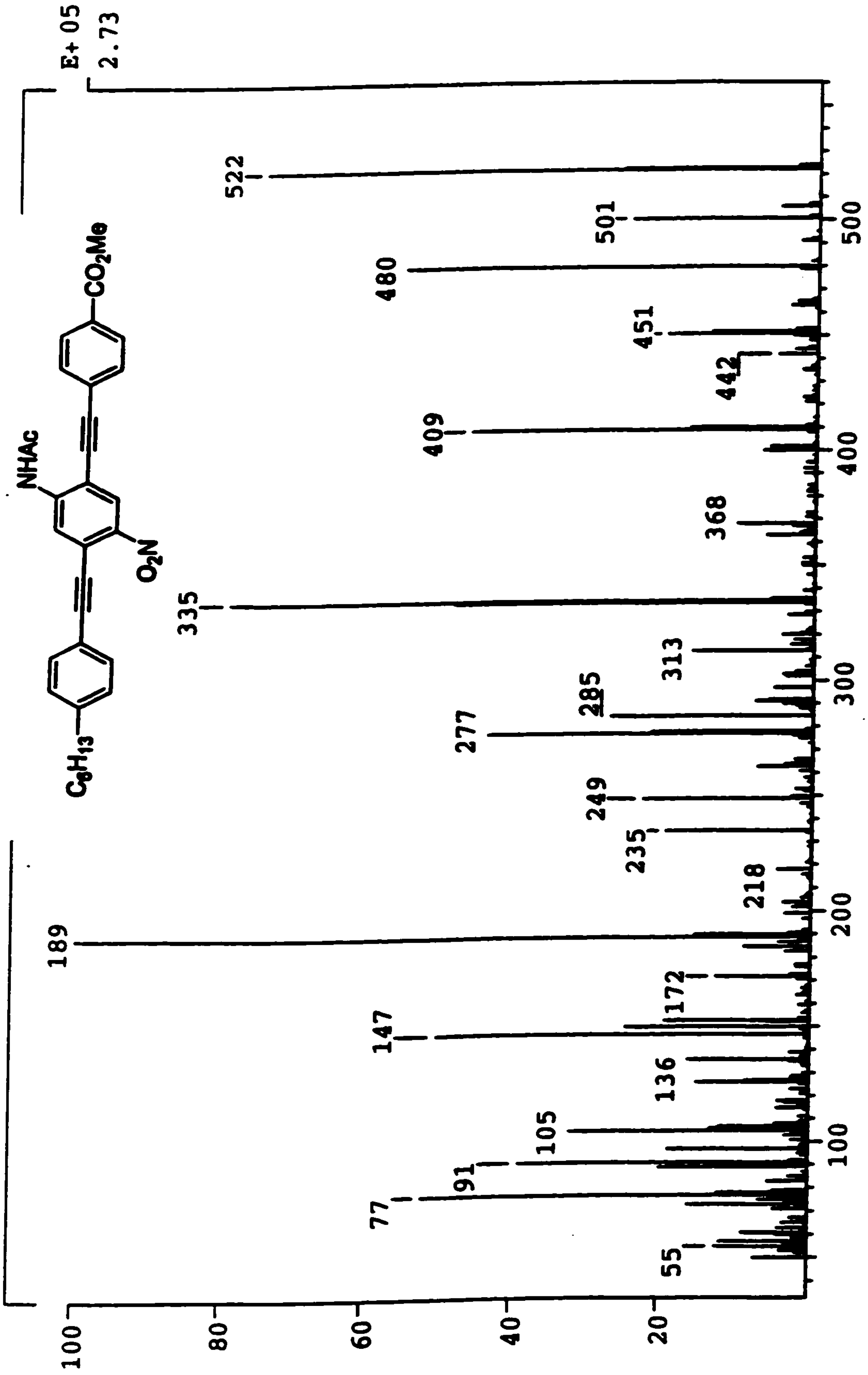

NHAc
Br
O_2N
C_6H_{13}
14.485
22.988
25.490
29.319
31.532
32.077
36.432
77.143
77.460
77.778
84.760
99.488
111.205
119.694
120.435
125.183
129.030
129.383
132.554
140.217
144.276
145.363
168.828
ppm
0
25
50
75
100
125
150
175
200
ppm

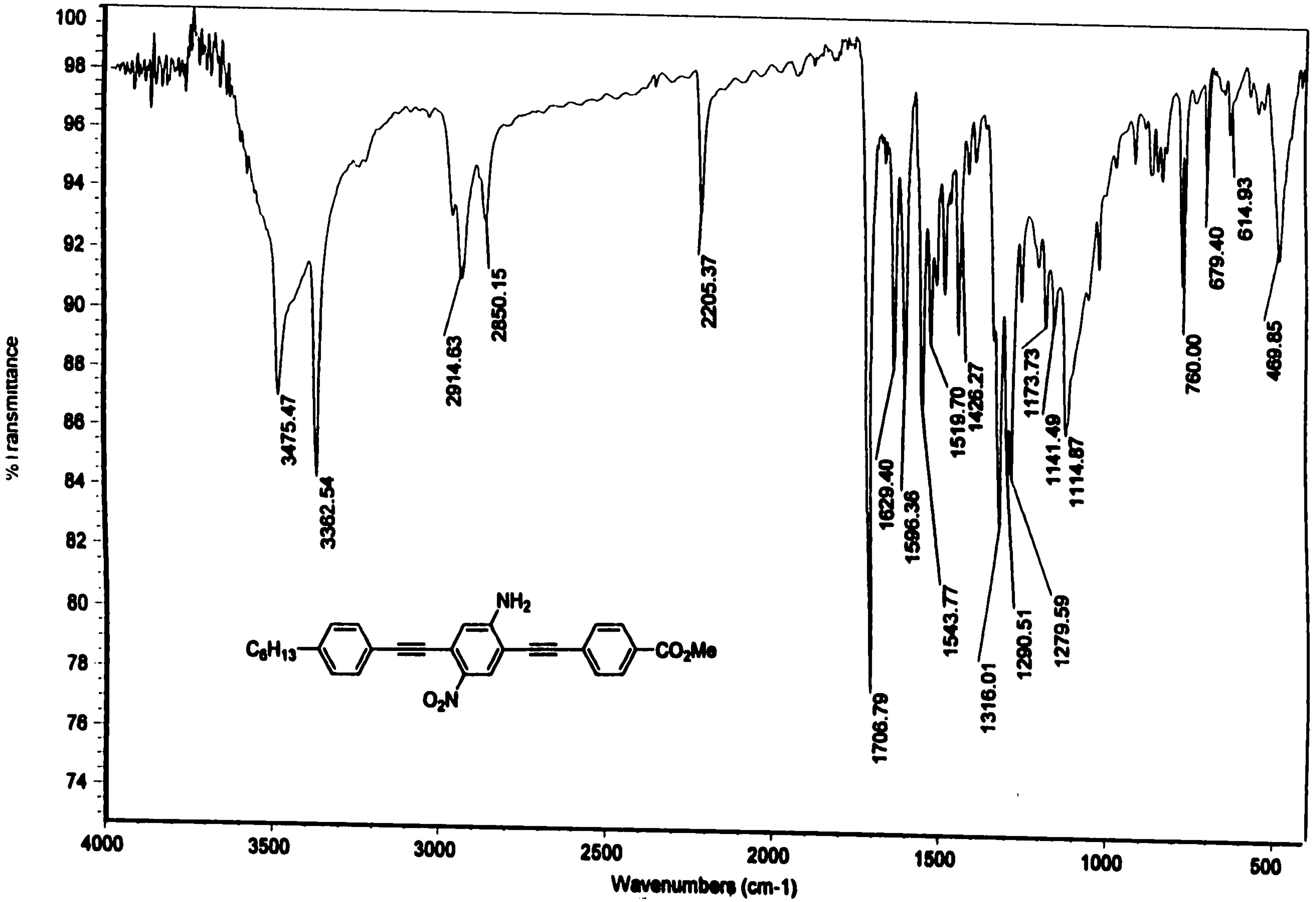

E+07
1.19
100
80
60
40
20
55
91
105
132
139
169
189
204
222
251
289
301
329
363
373
400
428
444
462
480
522
100
200
300
400
500
NHAc
Br
O_2N
C_6H_{13}

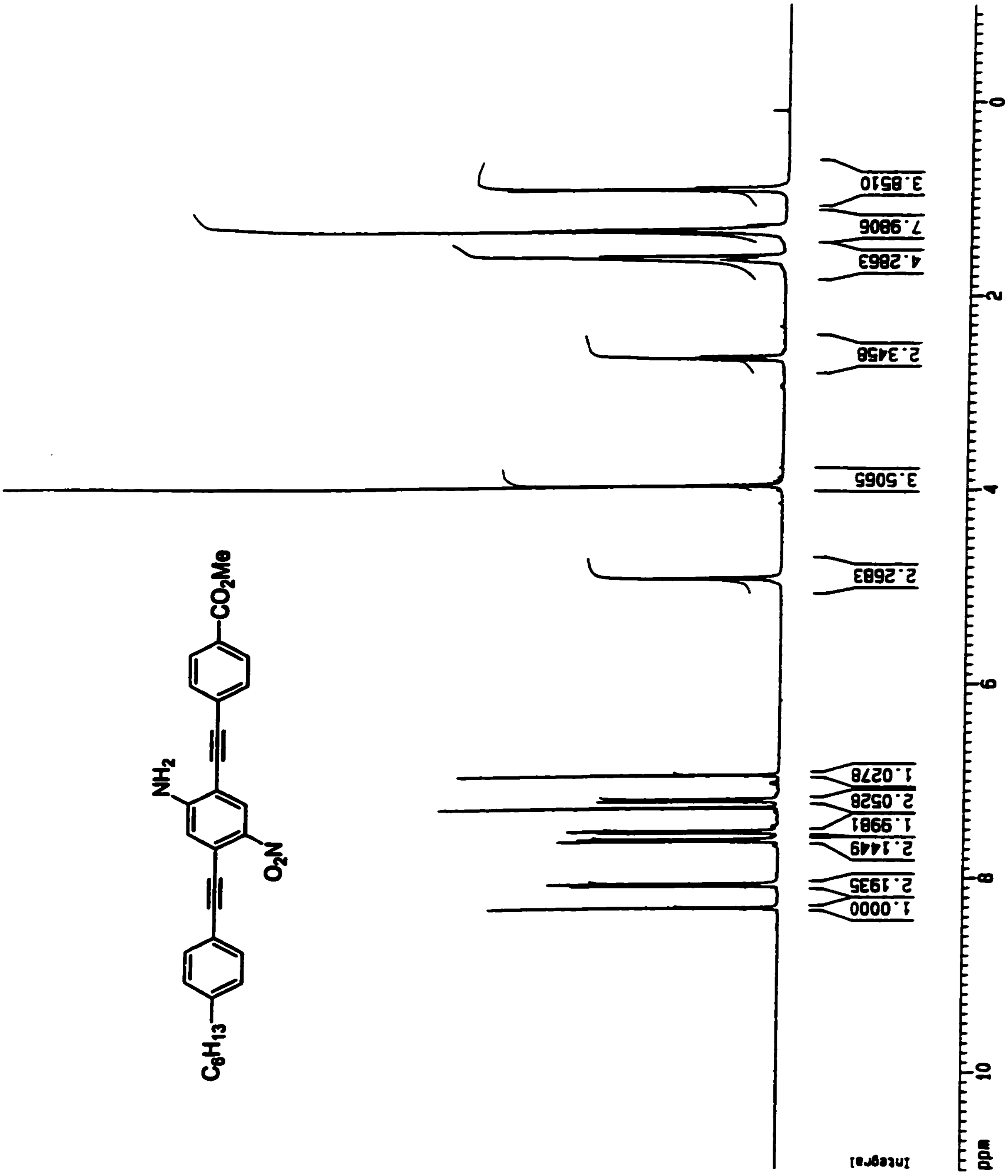

% Transmittance
96
94
92
90
88
86
84
82
80
78
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3426.99
3286.07
2926.72
2844.78
2361.19
2334.33
2194.63
1722.66
1671.72
1602.42
1546.11
1494.92
1426.27
1407.39
1338.77
1276.39
1173.17
1105.95
760.00
484.48
C_6H_{13}
NHAc
O_2N
CO_2Me

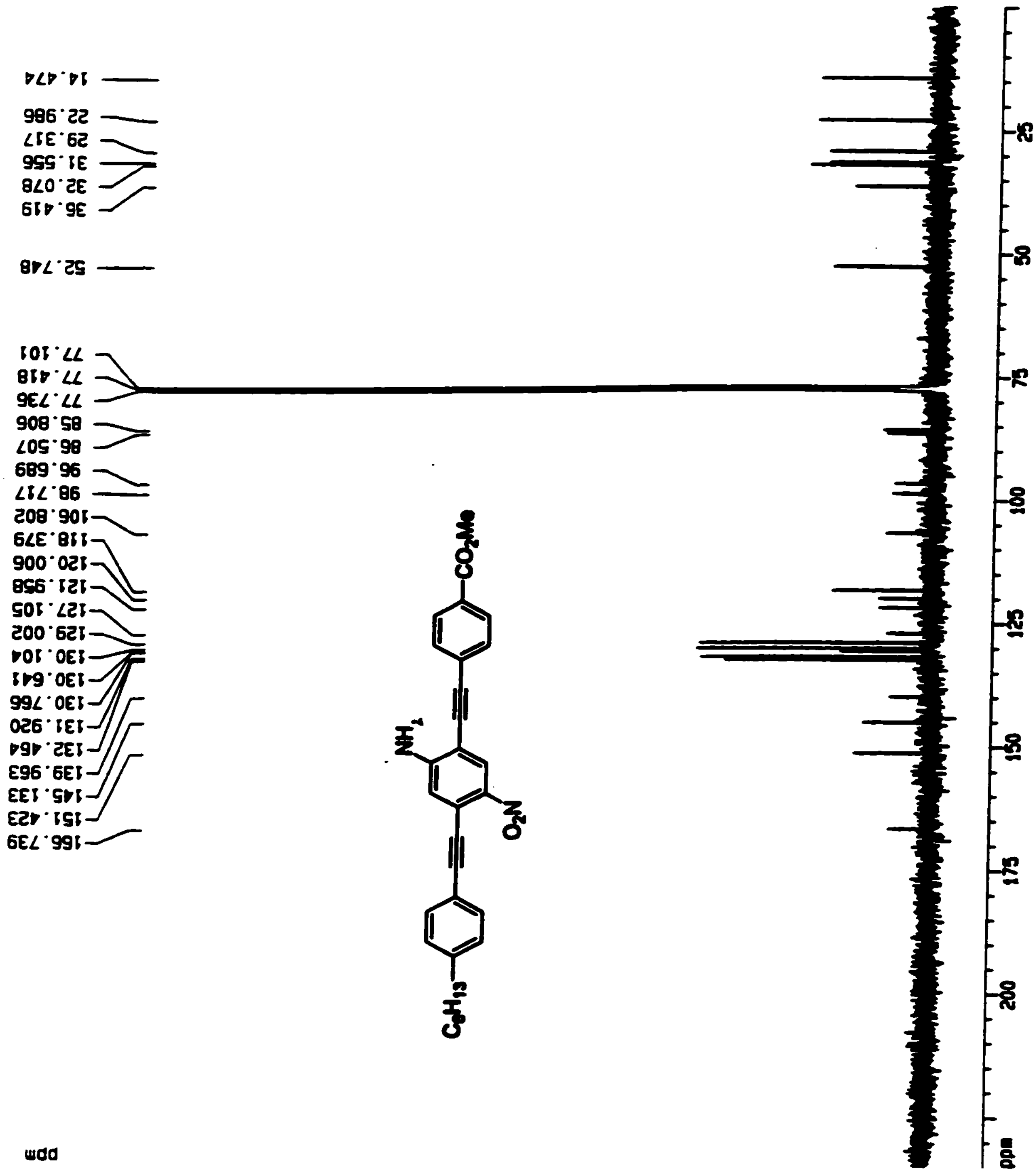

CO$_2$Me
NHAc
O$_2$N
C$_6$H$_{13}$
4.0935
7.6879
4.2623
3.7098
2.3844
3.8370
2.0458
2.1517
2.3169
1.1216
2.3303
1.1008
1.0000
Integral
0
2
4
6
8
10
ppm

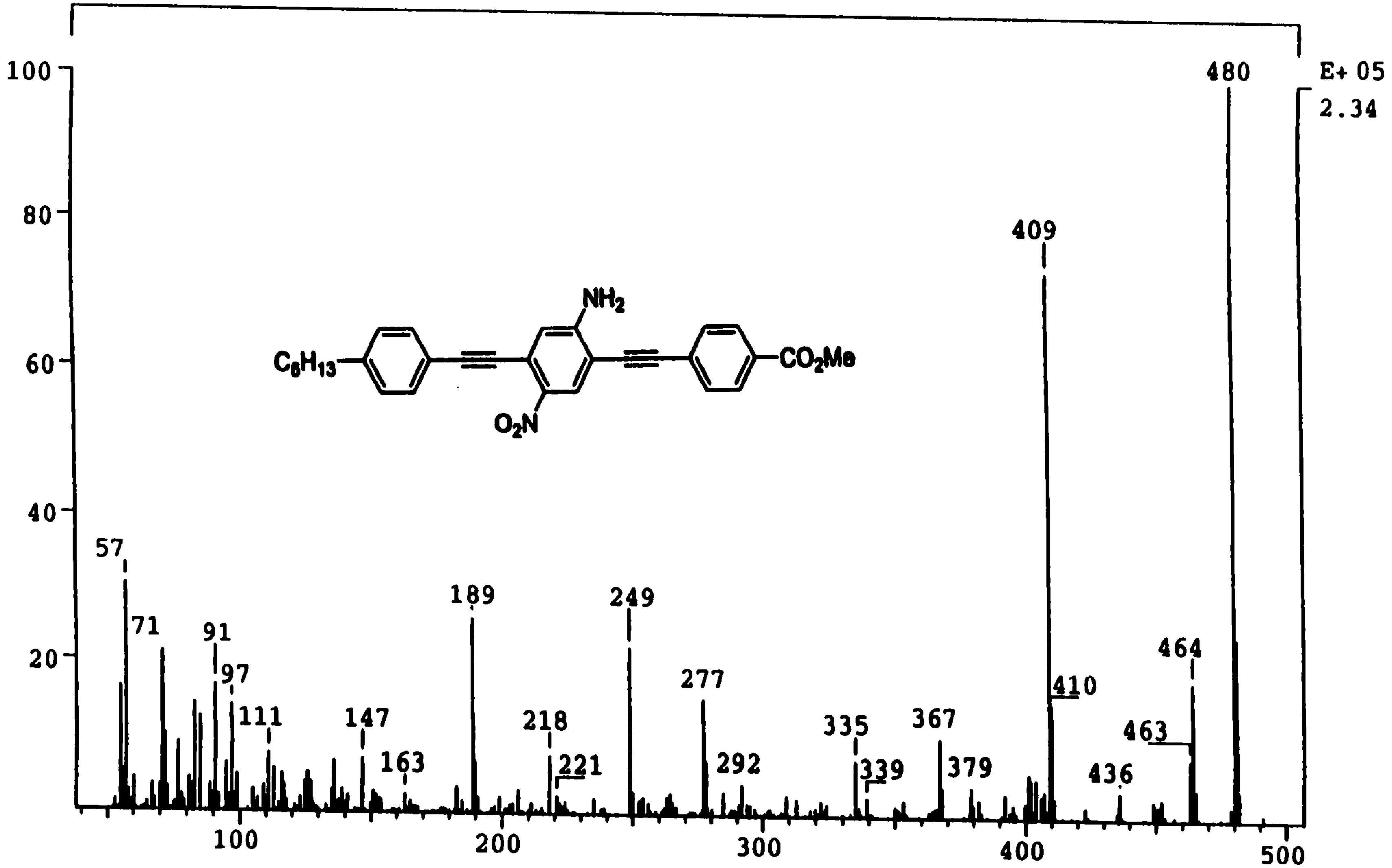

168.696
166.524
145.429
144.234
142.393
132.645
132.028
131.371
130.295
129.146
129.033
126.091
123.950
121.646
119.741
111.042
100.613
98.761
85.455
85.047
77.730
77.616
77.413
77.095
52.856
36.451
32.079
31.542
29.320
25.555
22.985
14.476
ppm
C_6H_{13}
NHAc
O_2N
CO_2Me
ppm
200
175
150
125
100
75
50
25
0

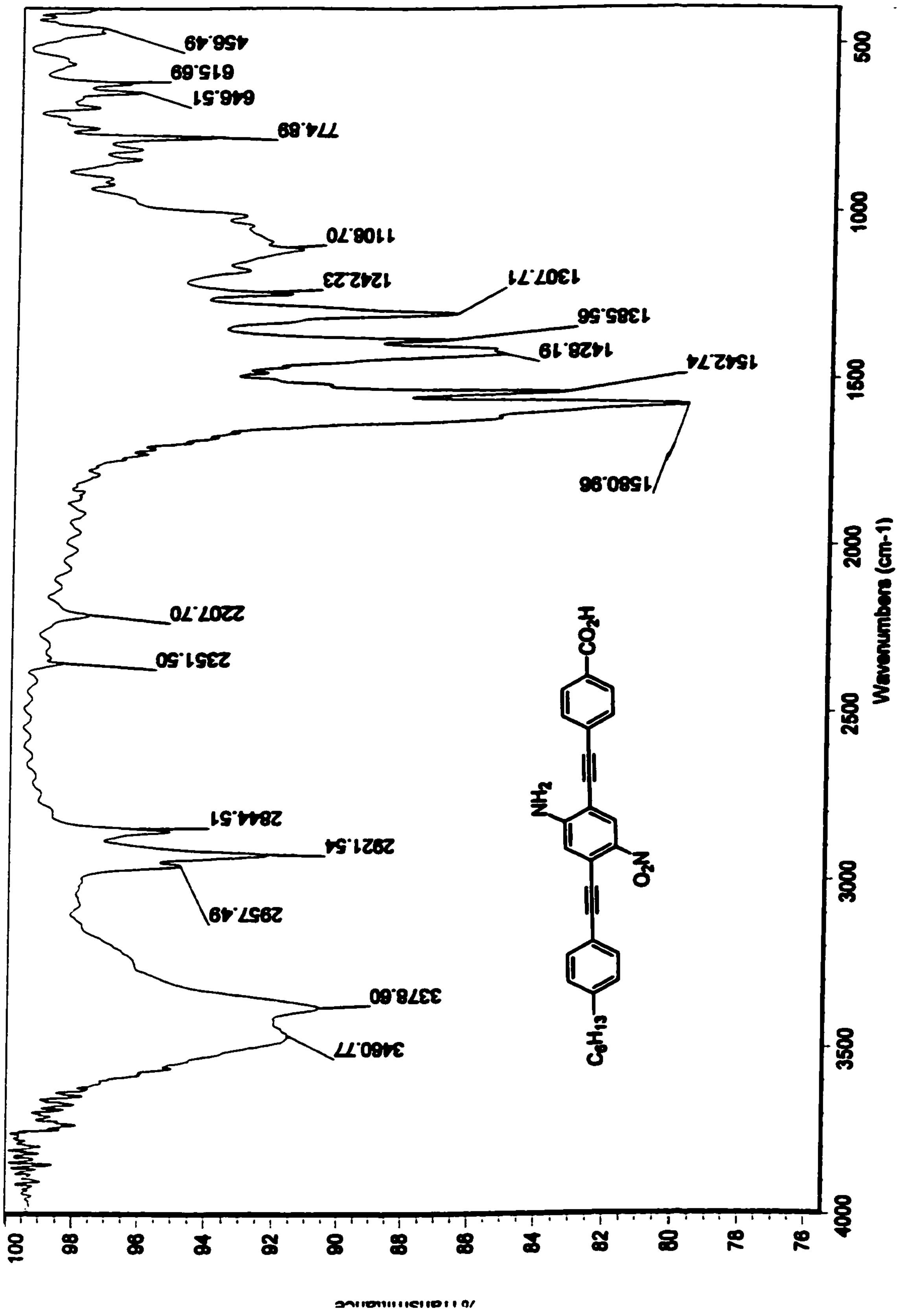

E+ 05
2.73
C_6H_{13}
NHAc
O_2N
CO_2Me
522
501
480
451
442
409
368
335
313
285
277
249
235
218
189
172
147
136
105
91
77
55
100
200
300
400
500
100
80
60
40
20

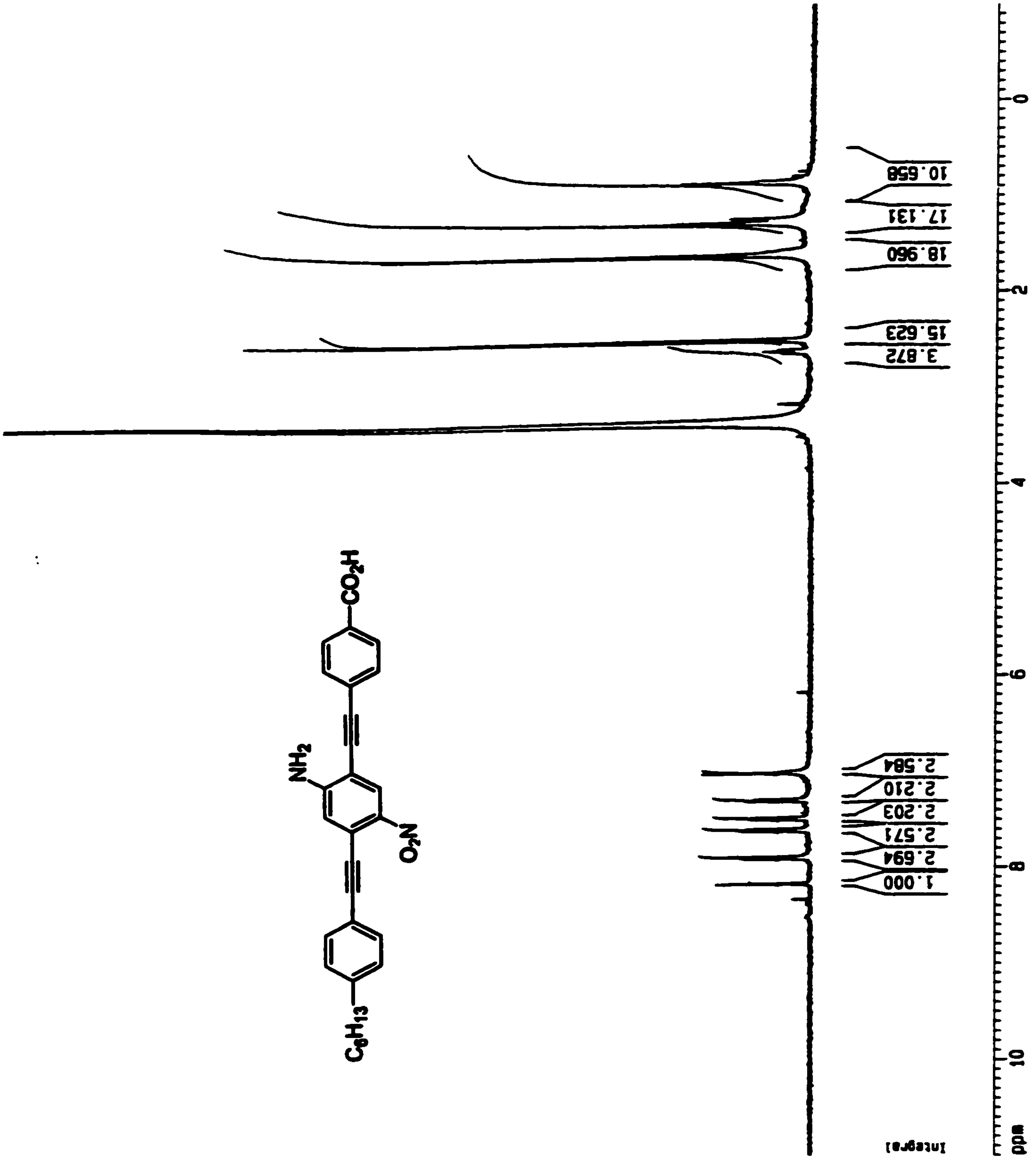

% Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3475.47
3362.54
2914.63
2850.15
2205.37
1706.79
1629.40
1596.36
1543.77
1519.70
1426.27
1316.01
1290.51
1279.59
1173.73
1141.49
1114.87
760.00
679.40
614.93
469.85
C_6H_{13}
NH_2
O_2N
CO_2Me

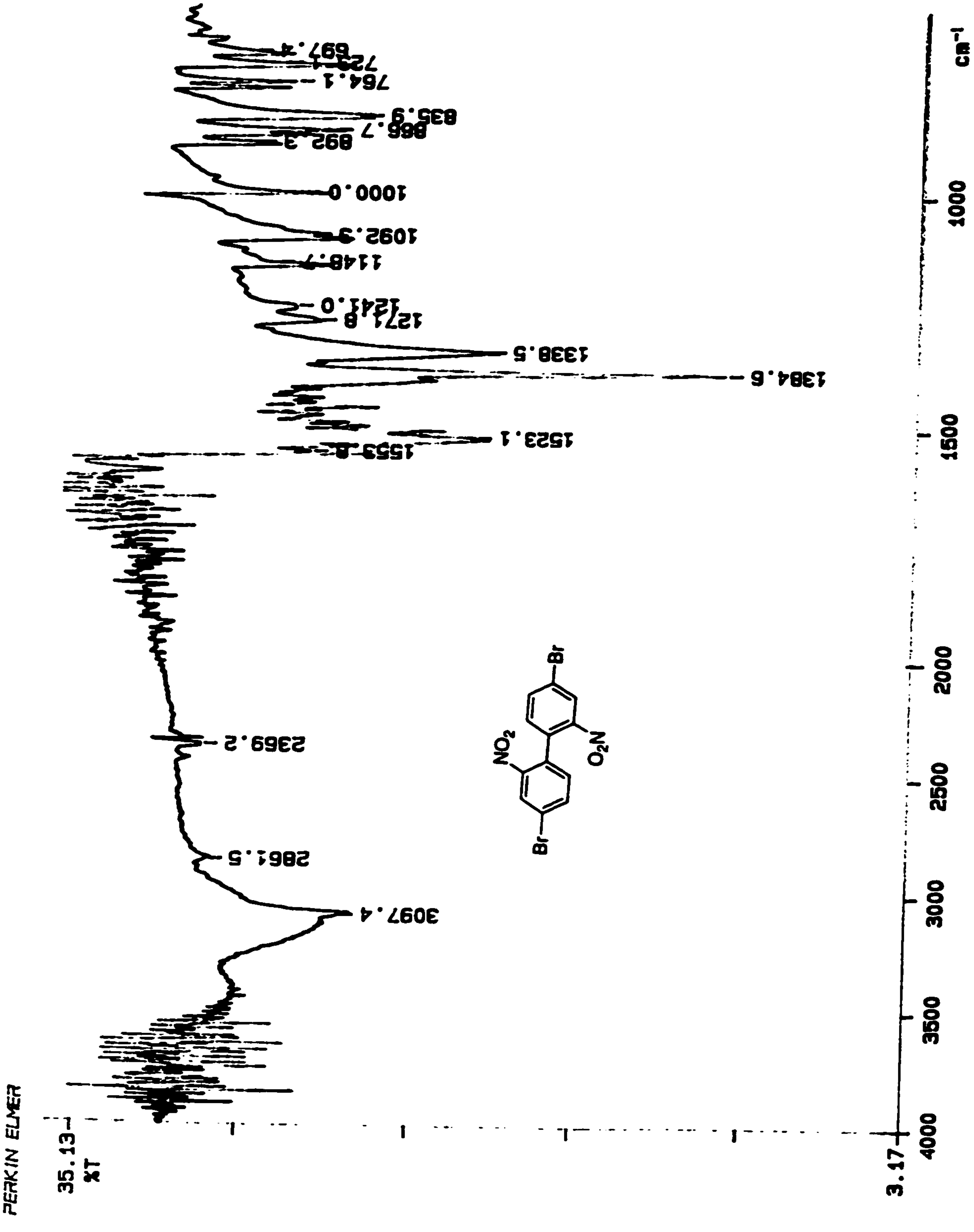

C$_6$H$_{13}$
NH$_2$
O$_2$N
CO$_2$Me
3.8510
7.9806
4.2863
2.3458
3.5065
2.2683
1.0278
2.0528
1.9981
2.1449
2.1935
1.0000
Integral
0
2
4
6
8
10
ppm

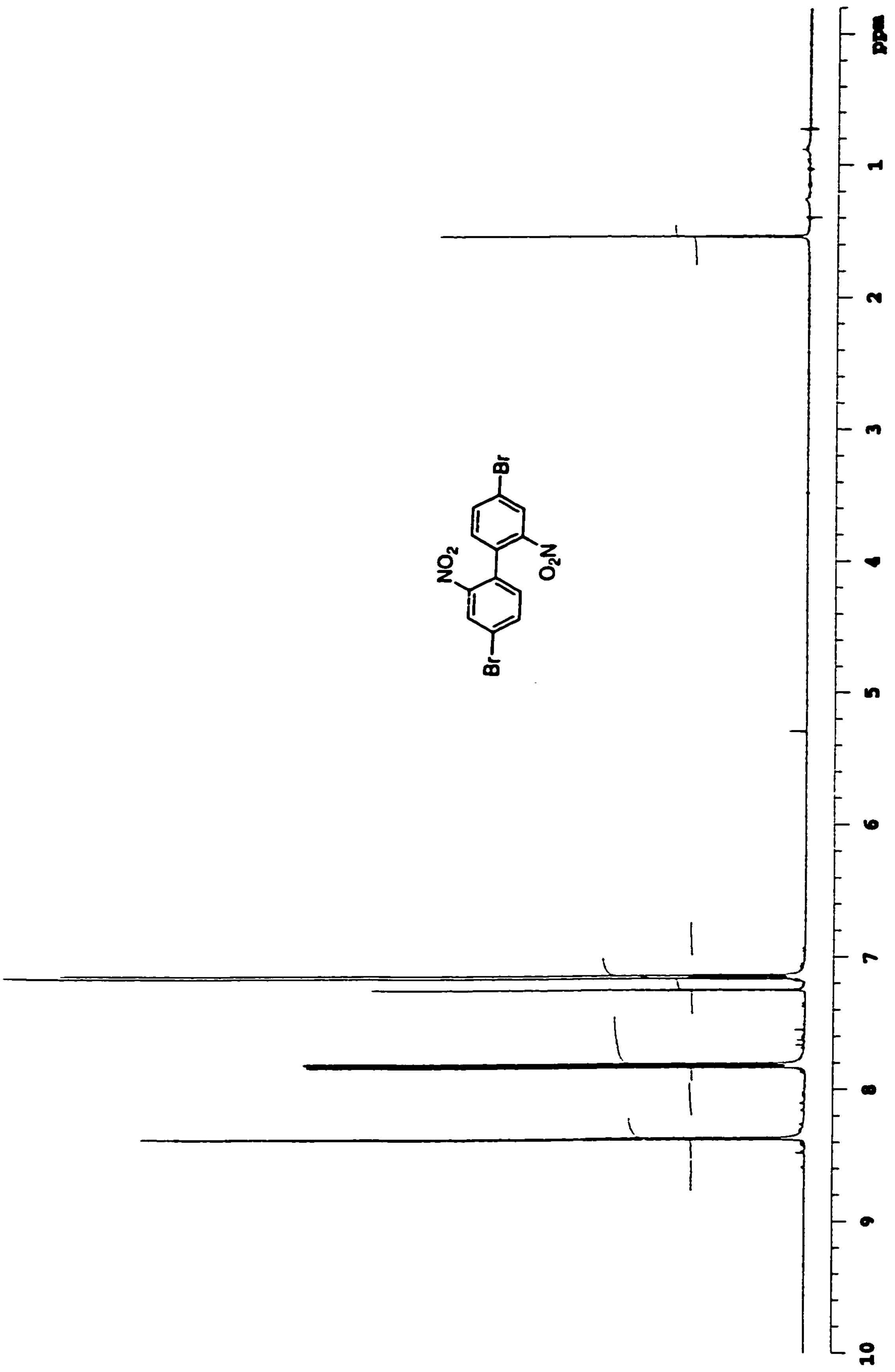

14.474
22.986
29.317
31.556
32.078
36.419
52.748
77.101
77.418
77.736
85.806
86.507
96.689
98.717
106.802
118.379
120.006
121.958
127.105
129.002
130.104
130.641
130.766
131.920
132.464
139.963
145.133
151.423
166.739
ppm
CO2Me
NH2
O2N
C6H13
25
50
75
100
125
150
175
200
ppm


E+ 05
2.34
100
80
60
40
20
100
200
300
400
500
57
71
91
97
111
147
163
189
218
221
249
277
292
335
339
367
379
409
410
436
463
464
480
NH2
C6H13
O2N
CO2Me

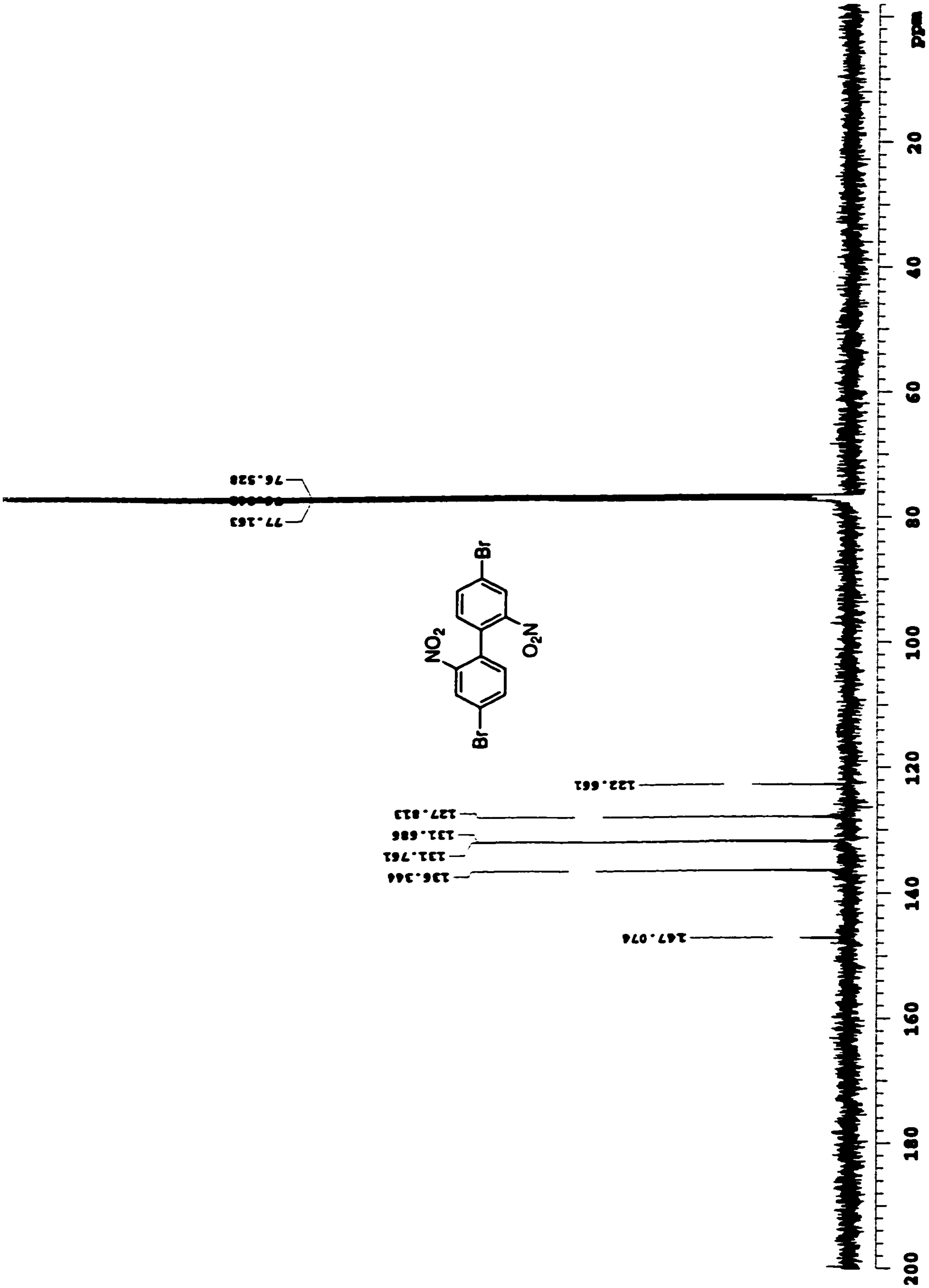

456.49
615.69
646.51
774.89
1108.70
1242.23
1307.71
1385.56
1428.19
1542.74
1580.96
2207.70
2351.50
2844.51
2921.54
2957.49
3378.60
3480.77
NH2
CO2H
O2N
C6H13
100
98
96
94
92
90
88
86
84
82
80
78
76
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)


10.658
17.131
18.960
15.623
3.872
2.584
2.210
2.203
2.571
2.694
1.000
Integral
ppm
0
2
4
6
8
10
CO2H
NH2
O2N
C6H13

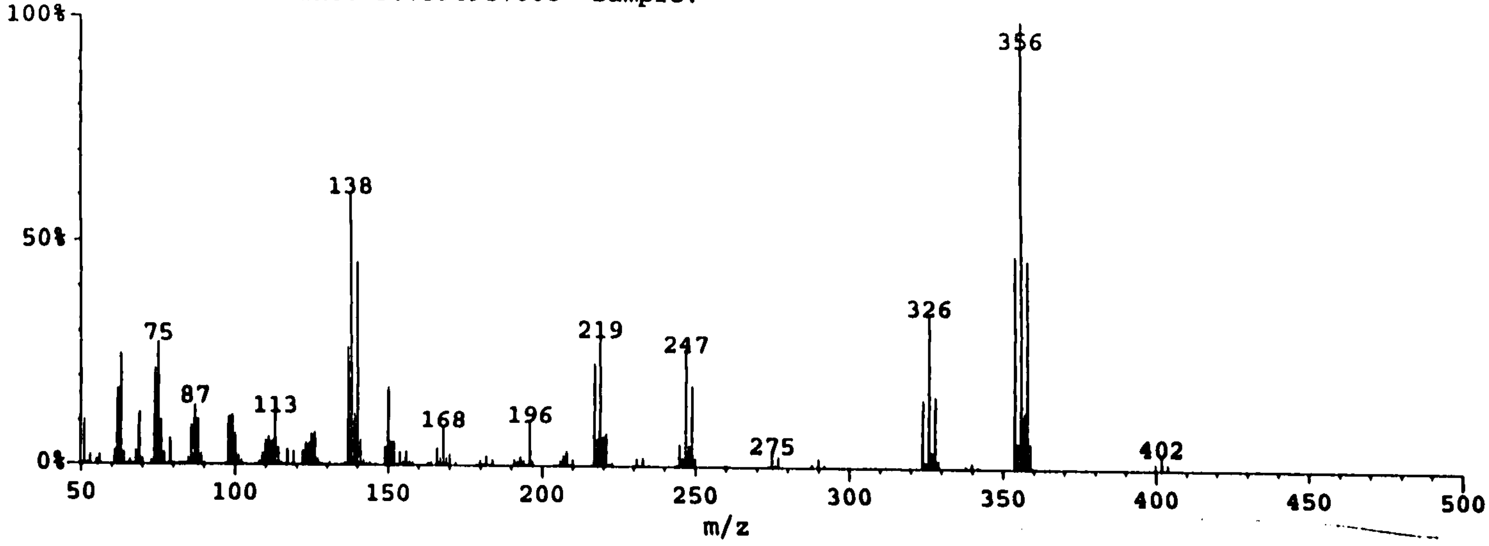

PERKIN ELMER
35.13
%T
3.17
4000
3500
3000
2500
2000
1500
1000
cm-1
3097.4
2861.5
2369.2
1553.8
1523.1
1384.6
1338.5
1271.8
1241.0
1148.7
1092.9
1000.0
892.3
866.7
835.9
764.1
729.1
697.4
Br
NO2
O2N
Br



ppm
1
2
3
4
5
6
7
8
9
10
Br
NO2
O2N
Br

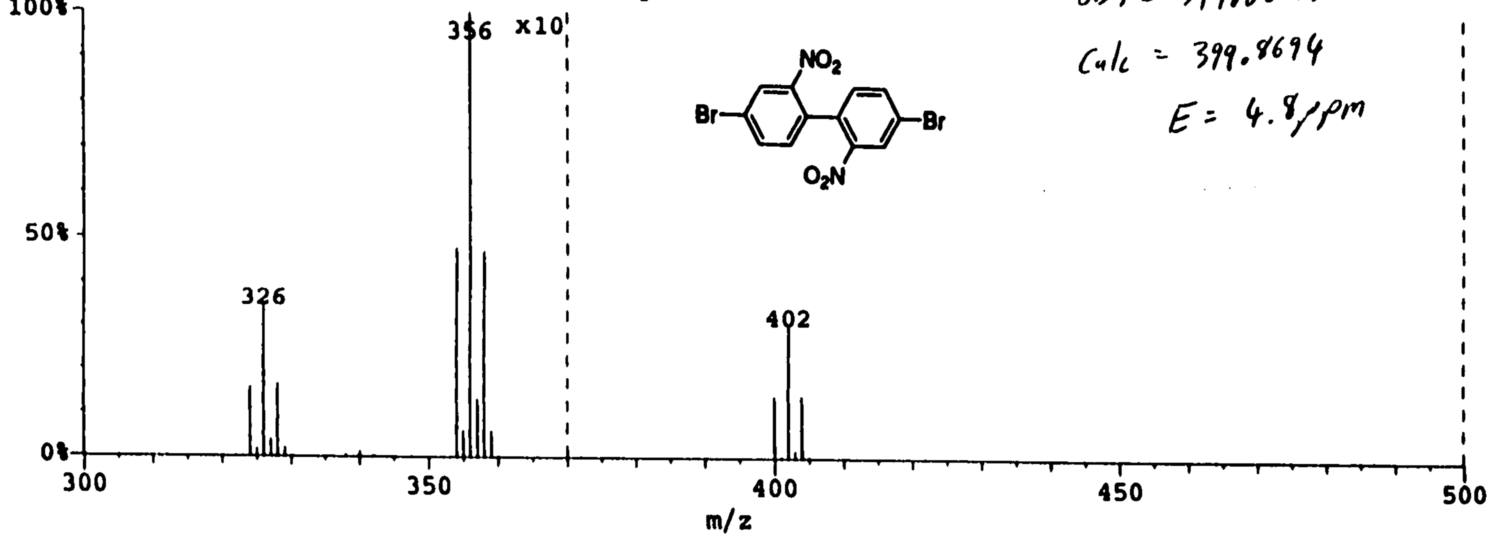

76.528
77.163
Br
NO2
O2N
Br
122.661
127.813
131.686
131.761
136.344
147.074
ppm
20
40
60
80
100
120
140
160
180
200

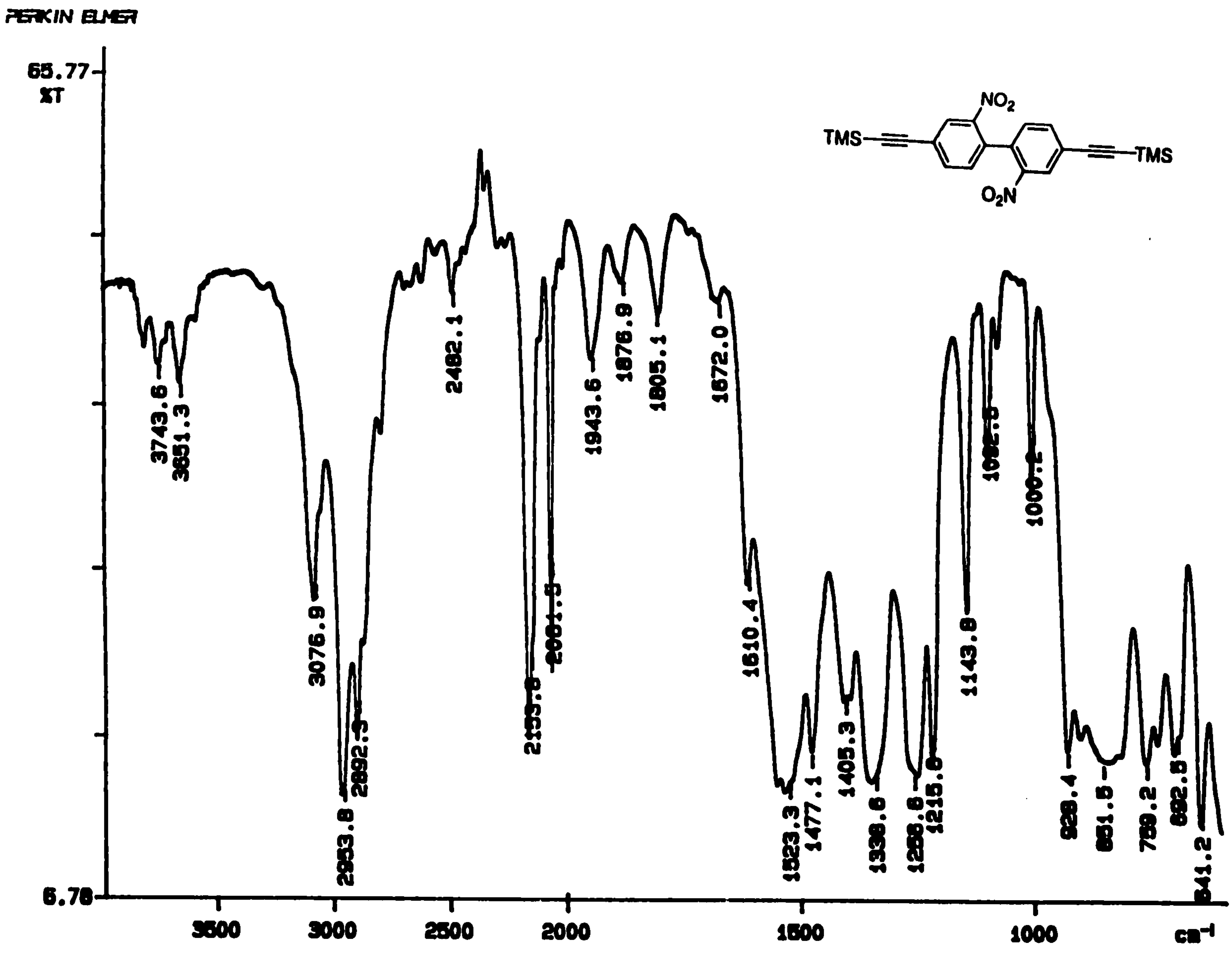
AMR81a: Scan Sum 1391-1401 (22.72 - 22.89 min)
Base: 356.00 Int: 5.75949e+006 Sample:

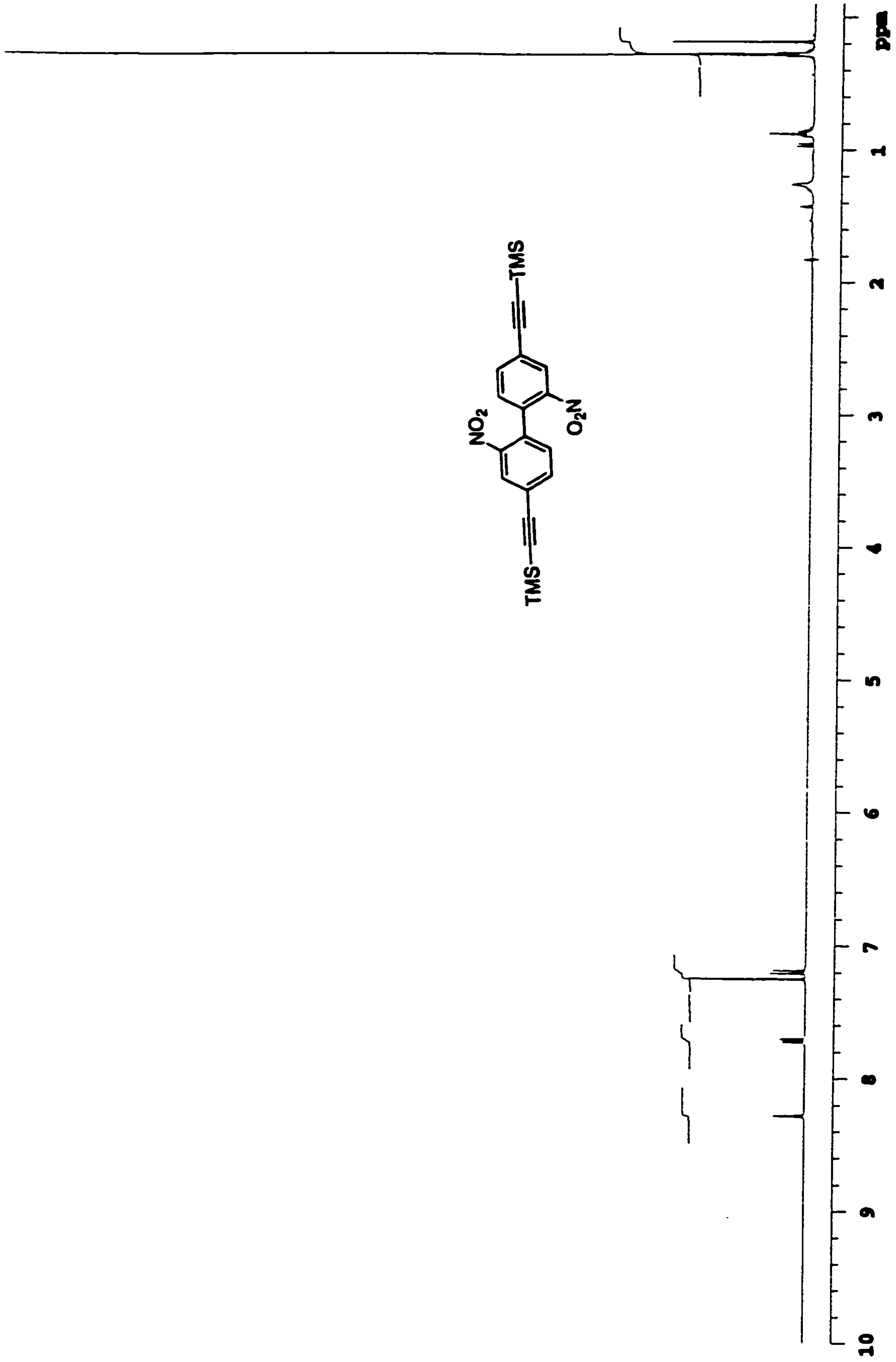


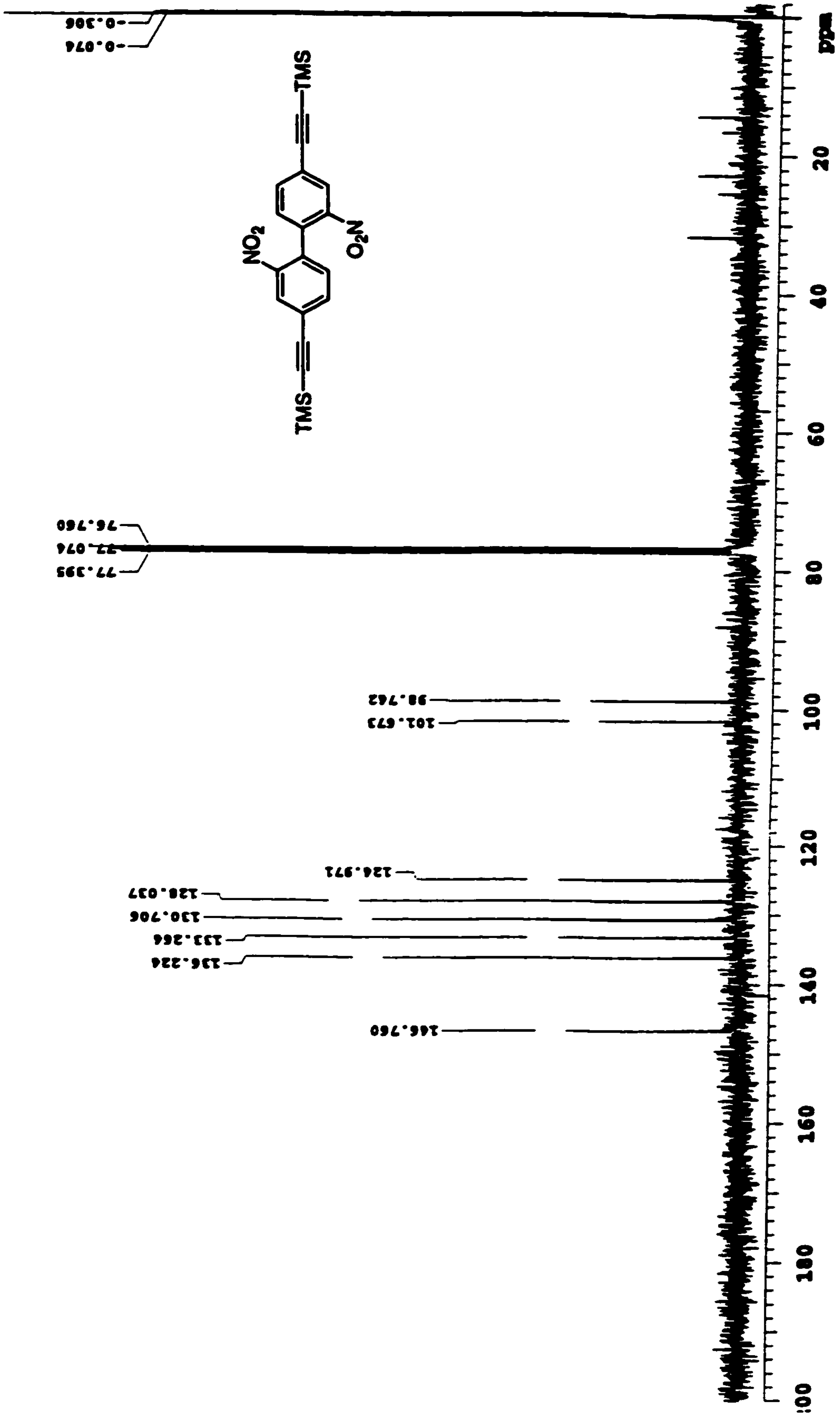
H. Res Direct Probe 1/28
obs = 399.8675
Calc = 399.8694
E = 4.8 ppm

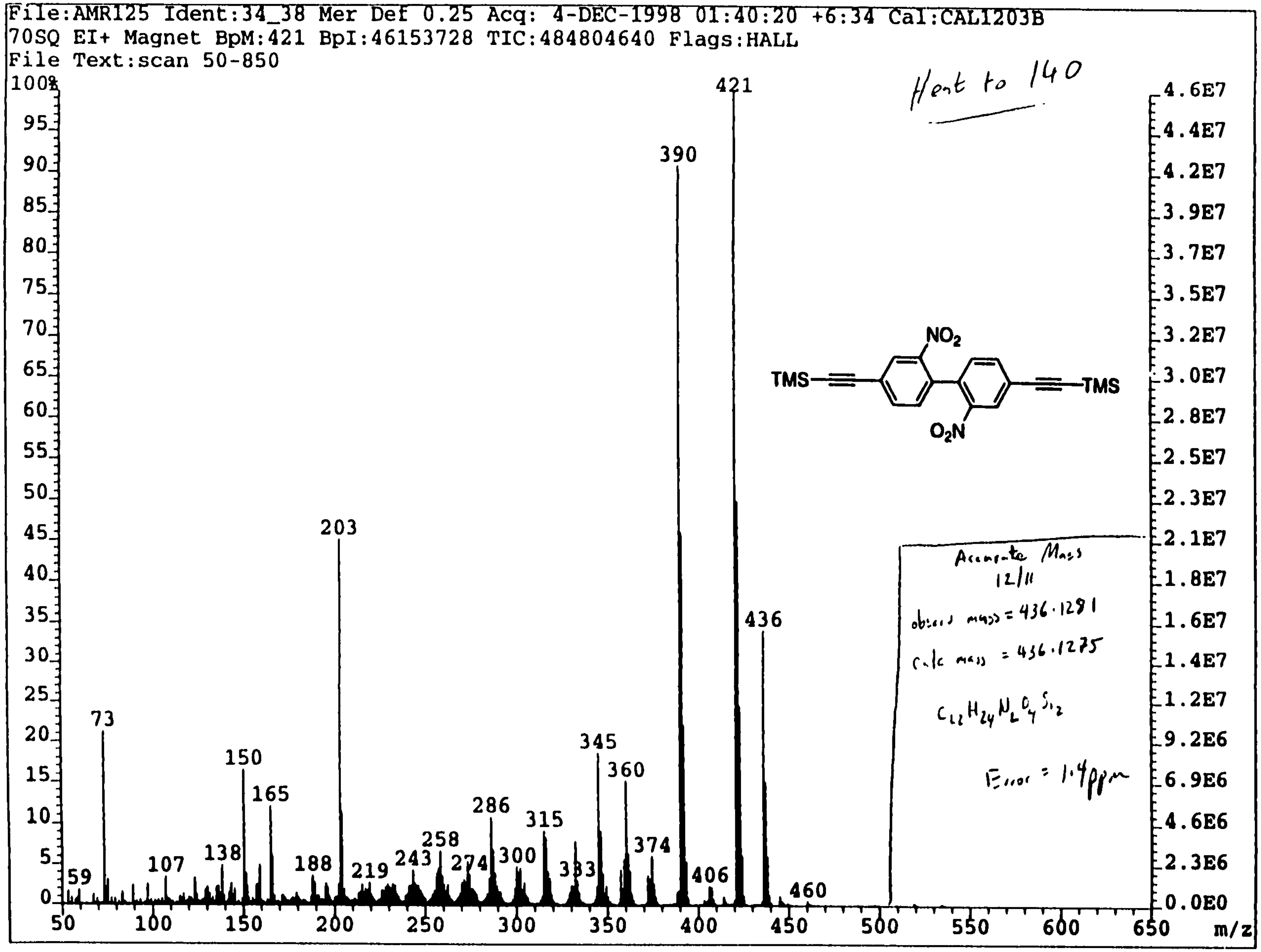
AMR81a: Scan Sum 1392-1400 (22.74 - 22.87 min)
Base: 356.00 Int: 5.72715e+006 Sample:




PERKIN ELMER
65.77
%T
6.78
3743.6
3651.3
3076.9
2953.8
2892.9
2482.1
2155.8
2061.5
1943.6
1876.9
1805.1
1672.0
1610.4
1523.3
1477.1
1405.3
1338.6
1258.6
1215.6
1143.8
1092.5
1000.2
928.4
851.5
759.2
692.5
641.2
3500
3000
2500
2000
1500
1000
cm⁻¹
TMS
NO₂
O₂N
TMS


TMS
NO2
O2N
TMS
ppm
1
2
3
4
5
6
7
8
9
10

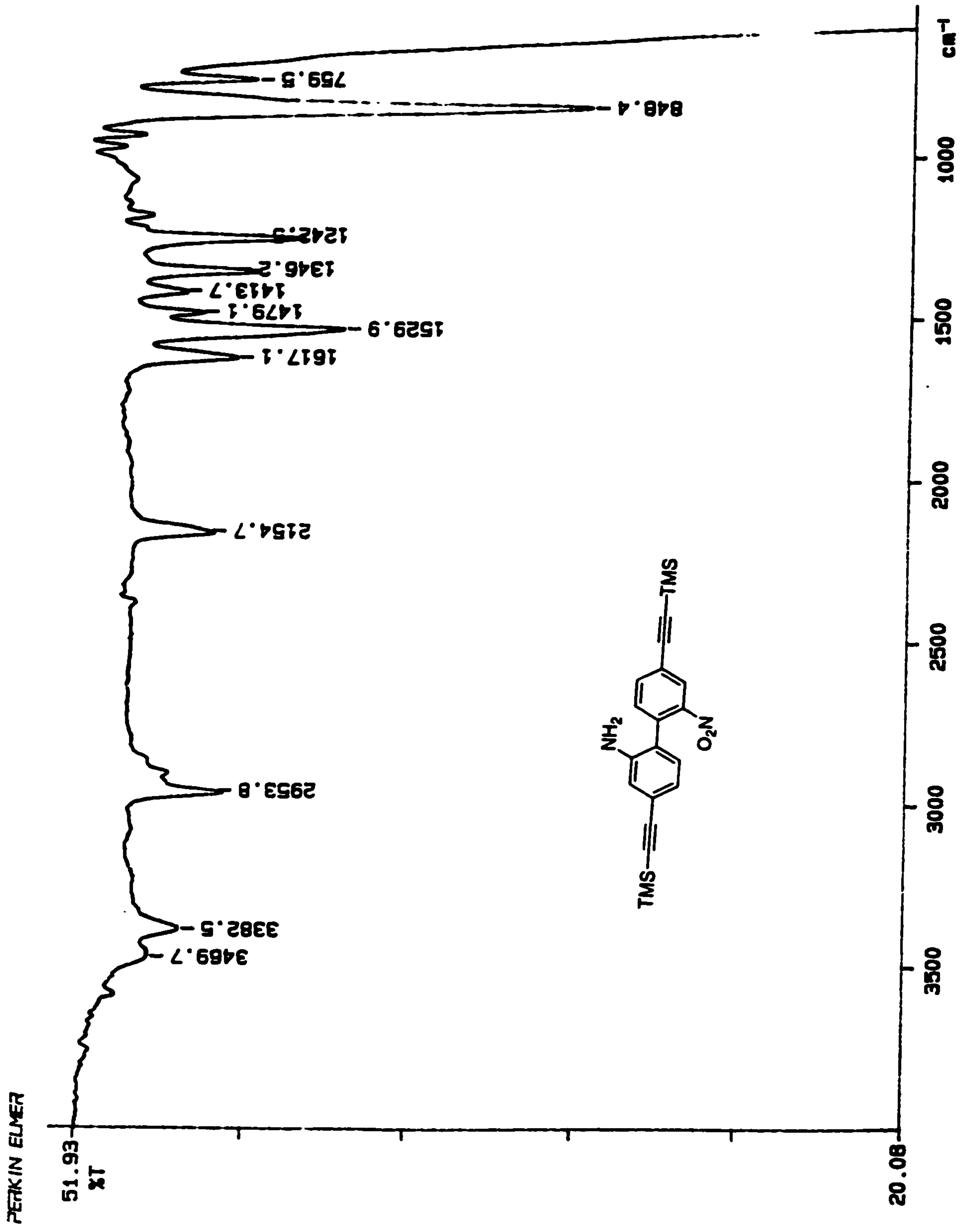

-0.306
-0.074
TMS
TMS
NO2
O2N
76.760
77.074
77.395
98.742
101.673
124.971
128.037
130.706
133.366
136.234
146.760
ppm
20
40
60
80
100
120
140
160
180
200

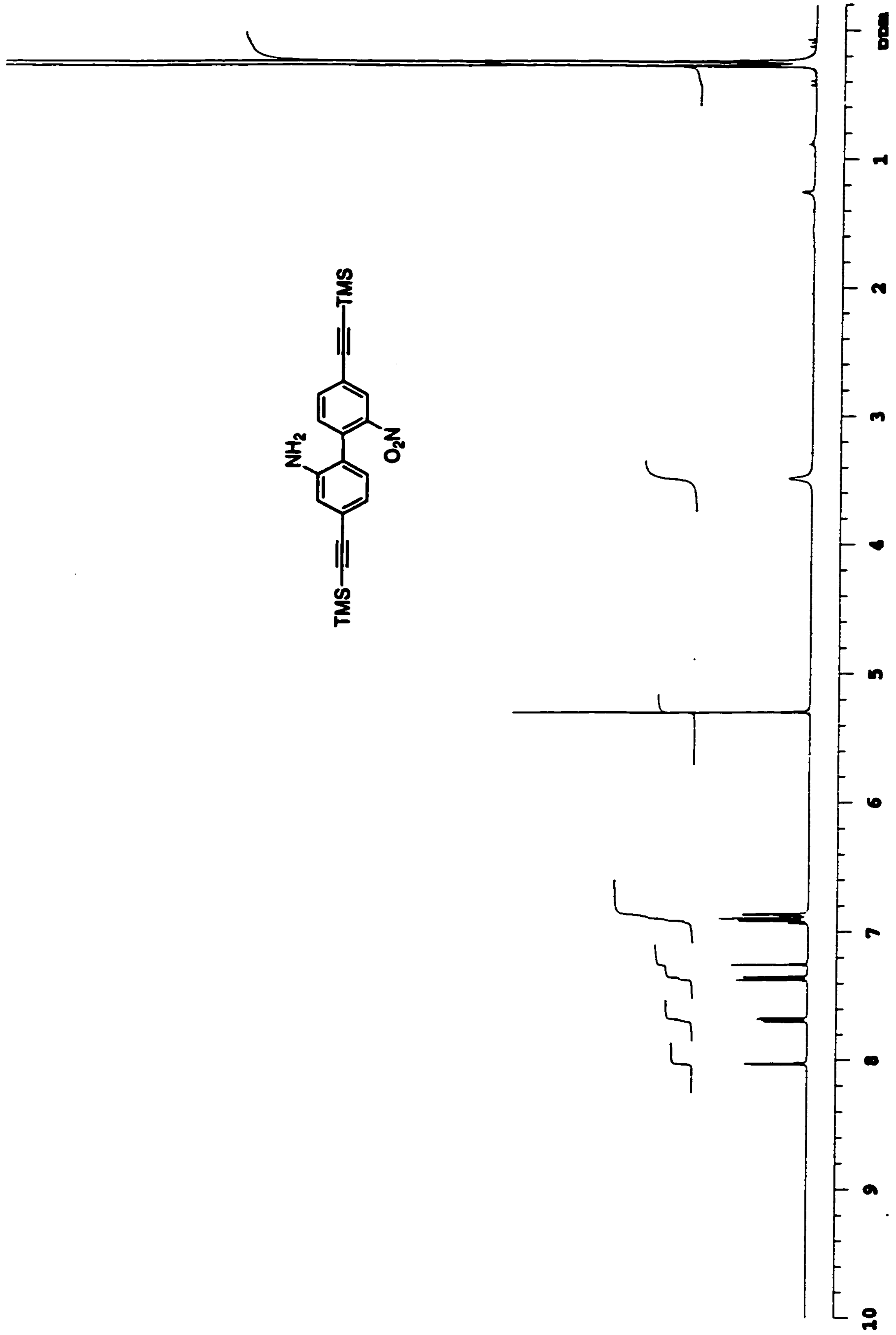


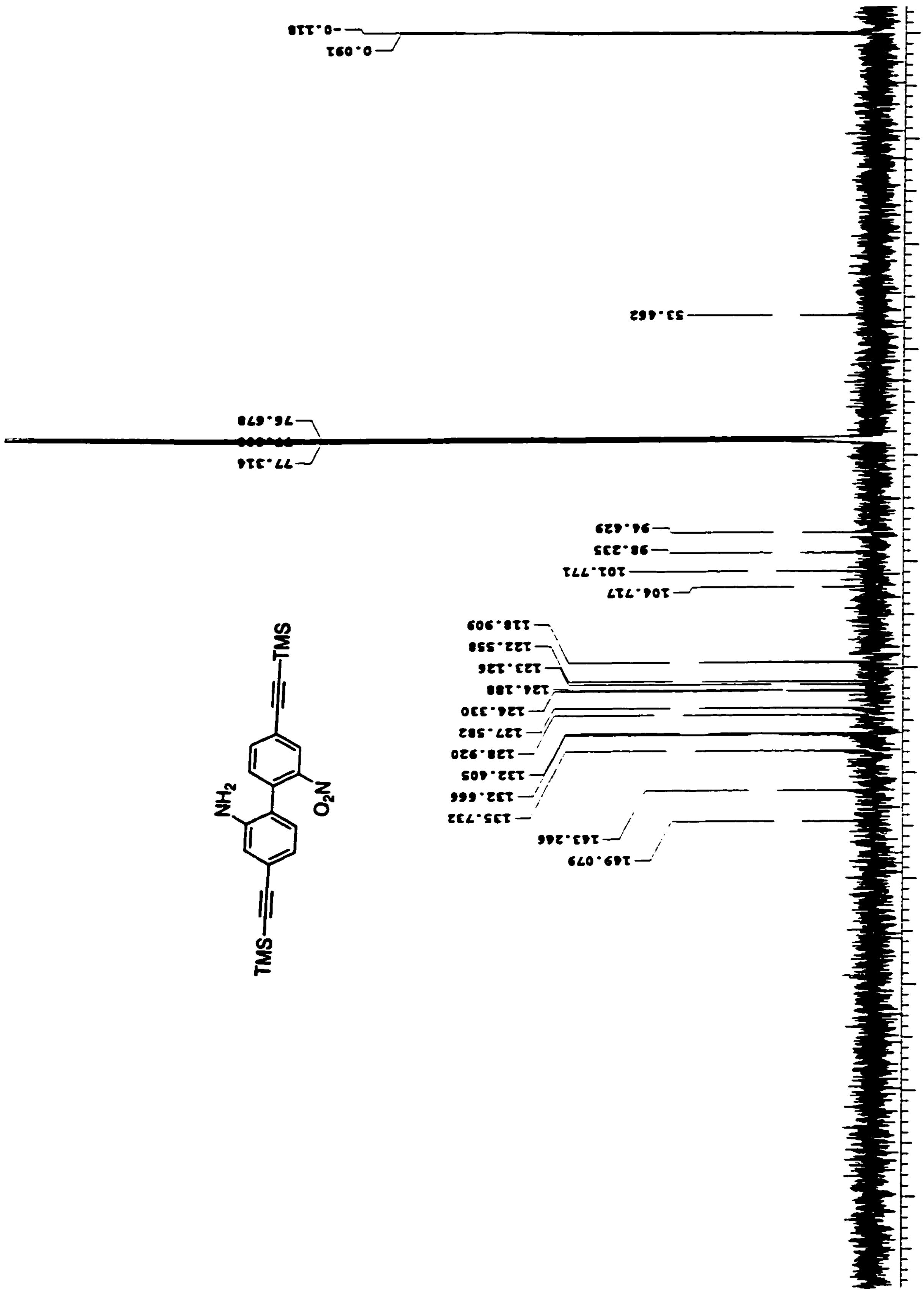
File:AMR125 Ident:34_38 Mer Def 0.25 Acq: 4-DEC-1998 01:40:20 +6:34 Cal:CAL1203B
70SQ EI+ Magnet BpM:421 BpI:46153728 TIC:484804640 Flags:HALL
File Text:scan 50-850

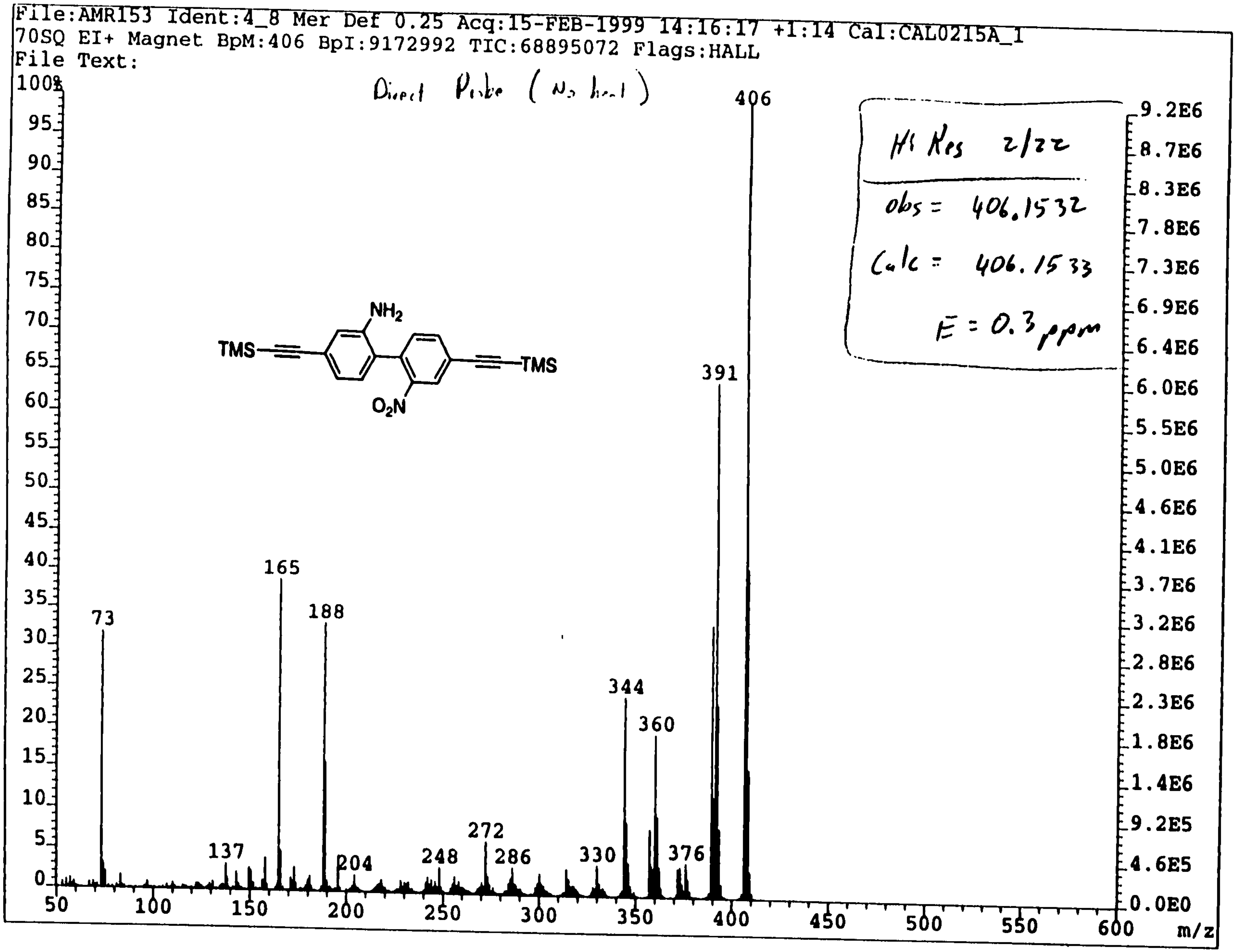
Heat to 140

Accurate Mass
12/11
observed mass = 436.1281
calc mass = 436.1275
$C_{22}H_{24}N_2O_4Si_2$
Error = 1.4ppm


PERKIN ELMER
51.93
%T
20.08
cm⁻¹
1000
1500
2000
2500
3000
3500
759.5
848.4
1242.5
1346.2
1413.7
1479.1
1529.9
1617.1
2154.7
2953.8
3382.5
3469.7
TMS
TMS
NH₂
O₂N


TMS
TMS
NH2
O2N
ppm
10
9
8
7
6
5
4
3
2
1


-0.118
0.091
53.462
76.678
77.000
77.314
94.629
98.235
101.771
104.717
118.909
122.558
123.126
124.188
124.330
127.582
128.920
132.405
132.666
135.732
143.246
149.079
ppm
20
40
60
80
100
120
140
160
180
200
220
TMS
TMS
NH_2
O_2N



```
File:AMR153 Ident:4_8 Mer Def 0.25 Acq:15-FEB-1999 14:16:17 +1:14 Cal:CAL0215A_1
70SQ EI+ Magnet BpM:406 BpI:9172992 TIC:68895072 Flags:HALL
File Text:
```

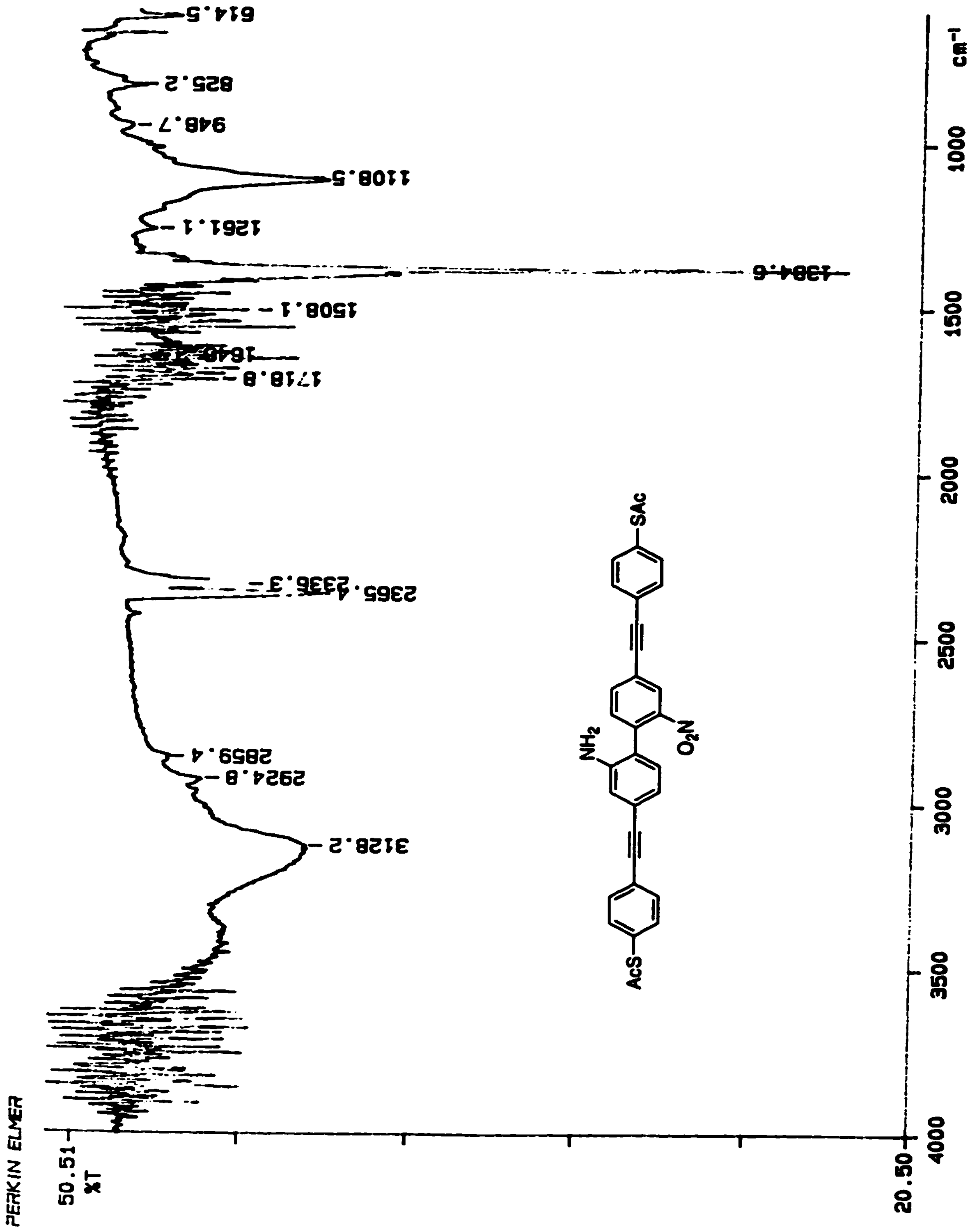
Direct Probe (No heat)

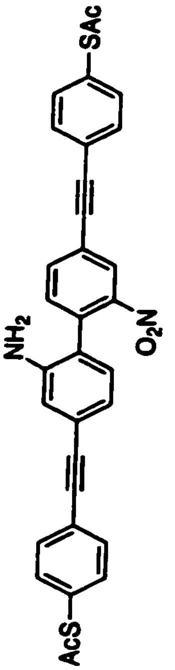
Hi Res 2/22

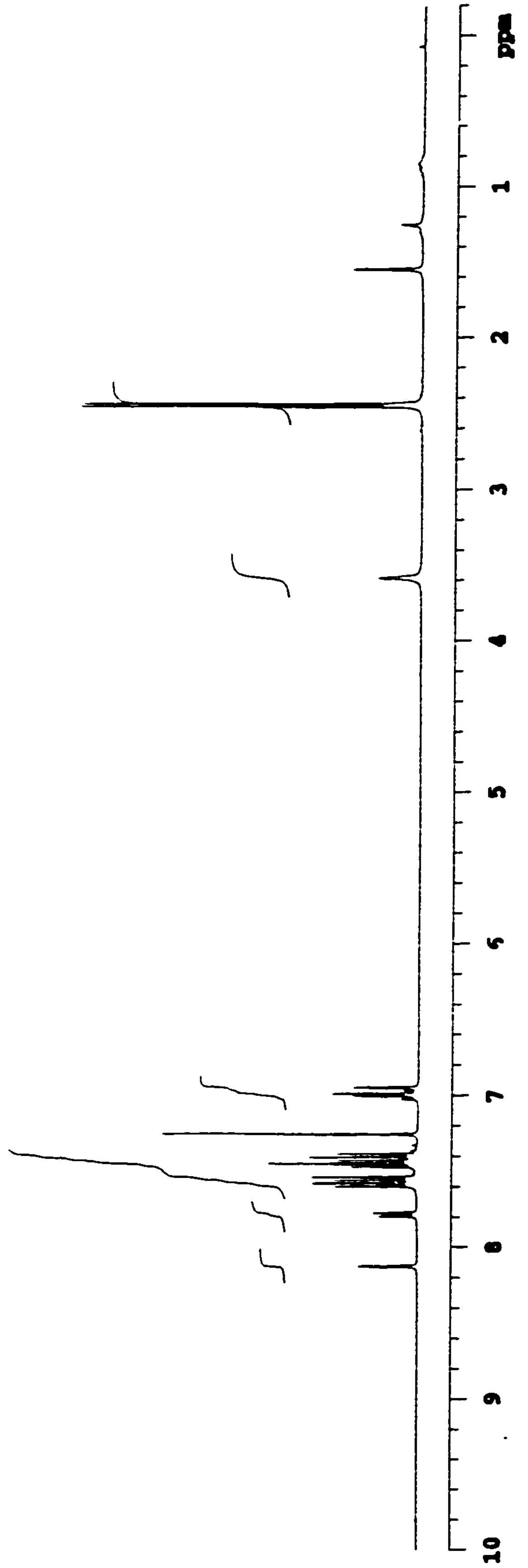
obs = 406.1532

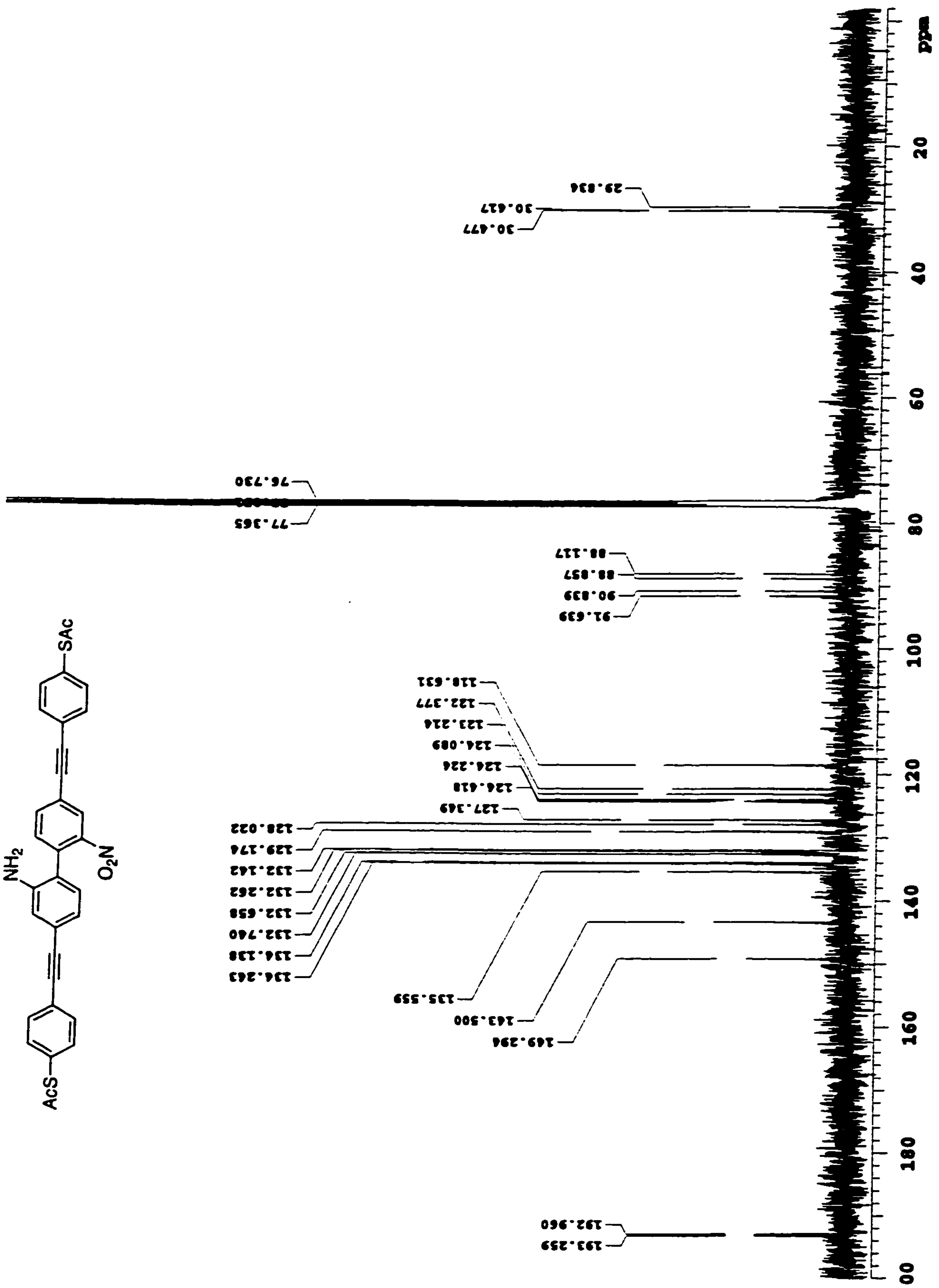
Calc = 406.1533

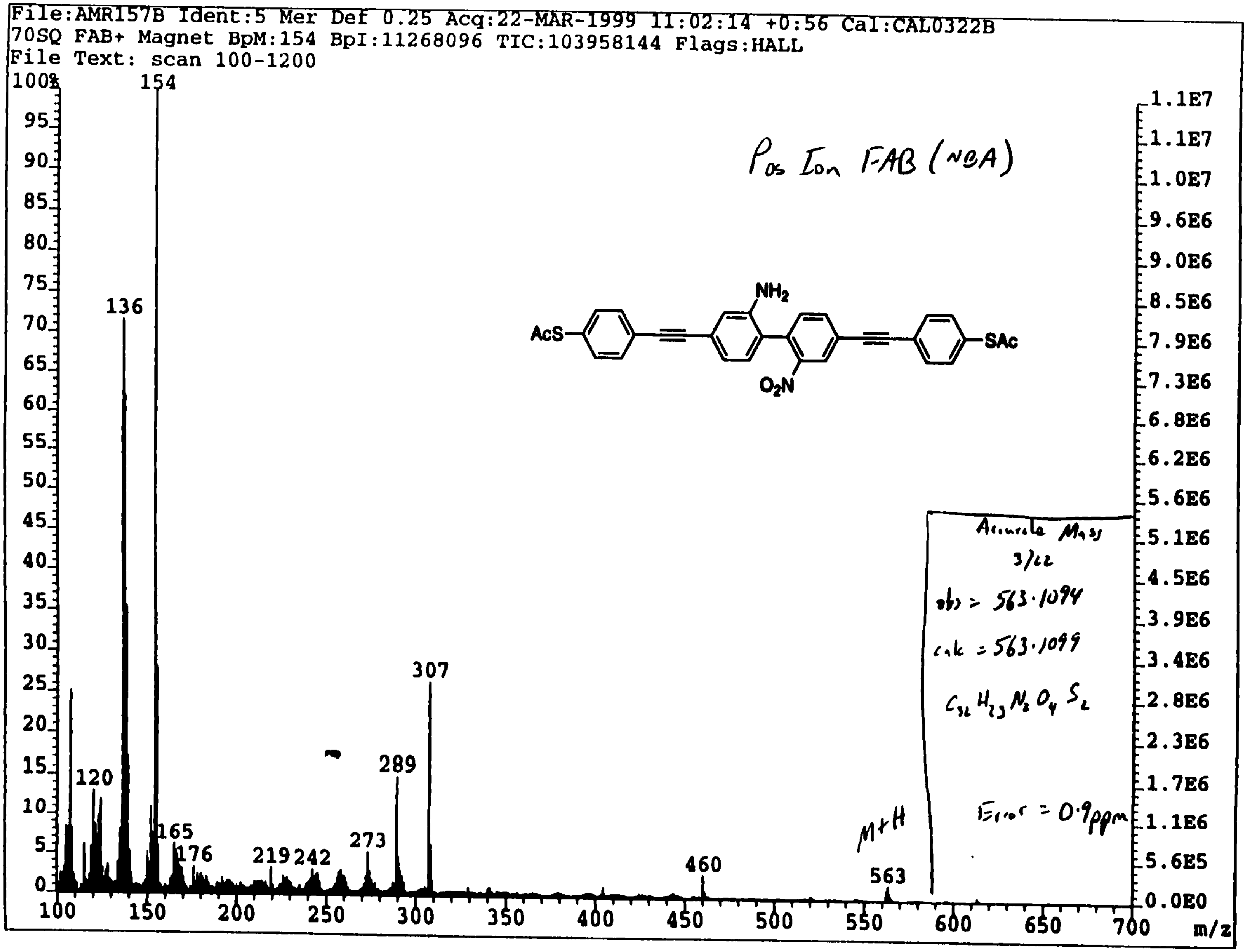
E = 0.3 ppm


PERKIN ELMER
50.51
%T
20.50
4000
3500
3000
2500
2000
1500
1000
cm-1
3128.2
2924.8
2859.4
2365.4
2336.3
1718.8
1640
1508.1
1384.6
1261.1
1108.5
948.7
825.2
614.5
AcS
NH2
O2N
SAc


SAc
NH2
O2N
AcS


ppm
1
2
3
4
5
6
7
8
9
10


SAc
NH$_2$
O$_2$N
AcS
29.834
30.417
30.477
76.730
77.365
88.117
88.857
90.839
91.639
118.631
122.377
123.214
124.089
124.224
124.418
127.349
128.032
129.174
132.142
132.262
132.658
132.740
134.138
134.263
135.559
143.500
149.294
192.960
193.259
ppm
20
40
60
80
100
120
140
160
180
00



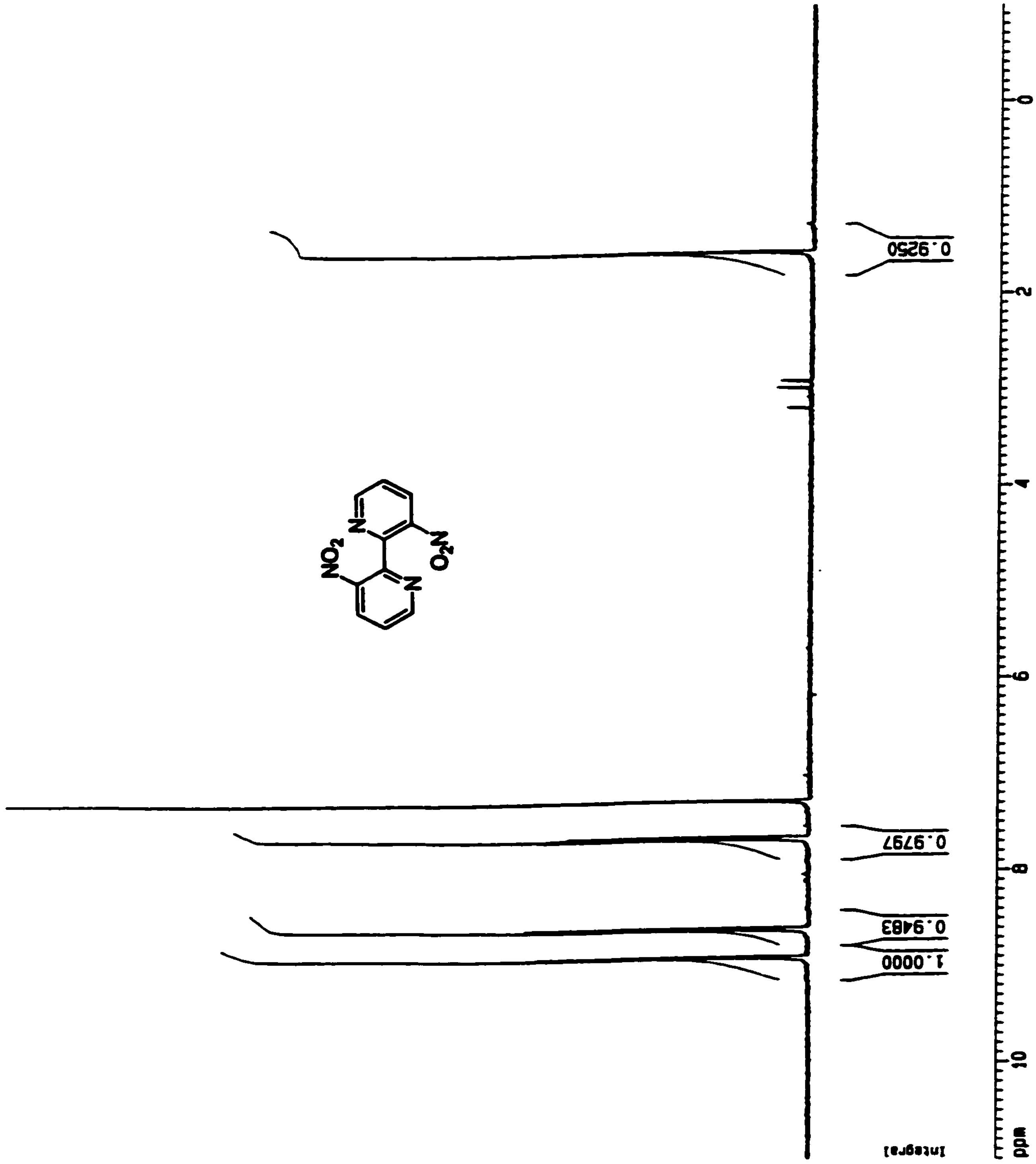
File:AMR157B Ident:5 Mer Def 0.25 Acq:22-MAR-1999 11:02:14 +0:56 Cal:CAL0322B
70SQ FAB+ Magnet BpM:154 BpI:11268096 TIC:103958144 Flags:HALL
File Text: scan 100-1200

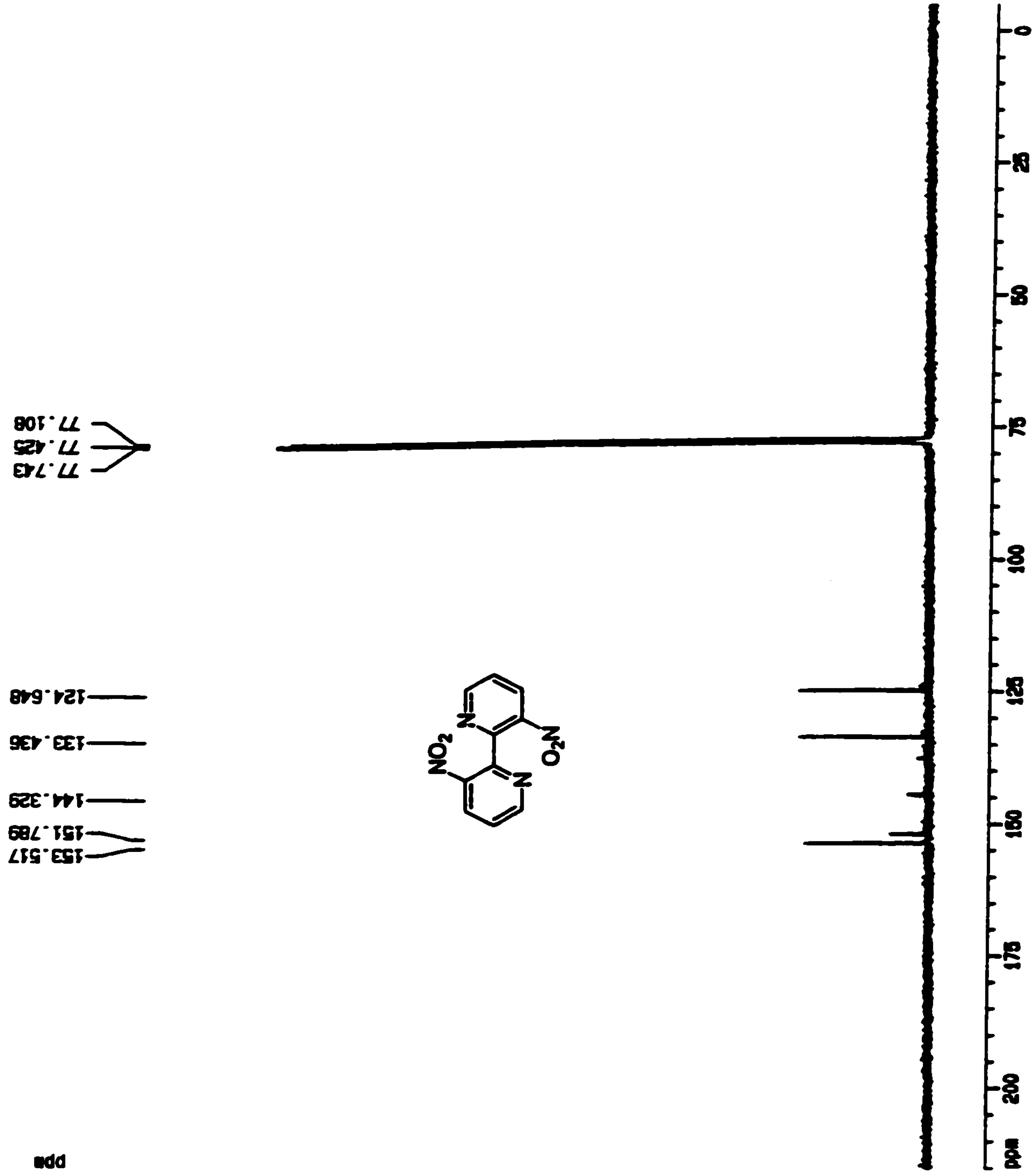
Pos Ion FAB (NBA)

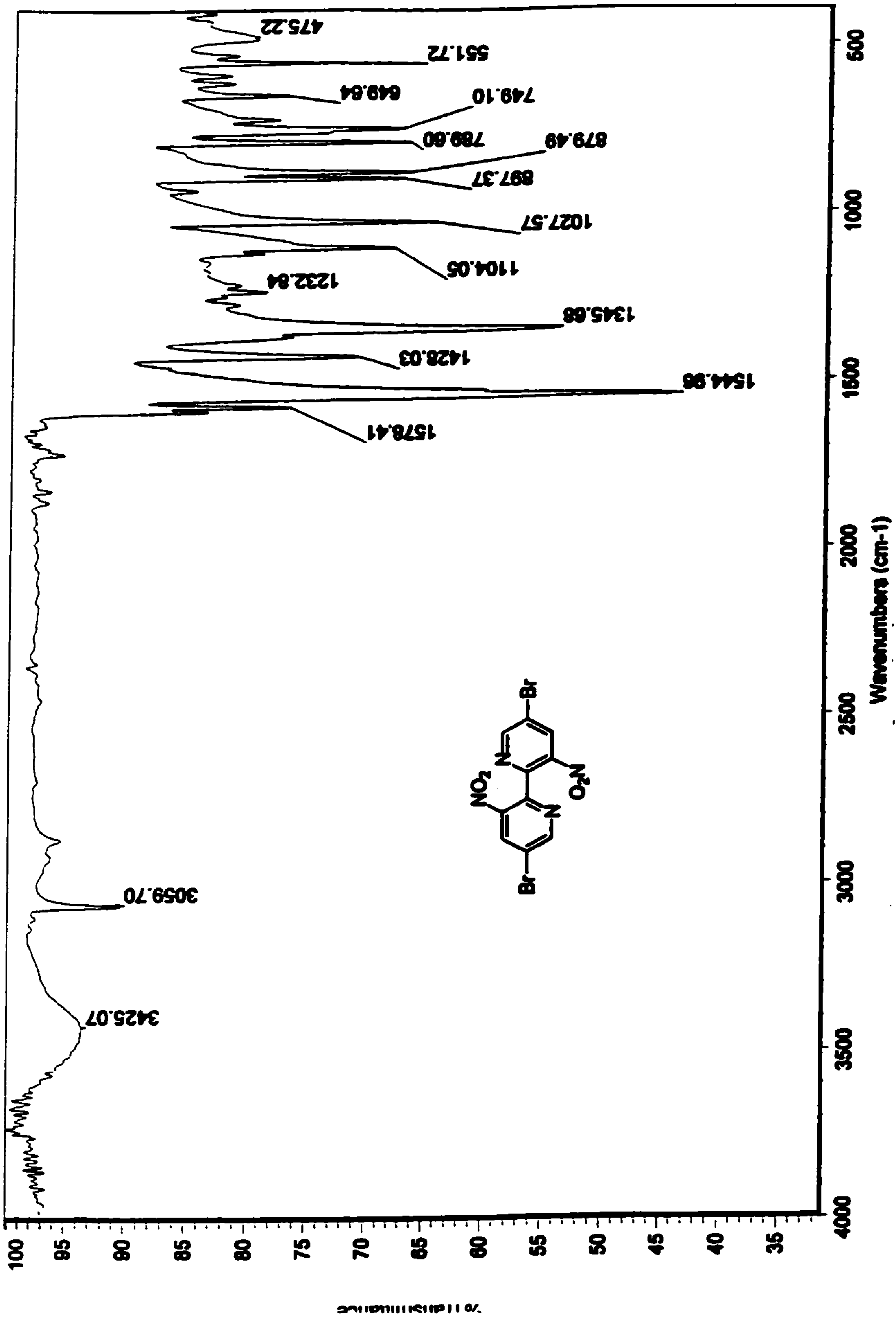
Accurate Mass
3/22
obs = 563.1094
calc = 563.1099
$C_{32}H_{23}N_2O_4S_2$

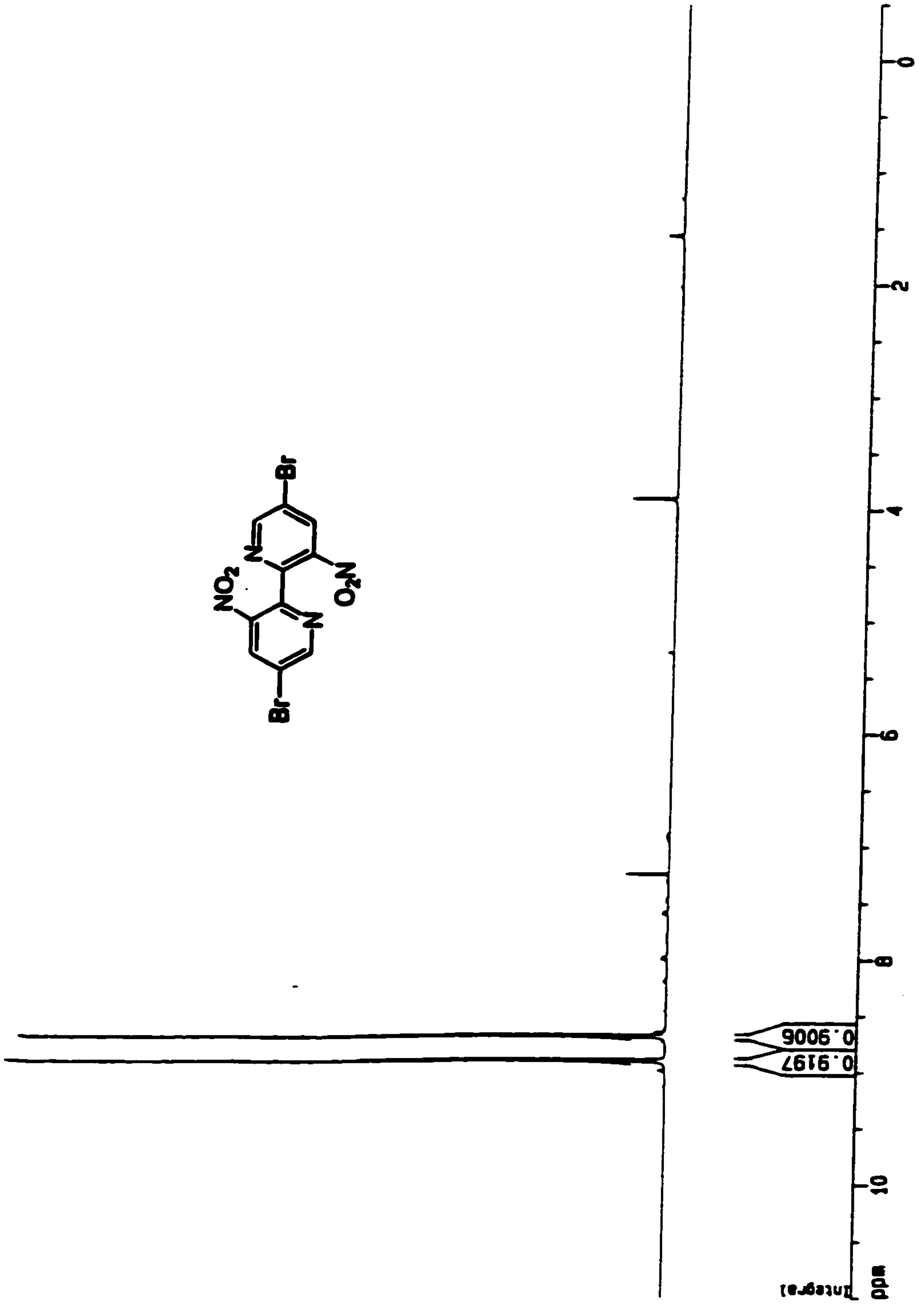
Error = 0.9ppm

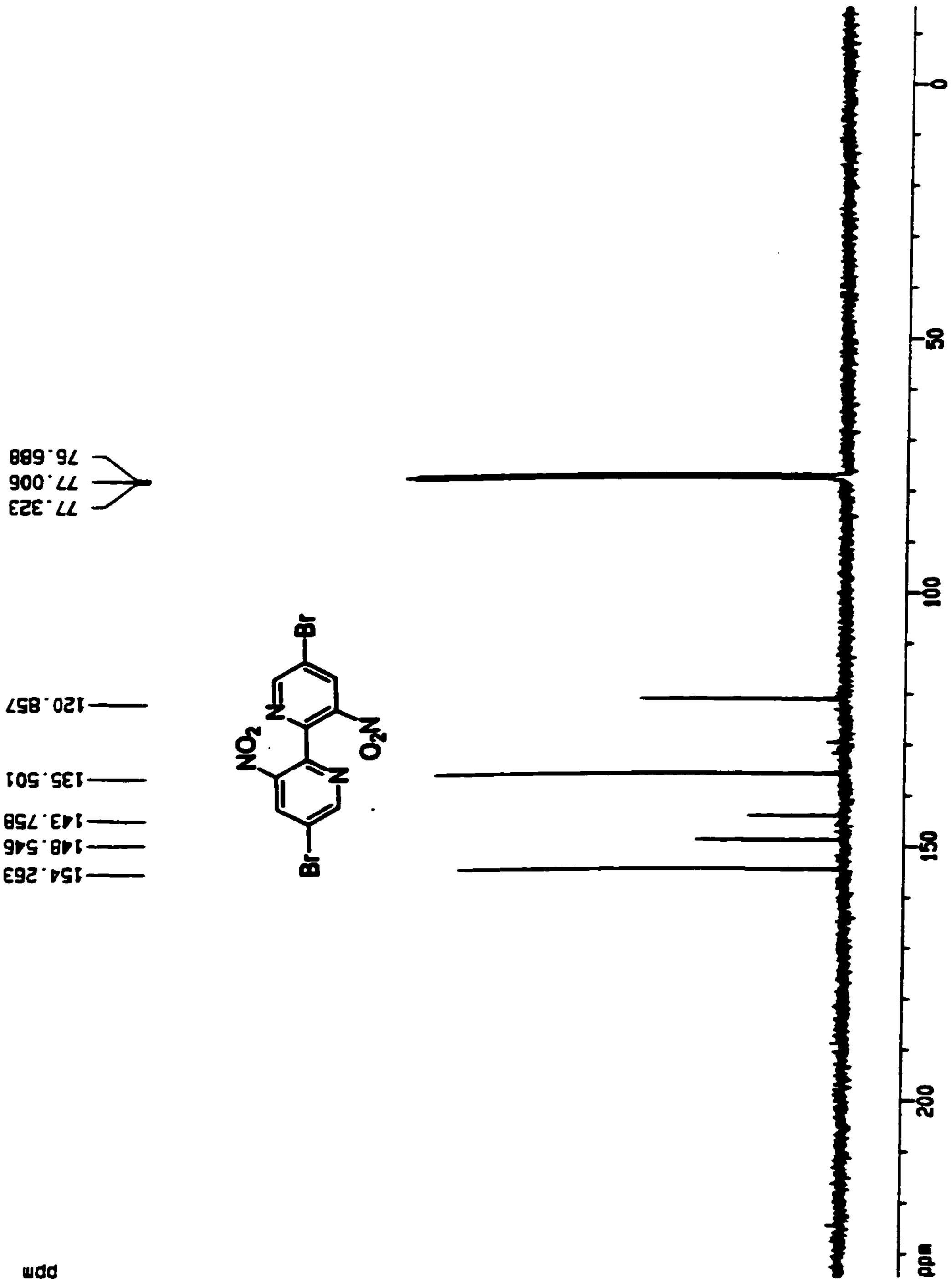
M+H

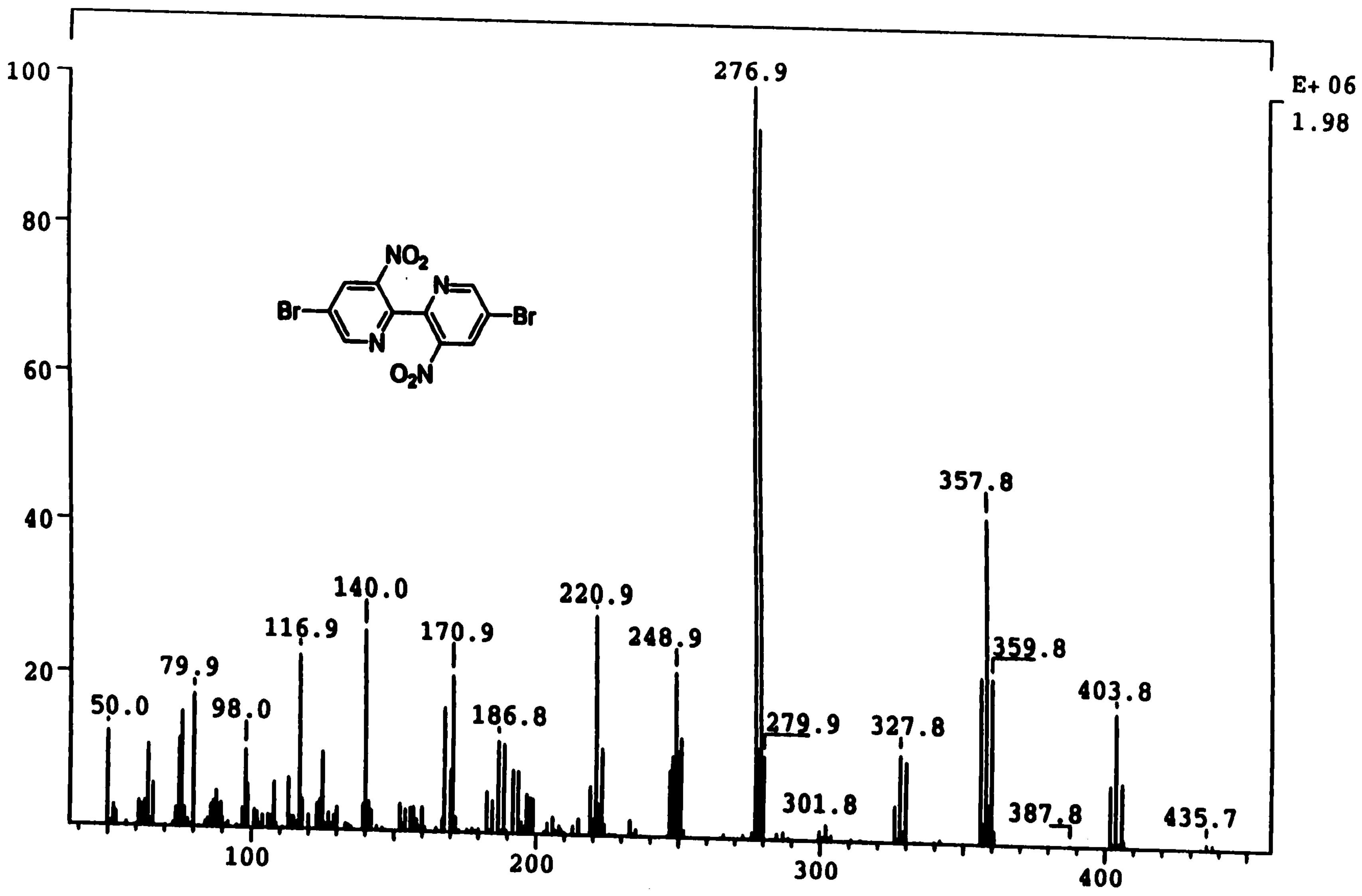

NO2
O2N
N
N
0.9250
0.9797
0.9483
1.0000
Integral
ppm
0
2
4
6
8
10

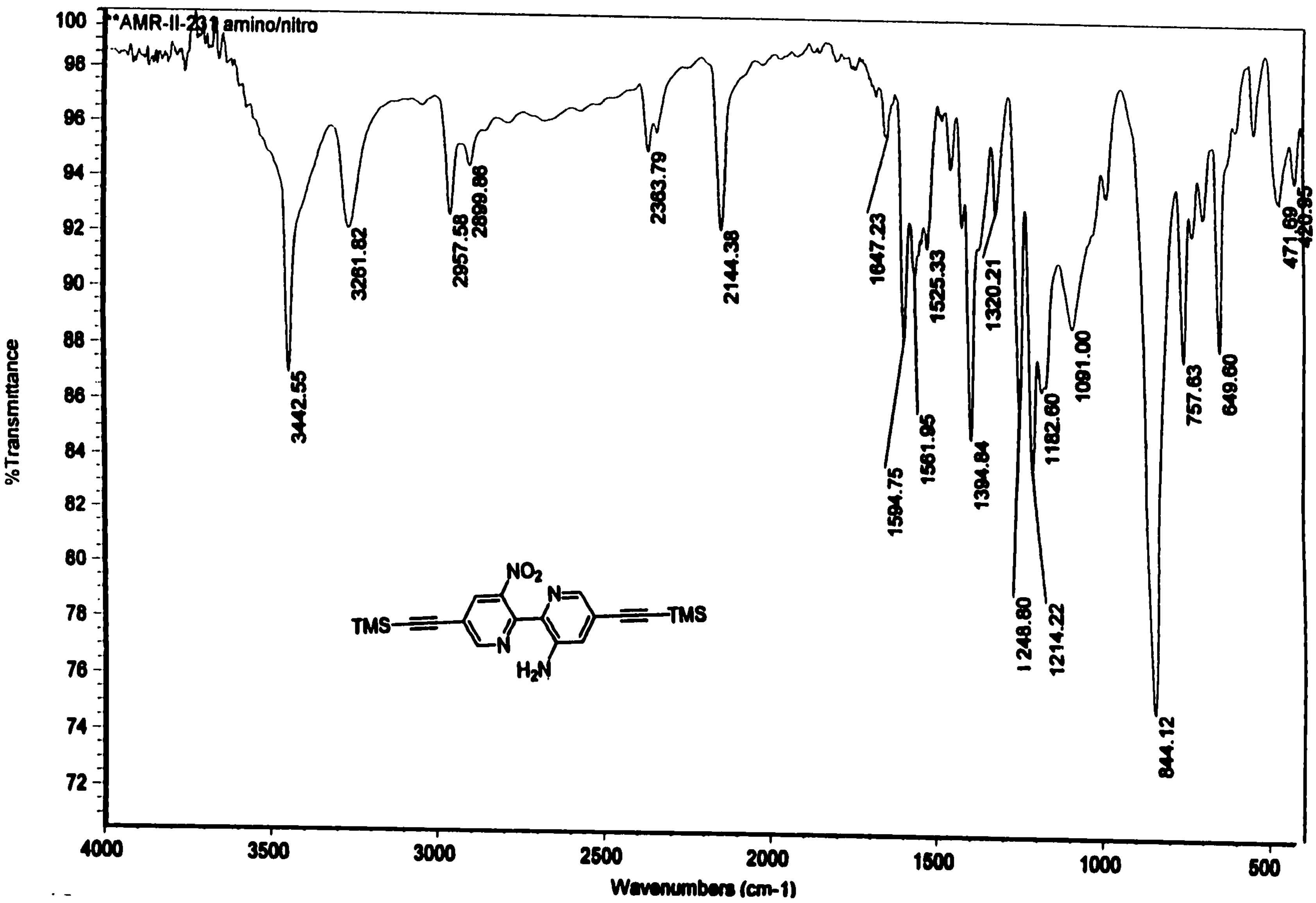

77.108
77.425
77.743
124.648
133.436
144.329
151.789
153.517
ppm
NO_2
O_2N
N
N
0
25
50
75
100
125
150
175
200
ppm

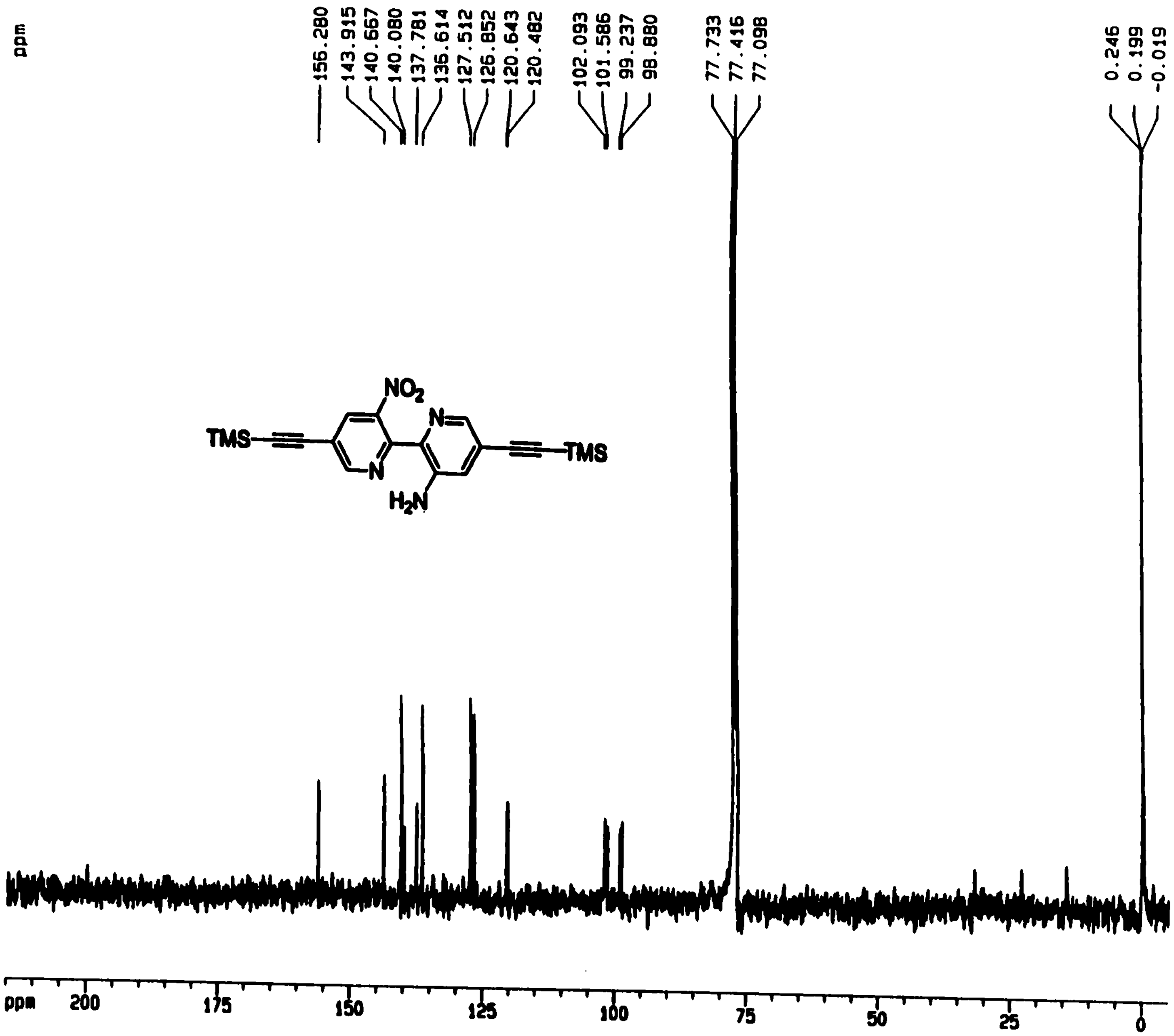

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
3425.07
3059.70
1578.41
1544.96
1428.03
1345.68
1232.84
1104.05
1027.57
897.37
879.49
789.60
749.10
649.64
551.72
475.22
Br
NO$_2$
N
N
O$_2$N
Br

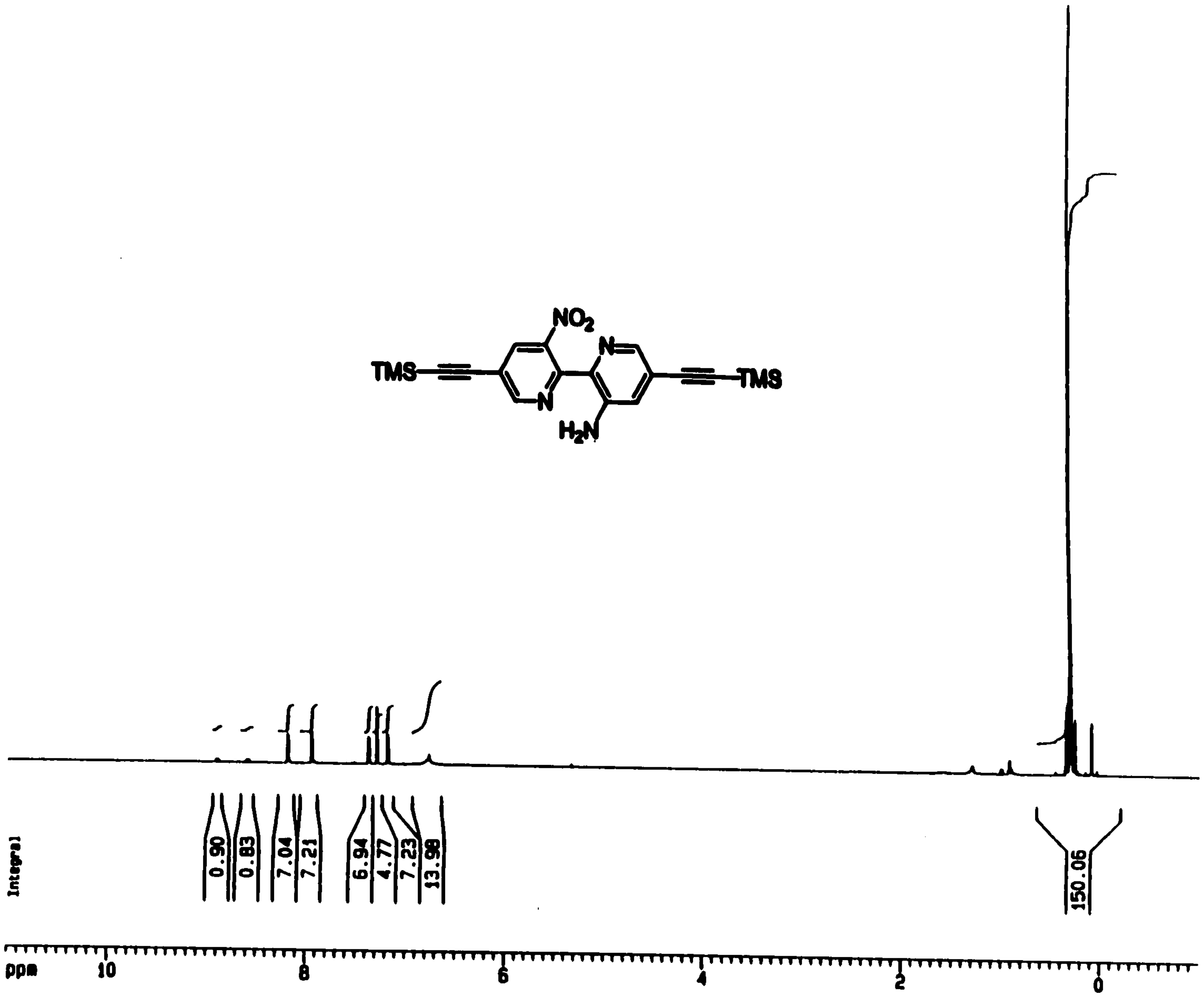

Br
Br
NO2
O2N
N
N
0.9006
0.9197
Integral
ppm
0
2
4
6
8
10

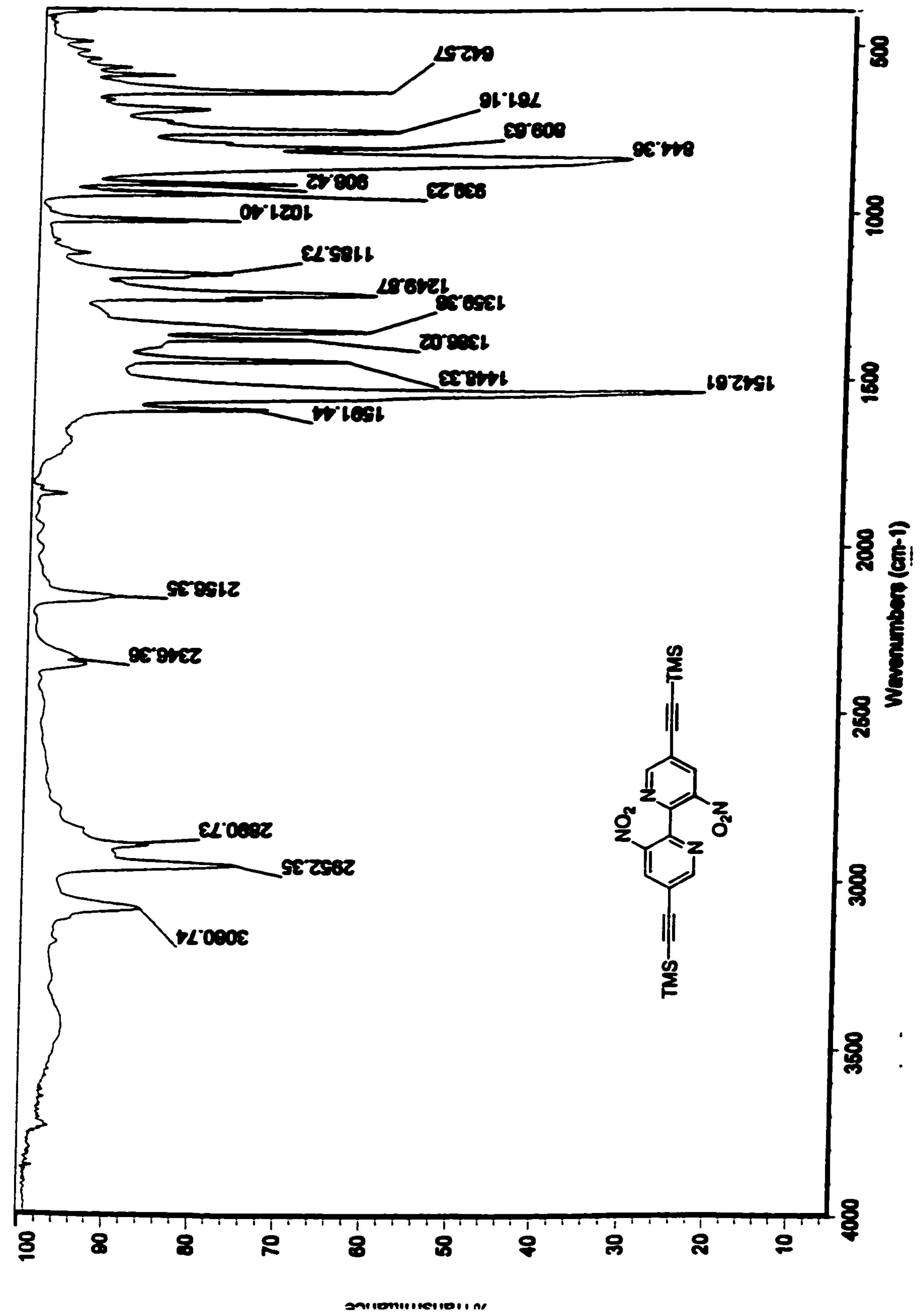

76.688
77.006
77.323
120.857
135.501
143.758
148.546
154.263
ppm
Br
NO2
O2N
N
N
Br
0
50
100
150
200
ppm

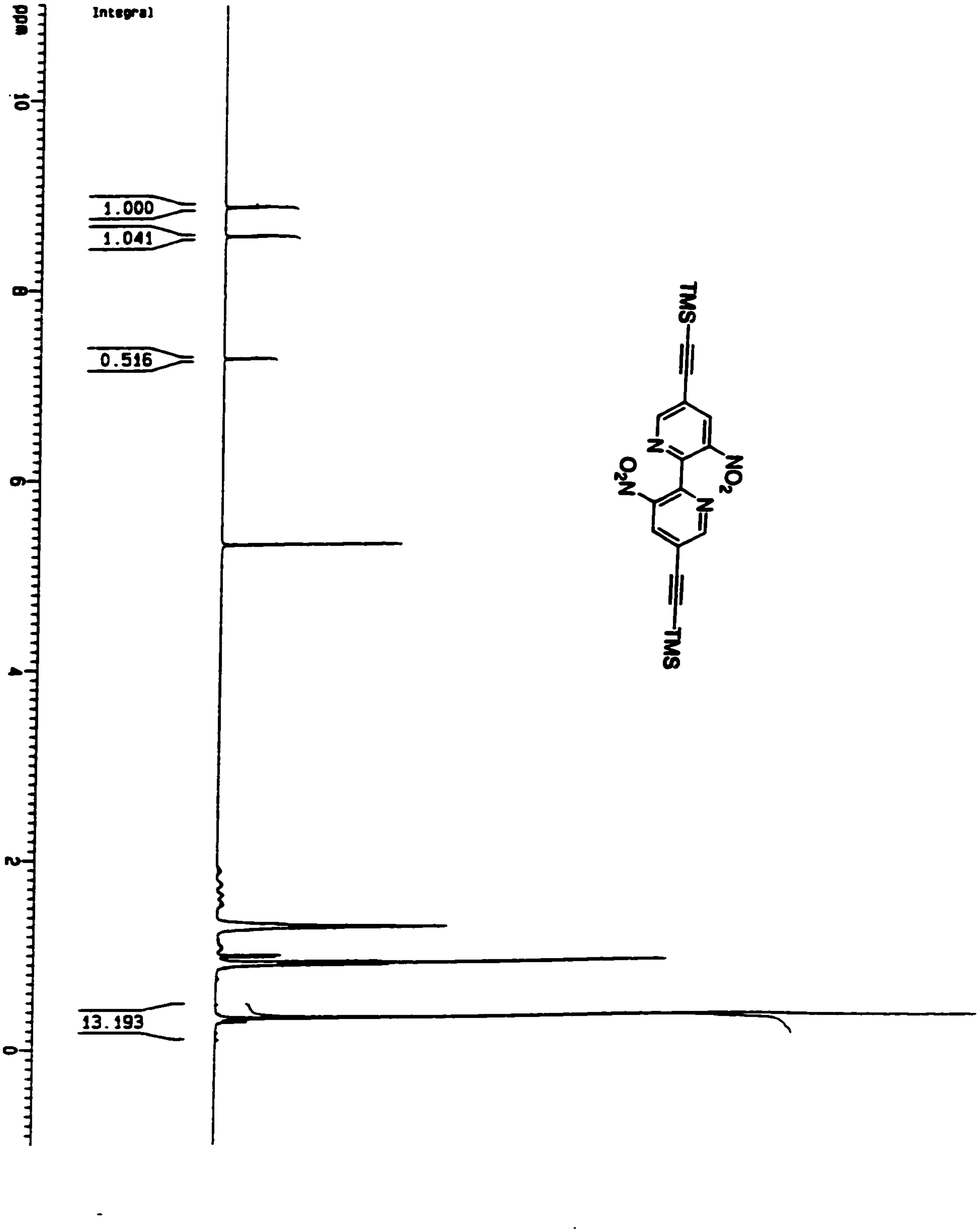

E+ 06
1.98
100
80
60
40
20
50.0
79.9
98.0
116.9
140.0
170.9
186.8
220.9
248.9
276.9
279.9
301.8
327.8
357.8
359.8
387.8
403.8
435.7
100
200
300
400
NO2
Br
N
N
Br
O2N

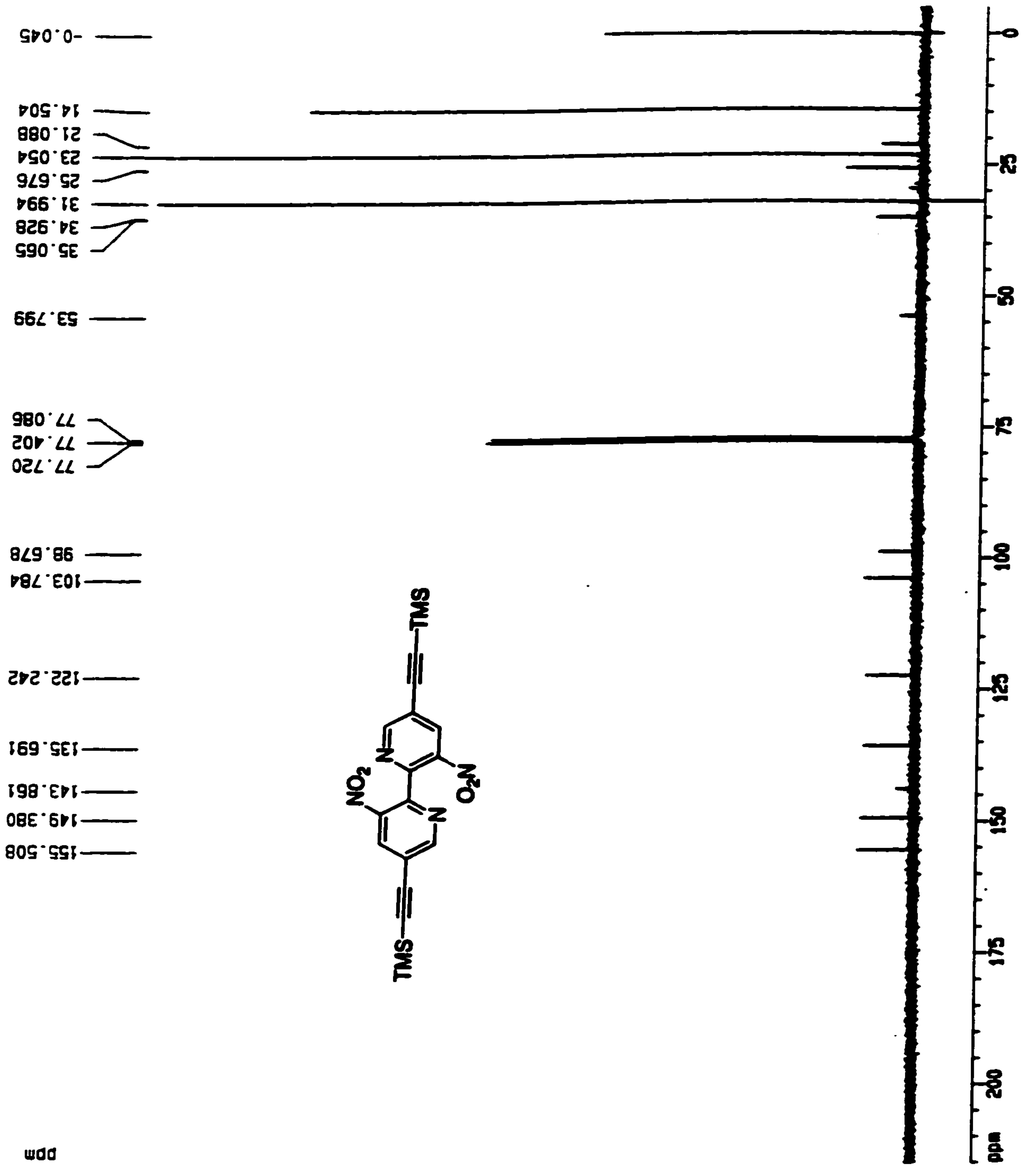

*AMR-II-231 amino/nitro
%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3442.55
3261.82
2957.58
2899.86
2363.79
2144.38
1647.23
1594.75
1561.95
1525.33
1394.84
1320.21
1248.80
1214.22
1182.60
1091.00
844.12
757.63
649.60
471.69
420.95
NO2
TMS
TMS
N
N
H2N

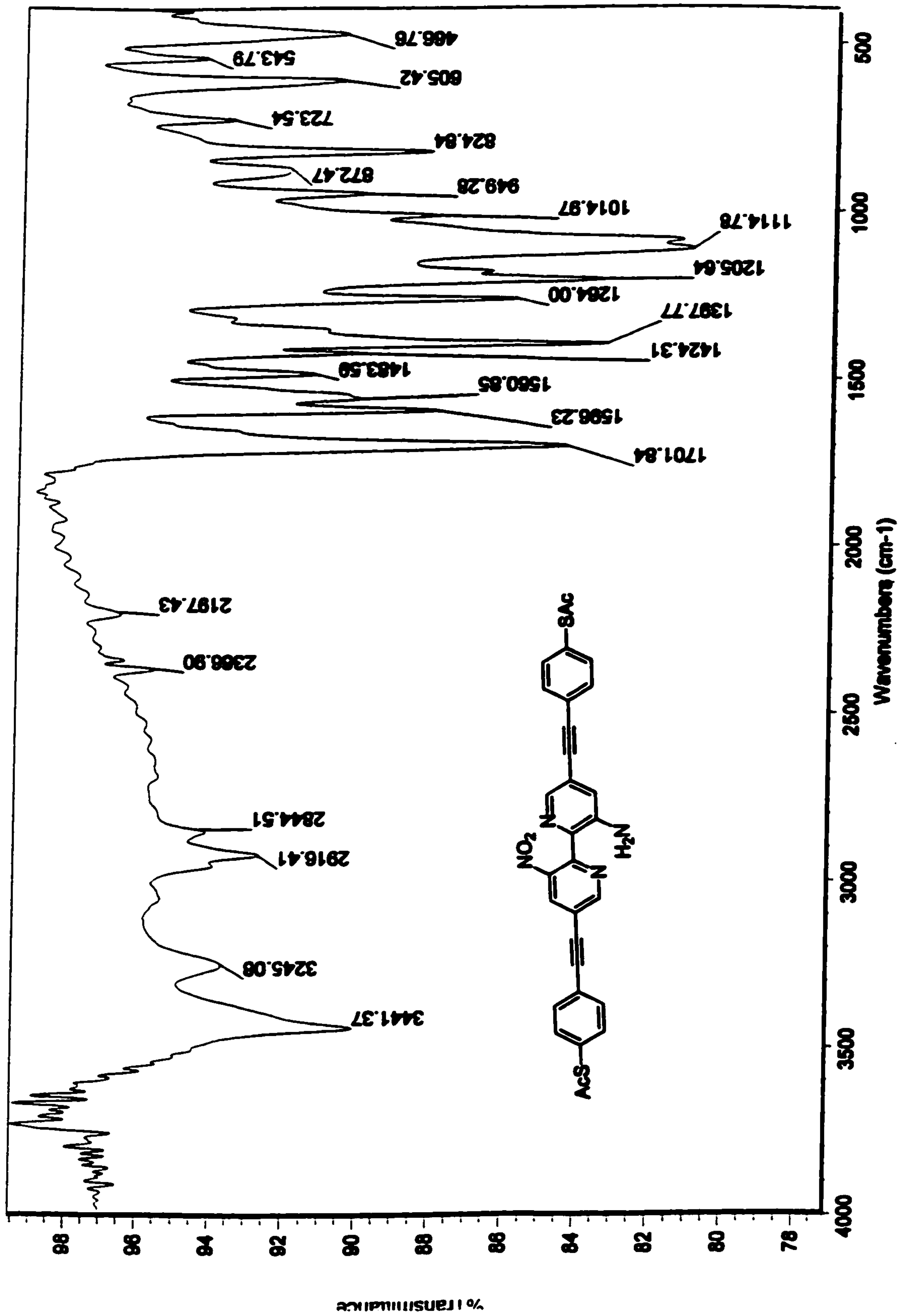

ppm
156.280
143.915
140.667
140.080
137.781
136.614
127.512
126.852
120.643
120.482
102.093
101.586
99.237
98.880
77.733
77.416
77.098
0.246
0.199
-0.019
NO2
N
N
TMS
TMS
H2N
ppm
200
175
150
125
100
75
50
25
0

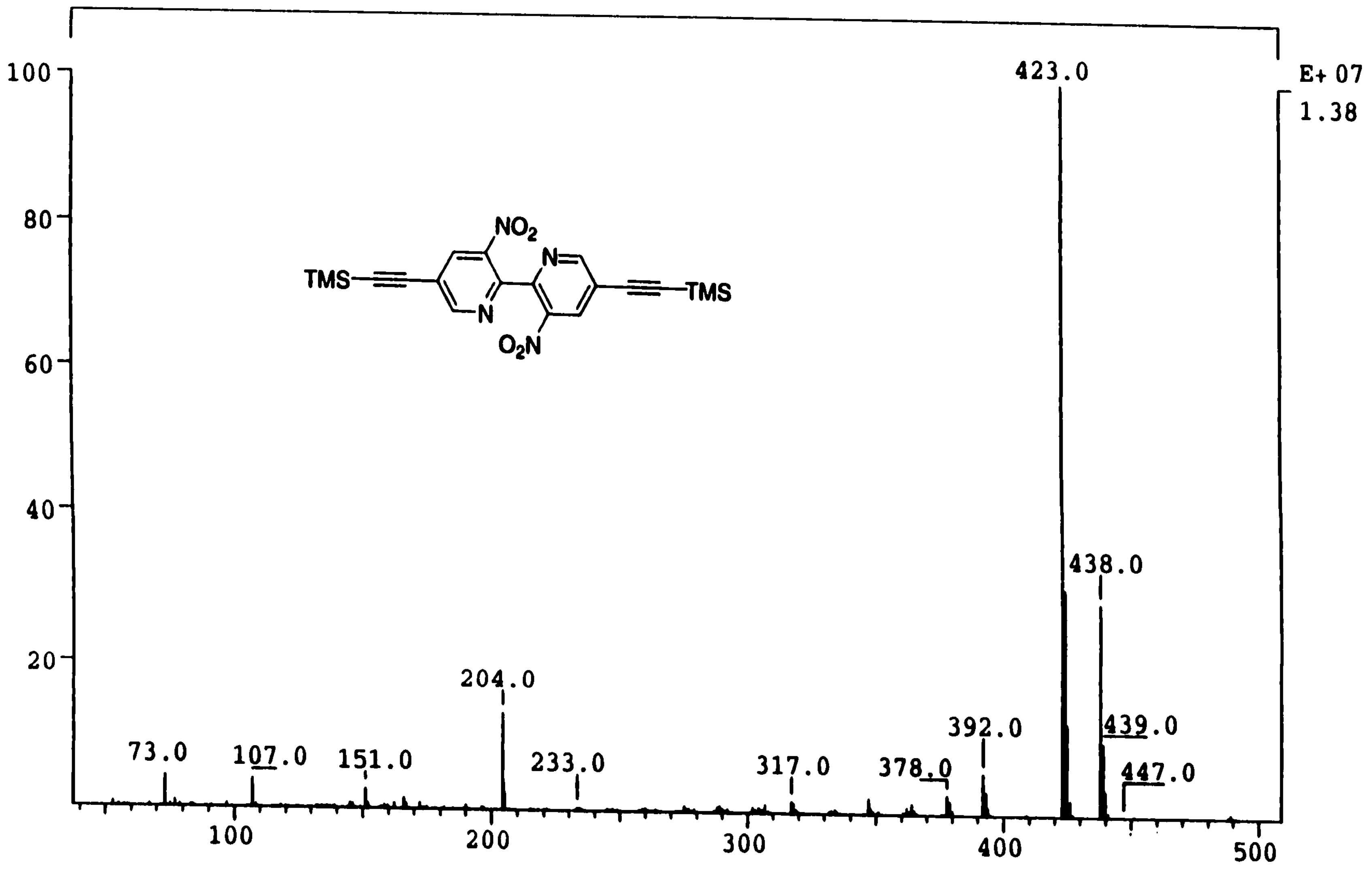

TMS
NO$_2$
N
N
H$_2$N
TMS
Integral
0.90
0.83
7.04
7.21
6.94
4.77
7.23
13.98
150.06
ppm
10
8
6
4
2
0

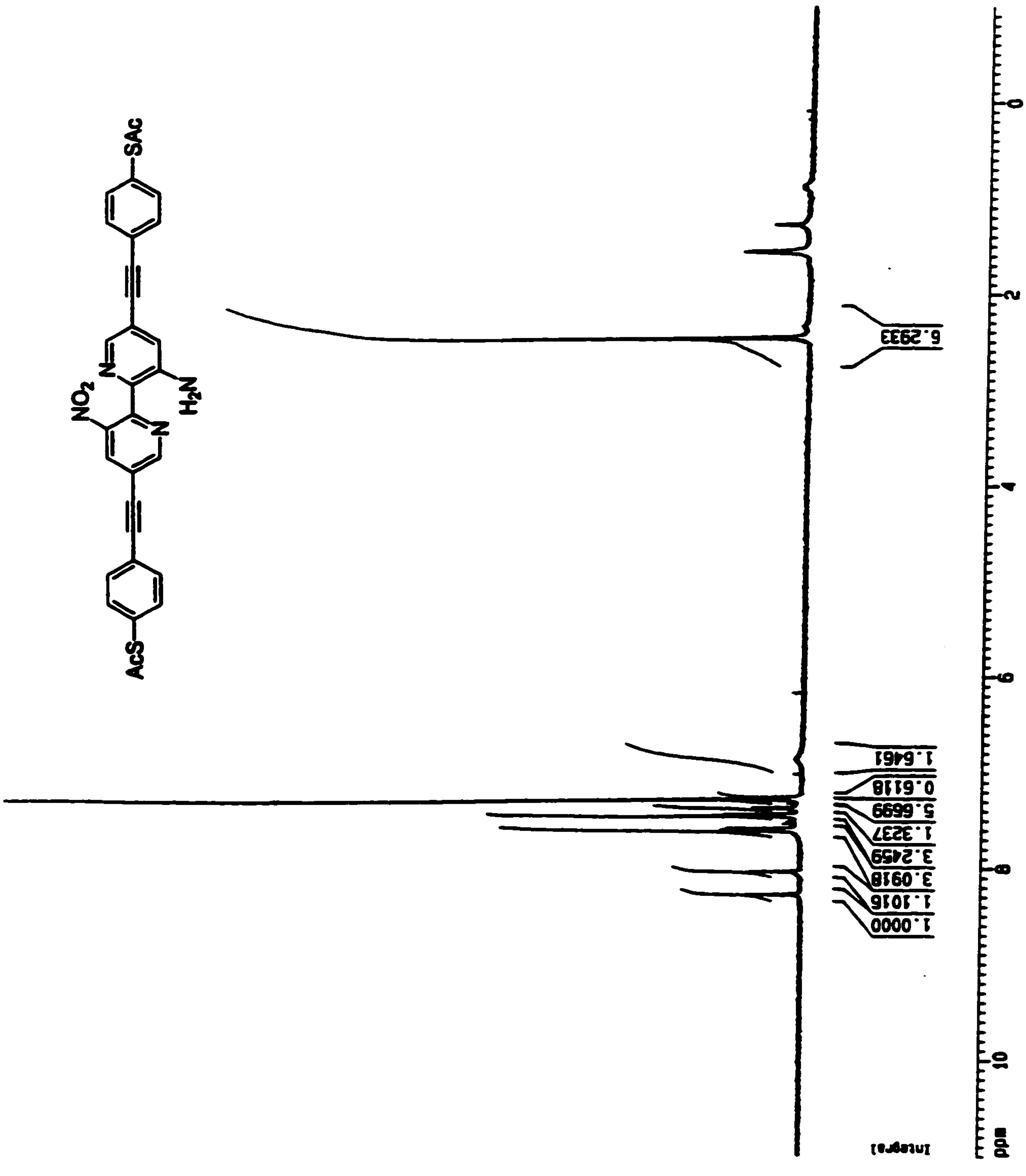

642.57
761.16
809.63
844.36
908.42
939.23
1021.40
1185.73
1249.87
1359.36
1386.02
1448.33
1542.61
1591.44
2156.35
2346.36
2880.73
2952.35
3080.74
TMS
NO_2
O_2N
N
N
TMS
500
1000
1500
2000
2500
3000
3500
4000
Wavenumbers (cm-1)
100
90
80
70
60
50
40
30
20
10
%Transmittance

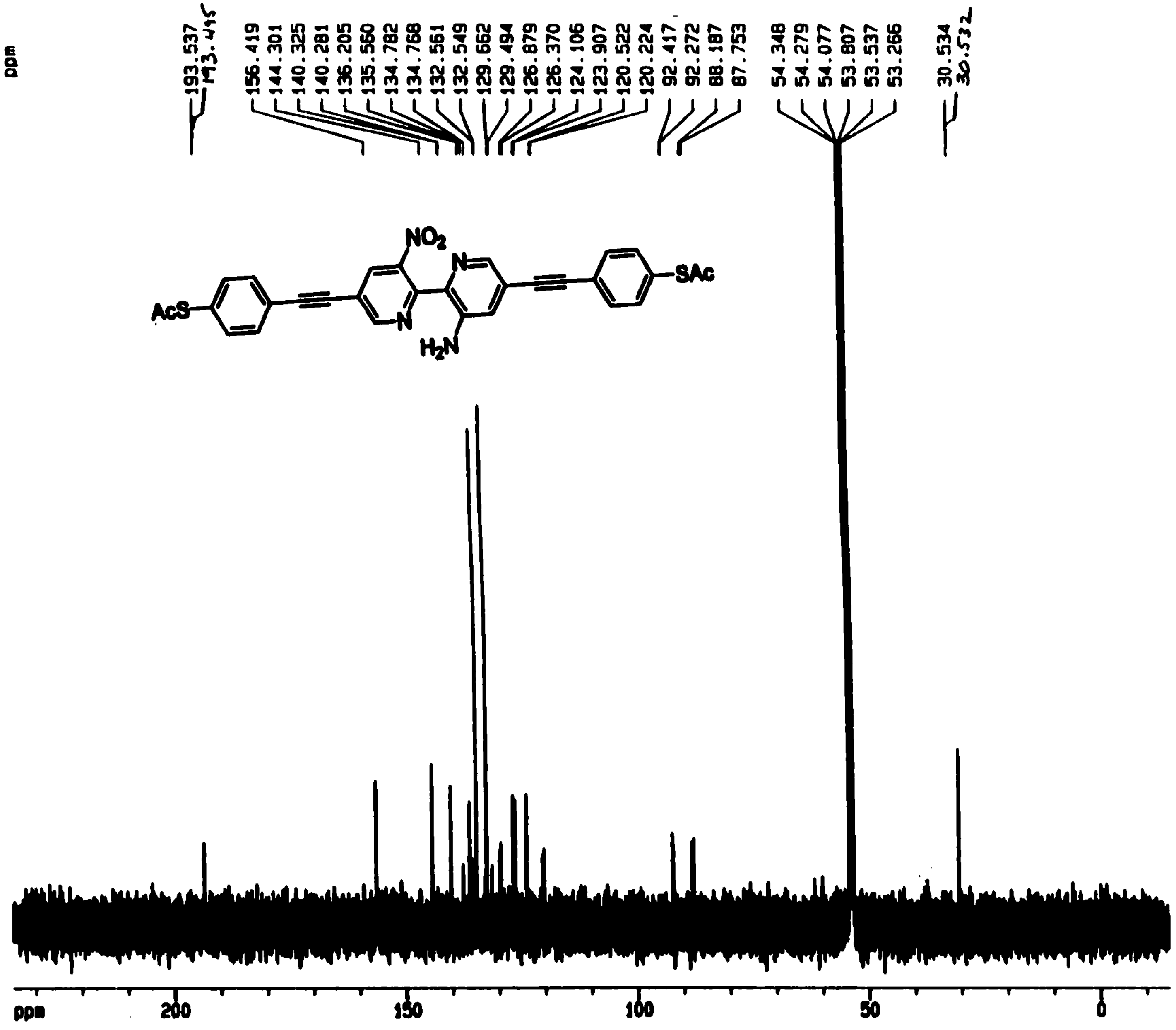

ppm
Integral
1.000
1.041
0.516
13.193
10
8
6
4
2
0
TMS
TMS
NO$_2$
O$_2$N
N
N


-0.045
14.504
21.088
23.054
25.676
31.994
34.928
35.065
53.799
77.086
77.402
77.720
98.678
103.784
122.242
135.691
143.861
149.380
155.508
ppm
TMS
TMS
NO2
O2N
N
N
0
25
50
75
100
125
150
175
200
ppm


3441.37
3245.08
2916.41
2844.51
2366.90
2197.43
1701.84
1596.23
1560.85
1483.59
1424.31
1397.77
1284.00
1205.64
1114.78
1014.97
949.28
872.47
824.84
723.54
605.42
543.79
466.76
AcS
NO2
H2N
N
N
SAc
% Transmittance
98
96
94
92
90
88
86
84
82
80
78
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500


100
80
60
40
20
E+ 07
1.38
423.0
438.0
439.0
447.0
392.0
378.0
317.0
233.0
204.0
151.0
107.0
73.0
100
200
300
400
500
TMS
TMS
NO2
O2N
N
N


AcS
SAc
NO$_2$
H$_2$N
N
N
6.2933
1.6461
0.6118
5.6699
1.3237
3.2459
3.0918
1.1016
1.0000
Integral
0
2
4
6
8
10
ppm


193.537
193.495
156.419
144.301
140.325
140.281
136.205
135.560
134.782
134.768
132.561
132.549
129.662
129.494
126.879
126.370
124.106
123.907
120.522
120.224
92.417
92.272
88.187
87.753
54.348
54.279
54.077
53.807
53.537
53.266
30.534
30.532
ppm
NO2
N
SAc
AcS
N
H2N
ppm
200
150
100
50
0

Chapter 2

Preparative Bench-top Enrichment of C_{60}, C_{70}, and the Higher Fullerene Allotropes Using a Brominated Polystyrene Stationary Phase

In 1985, Kroto *et al.*[1] discovered a third allotrope of carbon named buckminsterfullerene. It consists of 60 carbon atoms and is spherical, hollow and geodesic sphere shaped, the shape of a "soccer ball". Since that time, there have been discoveries of other related fullerenes, C_{70}, C_{76}, C_{78}, C_{84}, and higher. These higher fullerenes have similar properties but differ from C_{60} in reduction potentials,[2] magnetic susceptibility,[3-7] and possibly aromaticity. [3,6-7]

Buckminsterfullerene and higher fullerenes are easily made by a carbon arc method,[8] however purification of crude fullerenes remains difficult. The slight differences in molecular weight and solubility make them difficult to purify. These molecules have low solubilities in many common solvents, like hexanes, therefore chlorobenzene and other aromatic solvents must be used.[9,10] The low solubility in inexpensive, common solvents contributes to the ineffectiveness of performing separations on common stationary phases such as silica gel, using flash chromatography. Therefore, continued development is dependent on separation methods that facilitate isolation of gram quantities of fullerenes. This would enable the scientific community to fully evaluate the potential utility of these materials.

Early procedures for separating C_{60} employing neutral alumina as the stationary phase were found to be inefficient.[11] The cost of alumina, the amount of solvent needed, the duration of the separation, and the stationary phase's inability to separate any fullerenes higher than C_{60} called for a more effective way to purify fullerenes. Tour *et al.*[12] found that activated charcoal columns containing Norit A and silica gel, efficiently separated C_{60}. Further development led to an efficient method for isolation of C_{70} by modifying the mobile phase.[13] These two developments enabled gram quantities of these materials to be readily available. However, methods for efficient isolation of gram quantities of the higher fullerenes (>C_{70}) had not appeared prior to this work.

Higher fullerenes are currently separated by high pressure liquid chromatography (HPLC) employing the Buckyclutcher I stationary phase,[14] or by gel permeation chromatography (GPC).[11,15] These methods of purification have limitations. For example, they typically have (1) limited load capacities, (2) poor resolution of the higher fullerenes, (3) require multiple (as many as 30) passes through the column,[2] and (4) necessitate expensive specialty columns for efficient separation.

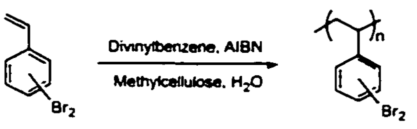
Gel permeation chromatography (GPC) separations typically functions by a size exclusion mechanism, whereas HPLC operates by an affinity mechanism. Fullerenes elute in ascending order, C_{60} initially, when introduced into a HPLC system. In GPC, the molecule that has the largest hydrodynamic volume typically elutes first, followed by the smaller molecules in descending order.[16] Previous GPC experiments showed that fullerenes elute in reverse order with reference to polystyrene standards.[17] C_{60} elutes first, followed by the higher fullerenes in ascending order. Therefore, the typical size exclusion mechanism is not operating for fullerenes using the typical styrene-based stationary phases.[18,19]

The aforementioned phenomenon has lead investigators to propose an affinity mechanism that supersedes the typical size exclusion mechanism. It has been hypothesized that a π-acidic (electron deficient) stationary phase might increase the retention and promote the discrimination of the π-basic (electron rich) fullerenes.[20] The possible differences in aromaticity[3,6] and their differing degrees of electron delocalization[21] of the fullerenes may lead to this affinity interaction. Aromatic hydrocarbons have shown large retention on polystyrene/divinylbenzene stationary phases that are believed to involve a $\pi-\pi$ or charge-transfer interaction between the fullerenes and the stationary phase. [22]

Building on the abovementioned stationary phase affinity for solute principle, we hypothesized that increasing the stationary phase's ability to interact with the more compatible components in the crude fullerene mixture would increase the retention times, giving a more effective separation. Thus, we investigated use of functionalized polystyrene stationary phases for the purification of fullerenes. We therefore investigated use of functionalized polystyrene stationary phases for the purification of fullerenes using various styrene monomers that were similar in structure to potent fullerene solvents.[18] The suspension polymerized resins prepared and screened for their efficacy in fullerene separations included polystyrene/DVB, poly(4-chlorostyrene)/DVB, poly(4-naphthylstyrene)/DVB, and poly(dibromostyrene)/divinylbenzene (PDBS/DVB). The PDBS/DVB stationary phase permitted a superior separation.

Outlined here is a simple method for the bench-top enrichment of preparative amounts of C_{60}, C_{70}, and the higher fullerenes ($<C_{100}$) from a crude fullerene mixture by a single elution through a column of PDBS/DVB using chlorobenzene as the mobile phase. PDBS-DVB stationary phase has been used in recent studies to separate the entire spectrum of chlorobenzene soluble fullerenes. A single elution through a column of poly(dibromo)styrene/divinylbenzene (PDBS-DVB) using chlorobenzene as the mobile phase, enabled us to separate seven fullerene fractions from a crude fullerene mixture.

The PDBS-DVB stationary phase has proven to be superior to current methods of fullerene separation because it (1) was inexpensive since the monomer is produced in bulk (the polymer is used as a flame-retarding additive for commodity plastics), (2) was easily produced in large quantities by a suspension polymerization, (3) permitted the use of potent fullerene solvents, and (4) could be easily reused. Numerous potent fullerene solvents[18] including chlorobenzene, 1,2-dichlorobenzene, carbon disulfide, and toluene were investigated as mobile phases; chlorobenzene gave the optimal separation for fullerenes in <C100 range.[27]



(1)

The production of the PDBS-DVB stationary involves a simple bead suspension polymerization using well known conditions according to equation 1.[24] The reaction conditions have been optimized to afford a 84% yield, mass to mass, for the polymerization, of which 50 weight % is the desired 200-400 mesh (37-74 μm) particle size range which is optimal for gravity column chromatography.

As expected, fullerenes elute from the PDBS-DVB stationary phase in the reverse order expected for a size exclusion mechanism.[18] C_{60} elutes first, followed by the higher fullerenes in ascending order. It is possible that the slight differences between the fullerenes may contribute to an affinity type mechanism for separation that supersedes the typical size exclusion mechanism. The stationary phase contains dibrominated aryl rings that are electron deficient (π acids) which interact with the fullerenes that are more electron rich (π bases).

Numerous solvents (including chlorobenzene, 1,2-dichlorobenzene, carbon disulfide, and toluene) which solubilize fullerenes well,[25] were investigated as mobile phases for this separation. Of the solvents investigated, chlorobenzene gave the best separation. In addition, separation by gravity filtration appears to be optimal because flash chromatography compresses the stationary phases, which adversely affects resolution.

A typical purification was performed as follows. A slurry of the PDBS-DVB stationary phase (140 g) and chlorobenzene (250 mL) was poured into a glass column (55 mm i.d., 270 mm long with a 500 mL solvent reservoir) containing a cotton plug. The slurry was allowed to settle until the solvent was approximately 1 mm above the stationary phase. The stationary phase should not be allowed to become solvent-free. A homogeneous, saturated chlorobenzene (20 mL) solution of 100.4 mg crude fullerenes (sonication of the mixture was used to facilitate the dissolution process) extracted from carbon soot, was introduced onto the top of the PDBS-DVB stationary phase. The column was then eluted at a flow rate of 1 mL/min using chlorobenzene as the mobile phase. The fractions were collected and tested by HPLC to determine purity.

Seven distinct colored bands, figure 1, were seen during the separation. Listed in Table 1 are the colors, purities, and the amounts recovered from this separation. The total column recovery was 95% of starting fullerenes.

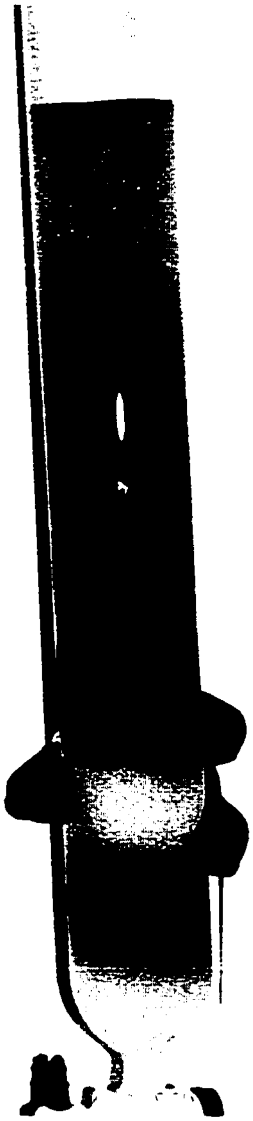


Figure 1. Fullerene allotrope fractions eluting from the PDBS-DVB stationary phase.

Band Number[a]	**Band Color**	**Constituent(s) (% purity)**[b]	**Isolated weight (mg)**
1	purple	C_{60} (99.3)	51.2
2	dark brown	C_{70} (98.8)	19.3
3	golden	C_{76} (30.0) C_{78} (61.1)	0.7
4	golden gray	C_{78} (98.7)	2.0
5	olive	C_{84} (84.3) C_{86} (10.0)	10.9
6	light gray	C_{90}, C_{92} (mix, 100%)[c]	1.0
7	dark gray	C_{90}, C_{92} (mix, 10.9)[c] C_{94}, C_{96} (mix, 89.1)[c]	10.0

Table 1. Fractions Collected From the PDBS/DVB Column. [a]The lower the band number, the faster the elution rate. [b]The purity was determined by HPLC on a C-18 column using a 55:45 MeOH/toluene mixture at a flow rate of 1 mL/min and UV detection at 340 nm. The peak identities were determined relative to authentic samples.[26] [c]The broadened peak did not have adequate resolution to permit quantitation of each of the two components in the mixture.

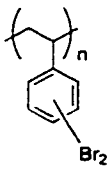
Additionally, the PDBS-DVB stationary phase column has been scaled up. A solution of chlorobenzene consisting of 506 mg of crude fullerenes was also separated on 140 g of stationary phase. Five distinct colored bands were seen, yet C_{76} and C_{78}, and the fullerenes higher than C_{84} co-eluted. It is believed that this column was overloaded. For this column, 395.1 mg of C_{60}, 111.6 mg of C_{70}, 17.0 mg of a mixture of C_{76} and C_{78}, 18.8 mg of C_{84}, and 6.7 mg of fullerenes higher than C_{84} were recovered.

A final set of columns was run on 507 mg of fullerene soot enriched in higher fullerenes ($>C_{70}$) from BuckyUSA. The procedures were the same except the material was purified by multiple columns and not by a single pass. 324.3 mg of C_{70}, 90.6 mg of C_{76}, 17.3 mg of C_{78}, 82.3 mg of C_{84}, and 34.6 mg of fullerenes higher than C_{84} were isolated.

The ability of the PDBS-DVB stationary phase to separate other organic molecules is being determined. Currently, silica gel, which is expensive, not easily reusable, and not able to resolve many compounds, is the predominate stationary phase that chemists use to separate organic compounds. The hope is that PDBS-DVB stationary phase will be able to purify many difficult to resolve molecules that silica gel cannot resolve. It is desired that this type of stationary phase will separate many organic compounds by simply tailoring the functionalities and the active sites on the polystyrene backbone.

Experimental

General. HPLC was carried out on a Waters C_{18} reverse phase column (3.9 mm x 300 mm i.d.) with 1:1 acetonitrile/toluene mixture at 1 mL/min using UV detection at 290 nm. Toluene and acetonitrile, both HPLC grade, were purchased from Aldrich. Chlorobenzene was purchased from Aldrich and used without purification. Dibromostyrene was donated by Great Lakes Chemical Corporation and purified by passage through neutral alumina. Divinylbenzene, tech. grade, 55% mixture of isomers, was purchased from Aldrich and purified by passage through neutral alumina. AIBN was purchased from Pfaltz and Bauer and used without purification. A Waring two speed commercial blender, model 5011, with a standard offset four blade stirrer was used for the suspension polymerization.



Poly(dibromo)styrene/divinylbenzene (2, AMR-I-10, 11, 12, 13, 14, 15, 16, 18, 19, 20, 21, 22, 23, 24, 25, 28, 29, 30, 31, 32, 33, 35, 36, 37, 38, 39, 40, 47, 48, 49, 50, 51, 52, 53, 54, 71, 72, 73, 74, 75, III-21, 27, 29). Inhibitor free dibromostyrene (50 mL, 344 mmol) and divinylbenzene (3.2 mL, 210 mmol) were mixed with AIBN (400 mg, 2.43 mmol), 12 mL of a pre-made solution of methyl cellulose (4 g in 800 mL of water) and 400 mL of distilled water. These components were stirred in an industrial blender set at low for 8 min. The resulting suspension was then heated at 75 °C for 2 d. The polymer beads were then poured into a 43 mm × 123 mm Soxhlet thimble and extracted with acetone for 12 h. The beads were then dried in a vacuum oven at 45 °C (1.0 mm Hg) overnight. Next the beads gently ground with a mortar and pestle and size fractionated using stainless steel full-height laboratory sieves. The suspension polymerization afforded 79.5 grams of product (84% yield) mass to mass, of which 50 weight % is the desired 200-400 mesh particle size range.

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Chapter 3

Synthetic Approaches To Self-assembled Monolayer Precursors For Sub-25 nm Devices Using Negative Tone Resists

Although there is a large effort in STM- and AFM-based direct modifications of surfaces for nano-fabrication as well as research into parallel exposure lithography tools using electrons, ions and atoms, there currently is no method of lithographic exposure that will enable the commercial application of device concepts with feature sizes below 25 nm.[1] Therefore, novel strategies for electronic device fabrication must be developed for future technologies. For device fabrication, a negative tone resist process based on ultra-thin resist layers appears to provide the most realistic approach to solve this problem. In order to address this goal, the materials currently under study as resists are overwhelmingly polymers. Polymers are limited by their molecular size and their inability to form durable ultra-thin layers for pattern transfer. Our integrated approach involving chemical synthesis, detailed surface analysis, and silicon device structure fabrication, increases the chances of developing a viable device fabrication method. We are using self-assembly in ways that take advantage of the chemical formation of high-quality functional thin layers that can be used to pattern arbitrary geometries with directly exposed features <25 nm. At these dimensions, the temperature of operation of a single electron transistor (SET) should approach room temperature.

Self-assembled monolayers (SAMs) have recently been successfully exposed by electrons, ions, UV photons, x-rays and excited atom beams, and they may offer an attractive new technology to attain sub-25 nm devices at reduced dimensions.[1,2] Regardless of the exposure process that will be used at these diminutive scales, they will require imaging surfaces that can acquire the lithographic patterns in very thin layers. This is necessary, in some cases, because of the extremely limited penetration depth of the exposing particles. However, a thin layer is primarily needed due to the inevitable spread in energy caused by scattering of the exposing particles. A thinner resist would cause less spreading of the exposing energy because the ultimate resolution is limited by scattering of the incident electron beam and the molecular dimensions of the resist layer (Figure 1).[1,2] Polymer resists are usually >50 nm thick due to the difficulty of preparing thinner continuous films. In polymer resists, the current resolution is 10-100 nm, with limited line width control.[1,3] The corresponding thicknesses of SAMs are 1-2 nm.[4] This order of magnitude decrease in resist thickness should greatly reduce the effect of exposing energy spread thereby improving resolution and feature size control to the required levels of better than 8 nm, Figure 1.[4] Therefore, the resist layer should be as thin as possible while retaining robustness and pattern transfer requirements. Properly designed SAMs can fulfill this goal.

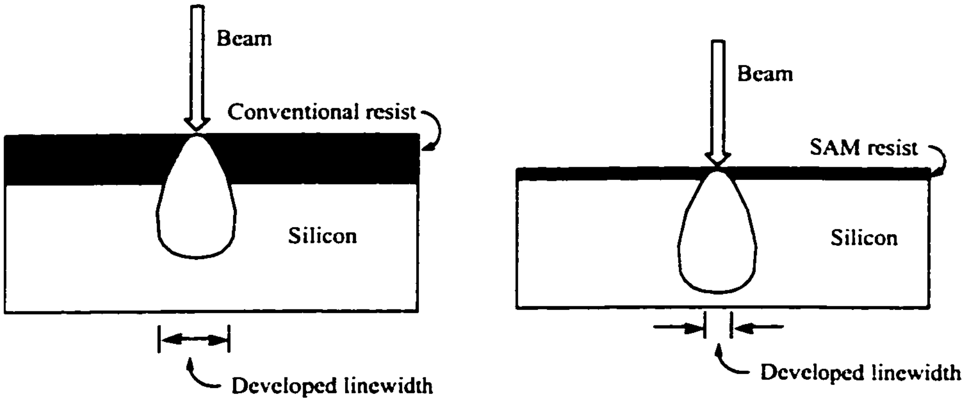


Figure 1: A thinner resist layer, based on a SAM, limits the effects of beam spreading in the resist layer.

There are a few examples that have been reported using SAMs as resists, but they have focused on positive tone processes.[1,2] However, for most line and device preparations, a negative tone resist process is preferred. In a negative tone resist, the exposed region forms a barrier layer that retards subsequent etching of the exposed region, Figure 2. Recently, we prepared a SAM wherein a negative tone resist was obtained and we hope to capitalize on this result.

Another feature that makes SAMs attractive is the exceedingly small amount of organic material needed for the process.[4] This could limit waste at the fabrication site, an important consideration for the development of future technologies.

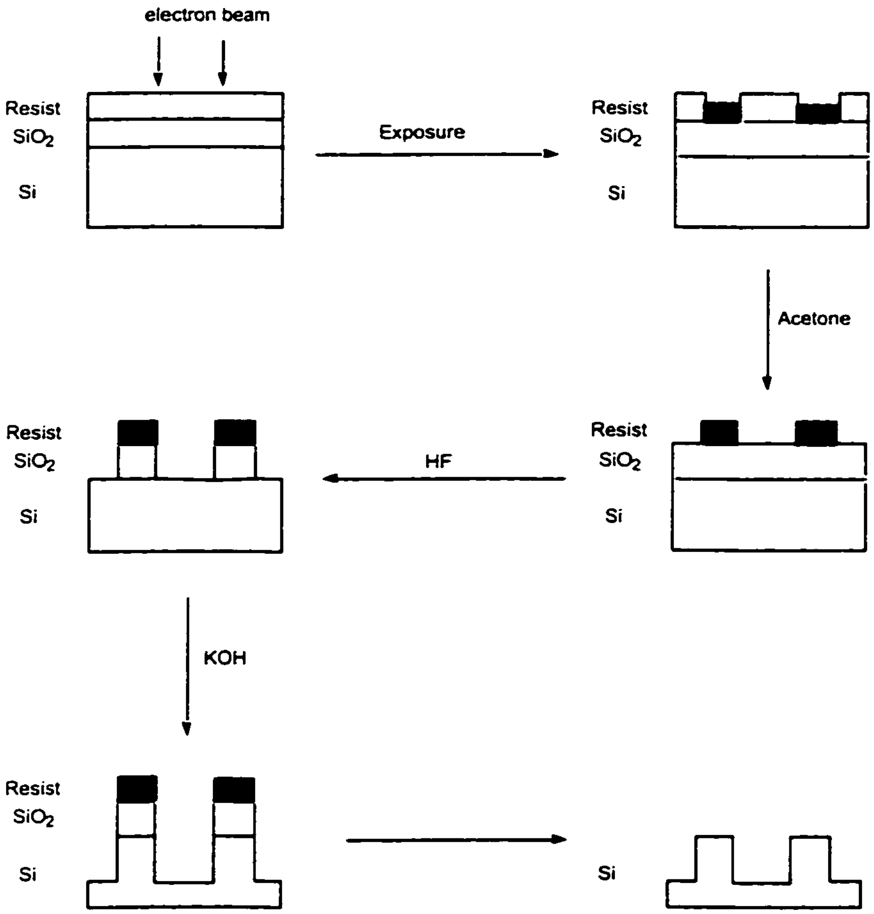

electron beam
Resist
SiO_2
Si
Exposure
Resist
SiO_2
Si
Acetone
Resist
SiO_2
Si
HF
Resist
SiO_2
Si
KOH
Resist
SiO_2
Si
Si

Figure 2: Schematic of a negative tone resist

Initial Result on a Negative Tone Resist Process

In our first effort toward the easily cleavable SAM route for a negative tone resist, we chose to construct a molecular system that had the following characteristics: (1) a long hydrophobic tail for the packing features necessary for SAM formation[4] (though our subsequent work showed that this feature is not a requirement for obtaining densely packed SAMs);[6] (2) an easily cleavable moiety close to the SAM surface which could significantly increase the throughput of the process by requiring lower beam dosages; (3) a $SiCl_3$ moiety on the end to bind to the hydrated SiO_2 surface; (4) the $SiCl_3$ moiety needed to be attached in the final synthetic step since it is a reactive group and subject to decomposition during other synthetic work-up procedures; (5) the attachment of the $SiCl_3$ group required a near quantitative yield reaction since purification by distillation was prohibitive due to the molecular weight of the final product; chromatography would lead to hydrolysis of the $SiCl_3$ group, and the long chain alkyl group would retard any crystallization scheme for purification, Figure 3.

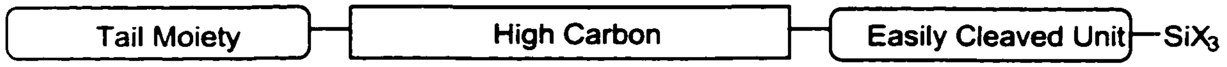
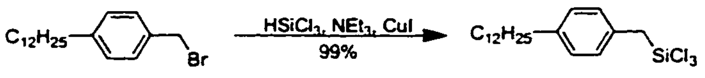


Figure 3: Optimal configuration of a SAM resist

We prepared the silane **1** according to the protocol outlined in equation 1. EIMS of **1'** (the methanolysis product of **1**) showed a base peak at 105 m/e ($[C_8H_9]^+$) resulting from ionization of the aryl ring.[7]



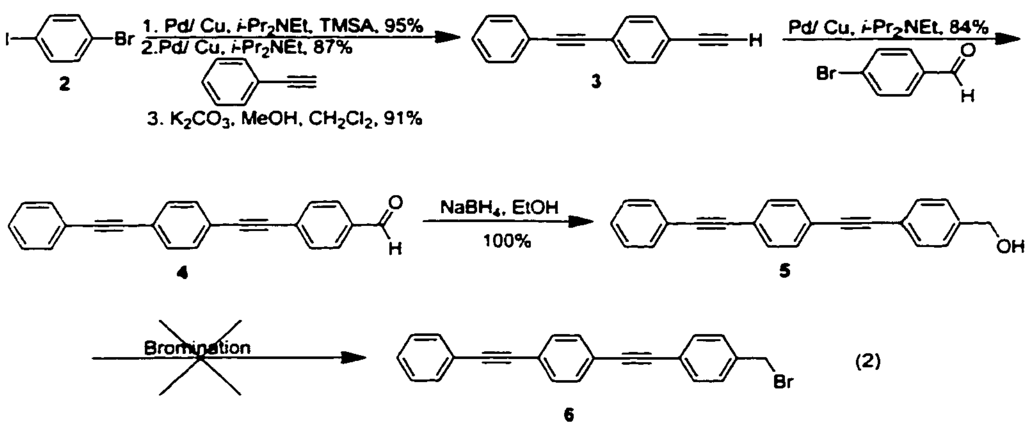
1

(1)

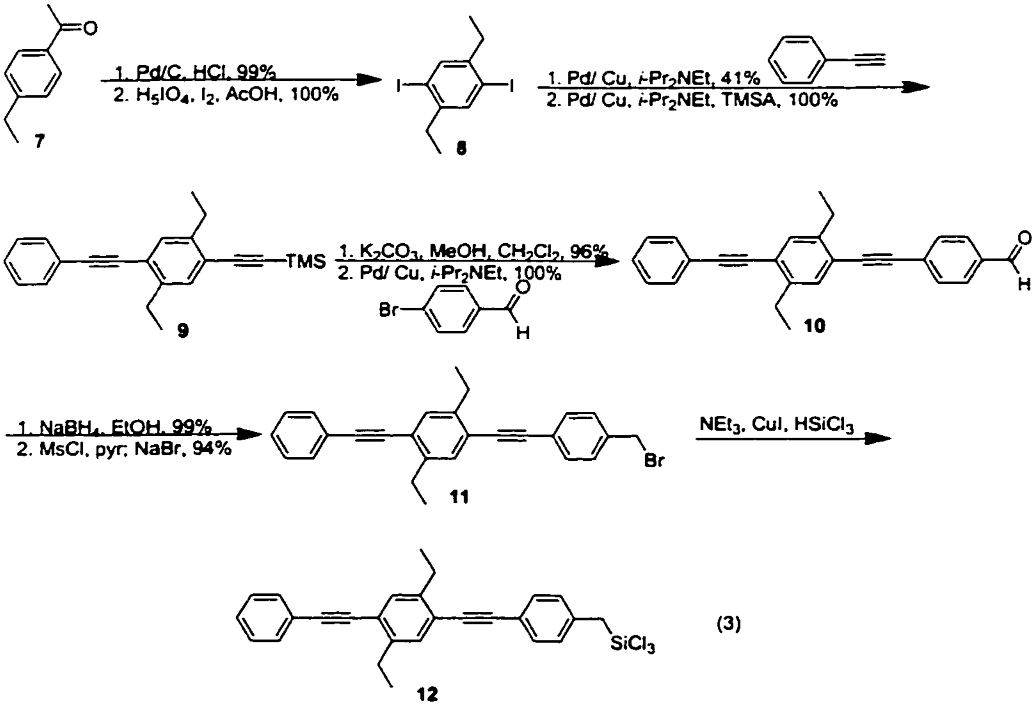
Remarkably, 1 responded as a negative tone resist. This suggested that with some molecular architectures, crosslinking can occur which causes a carbon residue to remain, thereby acting as a negative tone resist. To our knowledge, this is the first demonstration of molecular modification of a SAM precursor to afford a negative tone resist material.[7]

Current work on second generation negative tone resists is directed toward the synthesis of compounds that are highly conjugated phenylene ethynylenes that should crosslink with exposure to irradiation to form crosslinked carbon char that is desired for a negative resist. These compounds also possess an easily cleavable benzylic site and lack a hydrophilic tail that recently determined is not needed for SAM formation.[6] Further work will include the formation of SAMs these compounds and their irradiation to determine if they acts as negative tone resists.

The synthesis of a high conjugated phenylene ethynylene for the use as a SAM resist, eq 2, are facile with high yields of 84% and 100% for the coupling and reduction to the benzyl alcohol, respectively. Next the bromination did not occur as expected. The low solubility of the benzyl alcohol and the reactivity of the internal alkynes did not allow for the benzyl bromide formation.

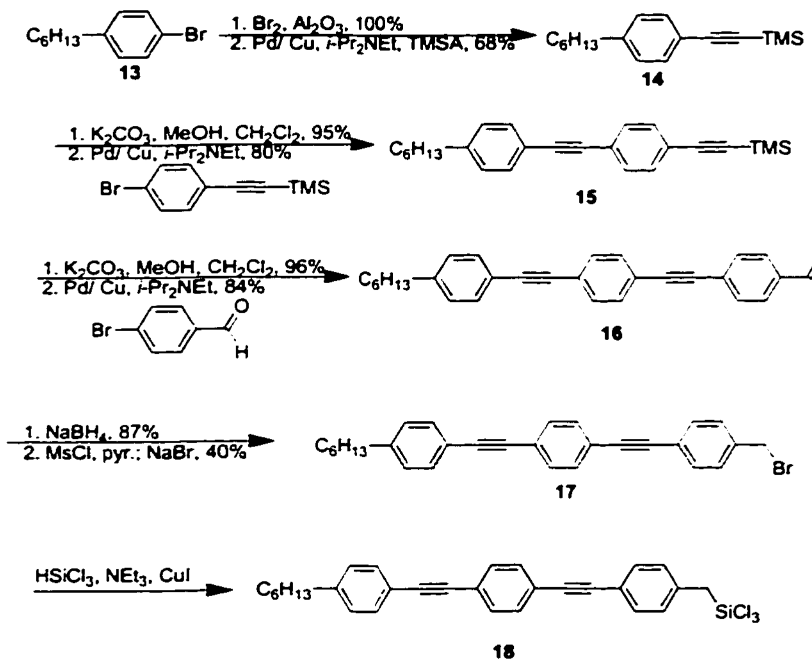

1. Pd/ Cu. i-Pr2NEt. TMSA. 95%
2.Pd/ Cu. i-Pr2NEt. 87%
3. K2CO3. MeOH. CH2Cl2. 91%
2
3
Pd/ Cu. i-Pr2NEt. 84%
4
NaBH4. EtOH
100%
5
Bromination
6
(2)

One major limitation to unsubstituted phenylene ethynylenes is that they are very insoluble in most organic solvents. Therefore, we determined that the best method for improving the solubility of these types of molecules is to attach side chain alkyl groups.


7
1. Pd/C. HCl. 99%
2. H5IO4. I2. AcOH. 100%
8
1. Pd/ Cu. i-Pr2NEt. 41%
2. Pd/ Cu. i-Pr2NEt. TMSA. 100%
9
1. K2CO3. MeOH. CH2Cl2. 96%
2. Pd/ Cu. i-Pr2NEt. 100%
10
1. NaBH4. EtOH. 99%
2. MsCl. pyr; NaBr. 94%
11
NEt3. CuI. HSiCl3
12
(3)

In eq 3, the addition of the diethyl subunits on the middle phenyl ring disrupted the π-stacking of the phenyl rings to greatly improve the solubility of this molecule. The synthesis commenced with the reduction and subsequent diiodonation of 4-ethylacetophenone that proceeded in very high yields from an inexpensive starting material.[8] The phenylene ethynylene core is built by four moderate yielding, subsequent Sonogashira couplings, and deprotections to the terminal alkyne to form the benzyl aldehyde **10**. In a facile reaction, the benzyl aldehyde was reduced to the benzyl alcohol with sodium borohydride in 99 % yield.

The transformation to the benzyl bromide **11** was surprisingly troublesome. The formation of the mesylate intermediate was very fast but the subsequent S_N2 attack of the bromide was very slow compared to the attack of the chloride even in acetone. The yield improved when the bromide source was changed from lithium or sodium bromide, due to less ionic interactions between sodium and bromine allowing for a more "naked" anion. During optimization of this reaction, it was determined that an aqueous workup with copper sulfate to remove pyridine before the addition of the sodium bromide, followed with refluxing the mesylate with sodium bromide in acetone was beneficial to this reaction. The attachment of the trichlorosilyl group to the phenylene ethynylene with copper iodide, trichlorosilane, and triethylamine is has been completed but has not been characterized due to the severe reactivity of the substituted trichlorosilane to atmospheric water. To decrease reactivity of **12**, the trimethoxysilane derivative may be beneficial.


C6H13
Br
13
1. Br2, Al2O3, 100%
2. Pd/Cu, i-Pr2NEt, TMSA, 68%
C6H13
TMS
14
1. K2CO3, MeOH, CH2Cl2, 95%
2. Pd/Cu, i-Pr2NEt, 80%
Br
TMS
C6H13
TMS
15
1. K2CO3, MeOH, CH2Cl2, 96%
2. Pd/Cu, i-Pr2NEt, 84%
Br
O
H
C6H13
O
H
16
1. NaBH4, 87%
2. MsCl, pyr.; NaBr, 40%
C6H13
Br
17
HSiCl3, NEt3, CuI
C6H13
SiCl3
18

(4)

Eq 4 shows the formation of an additional SAM resist with a hexyl subunit on a terminal ring to improve solubility. This subunit did improve solubility of this phenylene ethynylene but not to the extent of the compound **12** that possessed the diethyl subunits on the interior of the phenyl ring. This synthesis of **18** begins with the bromination of phenylhexane, which proceeds in high yield.[9] This compound was difficult to purify from minor side products such as ortho bromination and starting material. Therefore, it was reacted and purified after the next transformation. The next five steps entail three Sonogashira couplings and two deprotections to the terminal alkyne to ultimately form benzyl aldehyde **16** in high yield. After the reduction to the benzyl alcohol, the material became insoluble in most solvents except for THF and was only partially soluble in methylene chloride. This insolubility led to difficulties in the formation of the benzyl bromide that could only be achieved after multiple repetitions of this reaction. The attachment of the trichlorosilyl group to the phenylene ethynylene with CuI, trichlorosilane, and triethylamine is has been completed but has not been characterized due to the severe reactivity of the substituted trichlorosilane to atmospheric water.

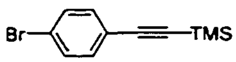
In conclusion, we have prepared the first self-assembled monolayer that upon irradiation acts as a negative tone resist. In addition, we have synthesized a phenylene ethynylene substituted trichlorosilane that should crosslink with exposure to irradiation to be a superior resist material. We are currently in the process of evaluating what functionalities are necessary to form negative tone resists at lower doses of energy. This will possibly allow the fabrication of device feature sizes below 8 nm.

Experimental Procedures

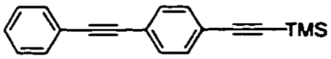
General. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Pyridine, methyl iodide, and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Trichlorosilane was distilled immediately before use. Toluene and benzene were distilled over CaH_2. Methylene chloride and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine was distilled over CaH_2. MeOH was dried over oven dried 3 Å molecular sieves. Silica gel plates were 150 μm thick, 60 F_{254} grade form EM Science. Silica gel was grade 60 (230-400 mesh) from EM Science. NMR spectra were observed at 300 MHz and 400 MHz on Brüker WH-400 and AM-300 spectrometers. Water sensitive samples for NMR analysis were run in $CDCl_3$ that was passed through flame-activated alumina using an oven-dried, septum-sealed NMR tube. Gas chromatography experiments were performed on a Hewlett-Packar GC model 5890A equipped with an Alltech column (cat # 932525, serial # 9059) 25 m × 0.25 mm D × 0.2 mm. Hydrogenations were performed on a Parr Instruments Company hydrogenator model number AP500MLAN15760.

General Procedure for the coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol)[10] To an oven dried round bottom flask equipped with a water cooled West condenser or screw capped pressure tube with a magnetic stirbar were added the aryl halide, bis(triphenylphosphine)palladium(II) chloride (3-5 mol % per halide), triphenylphosphine (12-20 mol % per halide), and copper(I) iodide (6-10 mol % per halide). The vessel was then sealed with a rubber septum under a N_2 atmosphere. A co-solvent of THF, benzene, or methylene chloride was added at this point depending on the solubility of the aryl halide. Then base, either triethylamine or *N,N*-diisopropylethylamine, was added and finally the terminal alkyne (1-1.5 mol % per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was then quenched with water, a saturated solution of NH_4Cl, or brine. The organic layer was diluted with methylene chloride or Et_2O and washed with water, a saturated solution of NH_4Cl, or brine (3×). The combined aqueous layers were extracted with methylene chloride or Et_2O (2×). Th combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each material.

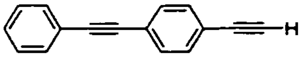
General Procedure for the Deprotection of a Trimethylsilyl Protected Alkyne. To a round-bottom flask equipped with a magnetic stirbar were added the trimethylsilyl protected alkyne, potassium carbonate (5 equivalents per alkyne), methanol, and methylene chloride. The reaction vessel was sealed with a septum under a N_2 atmosphere. The reaction mixture progress was monitored by thin layer chromatography. Upon completion of the reaction, the reaction mixture was then quenched with water or brine. The organic layer was diluted with methylene chloride and washed with water or brine (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each material.



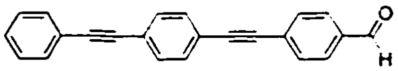
1-Bromo-4-(2′-trimethysilylethynyl)benzene.[11] See the general procedure for the Pd/Cu coupling reaction except that amine was added at 0 °C. The compounds used were 1-bromo-4-iodobenzene (2.83 g, 10.0 mmol), trimethylsilylacetylene (1.47 mL, 10.4 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol), CuI (0.11 g, 0.60 mmol), benzene (13 mL), and Et_3N (5.6 mL, 40 mmol). The mixture was stirred at room temperature for 10 h. Flash chromatography (silica gel, hexane) afforded 2.37 g (95 %) of the title compound as a yellow oil with slight impurities. The compound was used for the next step reaction without further purification. Spectra data were identical to those reported in the literature.



4-(Phenylethynyl)-1-(trimethylsilylethynyl)benzene (2, AMR-I-82). See the general procedure for the Pd/Cu coupling reaction. CuI (0.39 g, 2.03 mmol), bis(triphenylphosphine)palladium(II) chloride (0.70 g, 0.99 mmol), and 1-bromo-4-(2′-trimethysilylethynyl)benzene (5.00 g, 19.76 mmol) were added to a screw cap tube and purged with nitrogen for ~5 min. Phenylacetylene (3.04 mL, 27.66 mmol), triethylamine (9.64 mL, 69.16 mmol), and benzene (10 mL) were added with stirring at room temperature under an inert atmosphere. The tube was purged with nitrogen, sealed, and the reaction was stirred at 80 °C overnight. The mixture was diluted with methylene chloride and extracted with distilled water. The organic layer was dried with $MgSO_4$ and volatiles were removed via rotary evaporation. The resulting brown solid was eluted 2 × through a 4 × 20 cm column of silica gel using hexanes as the eluent. The product was obtained as a crystalline white solid (4.71 g, 87 %). TLC R_f=0.28 (hexanes). ^1H NMR ($CDCl_3$) δ 7.512 (m, 2 H), 7.441 (m, 4 H), 7.336 (m, 3 H), 0.253 (s, 9 H).

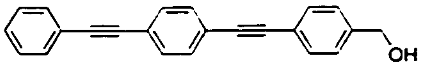


4-(Phenylethynyl)-1-(ethynyl)benzene (AMR-II-103, 123, 128, 138, 152, 167, 205, 239). See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. A mixture of 4-(Phenylethynyl)-1-(trimethylsilylethynyl)benzene (0.94 g, 3.4 mmol), K_2CO_3 (1.9 g, 14 mmol), methanol (2.5 mL), and methylene chloride (4 mL) was stirred for 30 min. Methylene chloride was added and the resulting mixture was extracted with distilled water. The organic layer was dried with $MgSO_4$ and the volatiles were removed via rotary evaporation. The product was obtained as a pale yellow solid (0.63 g, 91 %). IR (KBr) 3278, 3079, 3062, 3053, 3033, 3017, 1602, 1500, 1440, 1406, 1265, 1249, 1181, 1111, 1101, 1070, 1025, 922, 842, 834, 759, 690, 666, 629, 548, 527, 460 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.515 (m, 2 H), 7.462 (m, 4 H), 7.341 (m, 3 H), 3.159 (s, 1 H).



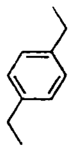
4-(4'-(Phenylethynyl)-1'-(ethynyl)phenyl)benzaldehyde (4, AMR-I-163, 240). See the general procedure for the Pd/Cu coupling reaction. Copper iodide (0.07g, 0.36

mmol), bis(triphenylphosphine)palladium(II) chloride (0.13 g, 0.18 mmol), 4-bromobenzaldehyde (1.00g, 5.42 mmol) and 4-(phenylethynyl)-1-(ethynyl)benzene (0.72 g, 3.56 mmol) were added to a screw cap tube and air removed in vacuo then purged with nitrogen (3×). Triethylamine(7.53 mL, 54.15 mmol), and THF (40 mL) were added with stirring at room temperature under an inert atmosphere. The tube was purged with nitrogen, sealed, and the reaction was stirred at ambient for 16 h. TLC of the reaction mixture indicated complete consumption of starting material. The mixture was diluted with THF and filtered through celite and extracted with ammonium chloride (3×). The organic layer was dried with $MgSO_4$ and volatiles were removed via rotary evaporation. Residue washed with hexanes to remove impurities. Reaction yielded 0.93 g (85%) of the desired compound. IR (KBr) 3200.0, 3117.9, 3046.2, 2933.3, 2841.0, 2738.5, 2205.1, 1702.6, 1651.3, 1594.9, 1559.0, 1543.6, 1512.6, 1497.4, 1435.9, 1405.1, 1384.6, 1302.6, 1282.1, 1205.1, 1164.1, 1107.7, 1015.4, 907.7, 861.5, 835.9, 800.0, 753.8, 717.9, 687.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1 H), 7.87 (d, *J*= 8.4 Hz, 2 H), 7.66 (d, *J*=8.2 Hz, 2 H), 7.51 (s, 6 H), 7.34 (m, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) 192.12, 136.22, 132.83, 132.43, 132.36, 132.34, 130.32, 130.04, 129.30, 129.13, 124.61, 123.59, 122.90, 93.79, 92.41, 90.94, 89.61. HRMS calcd for $C_{23}H_{14}O$: 306.1044. Found 306.1037.

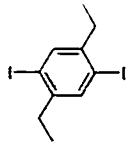


4-(4′-(Phenylethynyl)-1′-(ethynyl)phenyl)benzyl alcohol (5, AMR-I-159, 237). To a 500 mL round bottom flask equipped with a stir bar, was added 4-(4′-

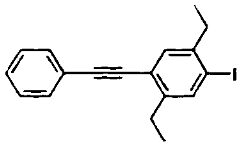
(phenylethynyl)-1′-(ethynyl)phenyl)benzaldehyde (0.35 g, 1.14 mmol), ethanol (100 mL), and methylene chloride (150 mL). The reaction mixture was cooled to 0° C and allowed to stir for 10 min. Sodium borohydride (0.05 g, 1.25 mmol) was added in small portions. The reaction flask was equipped with a condenser and the reaction mixture was heated to reflux for 30 min. The mixture was extracted with methylene chloride and washed with brine. The organic layer was dried with $MgSO_4$ and solvent was removed in vacuo. The residue washed with hexanes to remove the impurities to afford 0.347 g (99%) of the desired compound. IR (KBr) 3425.6, 3138.5, 2964.1, 2928.2, 2866.7, 1723.1, 1656.4, 1384.6, 1271.8, 1123.1, 1071.8, 835.9, 748.0, 687.2, 610.3 cm^{-1}. ^1H NMR (300 MHz, d_6-DMSO) δ 7.60-7.4 (m, 13 H), 5.32 (t, *J*= 6.5 Hz, 1 H), 4.53 (d, *J*= 6.5 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) 143.79, 131.68, 131.64, 131.44, 131.25, 129.06, 128.82, 128.68, 126.64, 122.60, 122.32, 121.99, 120.11, 91.62, 91.34, 88.89, 88.45, 62.47. HRMS calcd for $C_{23}H_{16}O$: 308.1201. Found 308.1212.



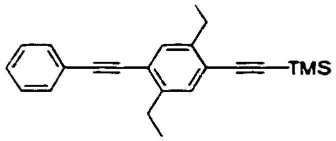
1,4-Diethylbenzene (AMR-I-276). To an oven dried thick walled Parr bomb vessel were added 4-ethylacetophenone (14.82 g, 100 mmol), HCl (20 mL), 10% Pd/C (2.0 g), and ethanol (100 mL). The vessel was attached to the hydrogenator and allowed to react for 2 d at 70 °C and 60 psi of H_2 pressure. Upon completion, the reaction mixture was filtered through a pad of Celite to remove the Pd/C. The reaction was quenched with NaOH (3 M, 150 mL). The reaction mixture was further diluted with methylene chloride and extracted with water (3×). The combined organic layers were dried over $MgSO_4$. The solvents were removed carefully in vacuo to afford the desired product (13.27 g, 99 % yield) as a clear liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4 H), 2.63 (q, *J*=7.5 Hz, 4H), 1.23 (t, *J*= 7.5 Hz, 6H).



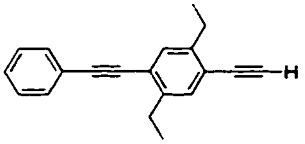
1,4-Diethyl-2, 5-diiodobenzene (8, AMR-I-202, 278).[8] To an oven dried round bottom flask was added 1,4-diethylbenzene (1.34g, 10 mmol), periodic acid (0.91g, 4 mmol), iodine (2.03g, 16 mmol), acetic acid (8.1 mL), water (1.62 mL), and sulfuric acid (0.24 mL). A West condenser was attached and the reaction was heated to 100 °C for 2.5 h. The reaction mixture was cooled and poured into an aqueous sodium bisulfite solution and the brown solids were collected. The solids were dissolved in diethyl ether and stirred with activated charcoal (Norit A) for 5 h. The mixture was filtered through a celite pad that was washed with additional diethyl ether. The ether was removed leaving a white crystalline material (3.92 g, 100%). IR (KBr) 3128.2, 2964.1, 2861.5, 1456.4, 1384.1, 1379.5, 1343.6, 1312.8, 1251.3, 1184.6, 1030.8, 979.5, 959.0, 882.0. 779.5, 712.8 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 2 H), 2.62 (q, *J*=7.5 Hz, 2 H), 1.16 (t, *J*=7.6 Hz, 3 H). ^{13}C NMR (400 MHz, C_6D_6) δ 145.67, 138.43, 100.13, 33.09, 14.43. HRMS calcd for $C_{10}H_{12}I_2$: 385.9029. Found: 385.9027.



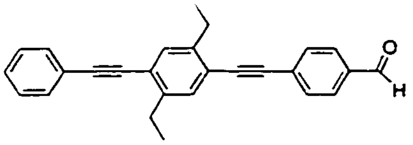
1,4-Diethyl-2-(phenylethynyl)-5-iodobenzene (AMR-I-251, II-3). See the general procedure for the Pd/Cu coupling reaction. 1,4-Diethyl-2,5-diiodobenzene (6.0 g, 15.55 mmol) was coupled to phenylacetylene (1.71 mL, 15.55 mmol) as described above using copper(I) iodide (0.30 g, 1.56 mmol), bis(triphenylphosphine)palladium(II) chloride (0.55 g, 0.78 mmol), triphenylphosphine (0.82 g, 3.11 mmol), THF (50 mL), and triethylamine (7.57 mL, 54.43 mmol) in a round bottom flask using a West condenser equipped with a magnetic stirbar. The reaction mixture was heated to reflux for 2 d. The resultant mixture was then subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride/ hexanes (19:1) as the eluent. The reaction afforded 2.32 g (41 % yield) of the desired clear liquid. IR (KBr) 3046.2, 2964.1, 2871.8, 1600.0, 1492.3, 1441.0, 1369.2, 1112.8, 1061.5, 989.7, 912.8, 987.2, 759.0, 687.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1 H), 7.53-7.48 (m, 2 H), 7.36-7.31 (m, 3 H), 7.31 (s, 1 H), 2.78 (q, *J*=7.5 Hz, 2 H), 2.67 (q, *J*=7.5 Hz, 2 H), 1.26 (t, *J*=7.5 Hz, 3 H), 1.20 (t, *J*=7.5 Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.01, 143.60, 138.53, 131.34, 131.25, 128.19, 128.12, 123.13, 122.49, 100.67, 93.50, 87.42, 33.48, 26.90, 14.68, 14.50. HRMS calcd for $C_{18}H_{17}I$: 360.0375. Found 360.0375.



1,4-Diethyl-2-(phenylethynyl)-5-(trimethylsilylethynyl)benzene (9, AMR-I-256, II-8). See the general procedure for the Pd/Cu coupling reaction. 1,4-Diethyl-2-(phenylethynyl)-5-iodobenzene (2.32 g, 6.34 mmol) was coupled to trimethylsilylacetylene (1.34 mL, 9.51 mmol) as described above using copper(I) iodide (0.14 g, 0.76 mmol), bis(triphenylphosphine)palladium(II)dichloride (0.18 g, 0.25 mmol), triphenylphosphine (0.26 g, 1.01 mmol), triethylamine (30.9 mL, 22.19 mmol), and THF (50 mL) in a large oven dried screw capped tube equipped with a magnetic stirbar. The reaction mixture was allowed to react at 50°C for 2 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by flash liquid chromatography using silica gel as the stationary phase and methylene chloride/ hexanes (1:1) as the eluent. The reaction afforded 2.09 g (100% yield) of the desired compound. IR (KBr) 3046.2, 2953.8, 2871.8, 2143.6, 1594.9, 1492.3, 1451.3, 1405.1, 1246.2, 1061.5, 851.3, 753.8, 687.2, 625.6 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51-7.50 (m, 2 H), 7.34-7.30 (m, 5 H), 2.83-2.71 (m, 4 H), 1.30-1.20 (m, 6 H), 0.24 (s, 9 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 143.81, 143.18, 131.71, 131.38, 128.28, 128.17, 127.58, 123.33, 122.53, 122.20, 103.76, 99.07, 94.00, 88.10, 27.23, 14.79, 14.61, 0.114. HRMS calcd for $C_{23}H_{26}Si$: 330.1804. Found: 330.1807.

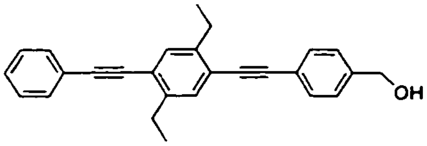


1,4-Diethyl-2-(phenylethynyl)-5-(ethynyl)benzene (AMR-I-263, II-9). See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. 1,4-Diethyl-2-(phenylethynyl)-5-(trimethylsilylethynyl)benzene (2.09g, 6.34 mmol) was deprotected to give the alkyne as described above using potassium carbonate (4.38 g, 31.70 mmol), methanol (25 mL), and methylene chloride (25 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.

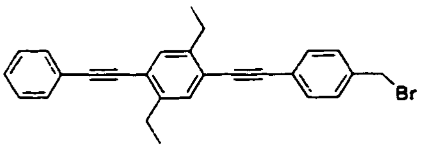


4-(4'-(Phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzaldehyde (10, AMR-I-264, II-10). See the general procedure for the Pd/Cu coupling reaction. 1,4-Diethyl-2-(phenylethynyl)-5-(ethynyl)benzene (1.58 g, 6.12 mmol) was coupled to 4-bromobenzaldehyde (1.52 g, 8.24 mmol) as described above using copper(I) iodide (0.14 g, 0.76 mmol), bis(triphenylphosphine)palladium(II) chloride (0.27 g, 0.38 mmol), triphenylphosphine (0.40 g, 1.52 mmol), triethylamine (13.22 mL, 95.10 mmol), and

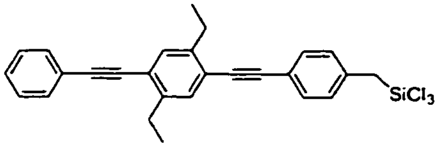
THF (50 mL) in an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar. The reaction mixture was allowed to heat to reflux for 2 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride/ hexanes (1:1) as the eluent. R_f(product): 0.3. The reaction afforded 1.49 g (64 % yield over two steps) of the desired material from 1,4-Diethyl-2-(phenylethynyl)-5-(trimethylsilylethynyl)benzene. IR (KBr) 3138.5, 2964.1, 2923.1, 1702.6, 1594.9, 1384.6, 1205.1, 1159.0, 1117.9, 830.8, 753.8, 687.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 7.86 (d, *J*=8.3 Hz, 2 H), 7.66 (d, *J*=8.3 Hz, 2 H), 7.56-7.52 (m, 2 H), 7.41 (s, 2 H), 7.38-7.32 (m, 3 H), 2.85 (overlapping q, *J*=7.3 Hz, 4 H), 1.31 (t, *J*=7.5 Hz, 6 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 191.01, 143.46, 143.28, 135.11, 132.16, 131.70, 131.51, 131.39, 131.27, 130.70, 129.49, 129.38, 128.16, 123.07, 121.35, 94.36, 92.93, 92.22, 87.85, 29.65, 27.11, 14.72, 14.63. HRMS calcd for $C_{27}H_{22}O$: 362.1671. Found: 362.1662.



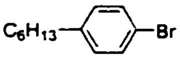
4-(4'-(Phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzyl alcohol (AMR-I-279, II-14). To an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar 4-(4'-(phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzaldehyde (0.80 g, 2.21 mmol) was added under a N_2 atmosphere. Methylene chloride (50 mL) and ethanol (50 mL) were added and the reaction mixture was cooled to 0 °C. Sodium borohydride (0.12 g, 3.09 mmol) was added slowly and the resultant reaction mixture was allowed to stir for 30 min and was then was heated to reflux for 30 min. Upon completion of the reaction, the reaction mixture was quenched with water. The organic layer was diluted with methylene chloride and washed with water (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. No further purification was needed. The reaction afforded 0.80 g (99 % yield) for the desired white material. IR (KBr) 3128.2, 2964.1, 2923.1, 2861.5, 1384.6, 1112.8, 1041.0, 1010.3, 882.1, 841.0, 810.3, 748.7, 687.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 4 H), 7.38 (s, 2 H), 7.37-7.32 (m, 5 H), 4.70 (s, 2 H), 2.85 (q, *J*=7.5 Hz, 4 H), 1.30 (t, *J*=7.5 Hz, 6 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.16, 140.73, 138.39, 131.41, 131.28, 131.23, 128.13, 128.01, 126.62, 123.20, 122.46, 122.24, 122.15, 93.88, 93.66, 88.13, 88.01, 64.84, 27.10, 14.66. HRMS calcd $C_{27}H_{22}O$: 364.1827. Found: 364.1818.



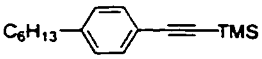
4-(4'-(Phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzyl bromide (11, AMR-II-38). To an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar was added 4-(4'-(phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzyl alcohol (0.10 g, 0.27 mmol). The vessel was capped under a N_2 atmosphere, methylene chloride (3 mL) was added, and the reaction was cooled to 0 °C. Pyridine (0.11 mL, 1.35 mmol) and mesyl chloride (0.03 mL, 0.41 mmol) were added and the resultant mixture was allowed to stir at ambient temperature for 4 h. Sodium bromide (0.14 g, 1.35 mmol) and acetone (5 mL) were added to the reaction mixture. The reaction mixture was then allowed to reflux for 12 h. Upon completion of the reaction, the reaction mixture was then quenched with water. The organic layer was diluted with methylene chloride and washed with water (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo. ^1H NMR showed mostly benzyl chloride; therefore, the material was placed in an oven dried round bottom flask equipped with a stirbar and a West condenser. Sodium bromide (0.14 g, 1.35 mmol) and acetone (5 mL) were added and the reaction mixture was allowed to heat to reflux for 12 h. Upon completion of the reaction, the reaction mixture was quenched with water. The organic layer was diluted with methylene chloride and washed with water (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo. No further purification was needed. The reaction afforded 0.11 g (94 % yield) of the desired product. IR (KBr) 3133.3, 2966.7, 2922.2, 2844.4, 1377.8, 1133.3, 888.9, 833.3, 750.0, 688.9, 605.6 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.59-7.52 (m, 4 H), 7.45-7.36 (m, 7 H), 4.55 (s, 2 H), 2.88 (overlapping q, J=7.6 Hz, 4 H), 1.33 (overlapping t, J=7.5 Hz, 6 H). ^{13}C NMR (400 MHz, CD_2Cl_2) δ 143.63, 143.57, 138.12, 131.78, 131.73, 131.54, 131.43, 129.18, 128.73, 128.40, 123.50, 123.33, 122.65, 122.23, 94.19, 93.56, 89.04, 88.09, 46.13, 33.37, 29.90, 27.34, 14.78. HRMS calcd $C_{27}H_{23}Br$: 426.0983. Found: 426.0982.



4-(4'-(Phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzyl trichlorosilane (12, AMR-II-27, 43, 77). To a flame dried 100 mL round bottom flask equipped with a magnetic stirbar solids 4-(4'-(Phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzyl bromide (0.16 g, 0.36 mmol) and copper iodide (0.01 g, 0.01 mmol) were added and air removed and nitrogen backfilled (3×). The solids were dissolved in methylene chloride (5 mL) and cooled to 0 °C for 5 min. Then triethylamine (0.15 mL, 1.37 mmol) followed by freshly distilled trichlorosilane (0.15 mL, 1.37 mmol) were added. The reaction mixture was allowed to sitr at room temperature for 2 d. The solvents in the reaction mixture were removed in vacuo. Solid material was dissolved in diethylether and transferred via syringe filtration with celite to another dry flask. Solvent removed in vacuo. Material determined to be insoluble in numerous solvents and the extreme reactivity of the trichlorosilane derivative did not allow for characterization.

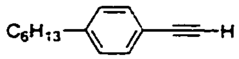


4-Bromo-1-*n*-hexylbenzene (AMR-I-261, 268).[9] In an 125 mL Erlenmeyer flask, bromine (0.52 mL, 10 mmol) was absorbed on neutral, Brockmann grade I alumina (10 g). 1-Phenylhexane (1.88 mL, 10 mmol) was absorbed on neutral alumina (10 g) in a second 125 mL Erlenmeyer flask. The contents of both flasks were combined in a 250 mL Erlenmeyer flask equipped with a magnetic stirbar. The reaction was complete within 1 min when the dark orange color of the bromine became light yellow. The solid mass was then poured in a column that contained a short plug of silica gel. The desired product was eluted with methylene chloride to give 2.58 g (100 % yield) of the desired clear oil. According to ^{1}H NMR, there was a ratio of products; 80:15:>5 (desired product: starting material: ortho substituted product). Isolation of the desired material was deemed to be more facile after the subsequent step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J*=8.2 Hz, 2 H), 7.03 (d, *J*=8.2 Hz, 2 H), 2.54 (t, *J*=7.5 Hz, 2 H), 1.60 (p , *J*=7.1 Hz, 2 H), 1.38-1.24 (m, 8 H), 0.92-0.84 (m , 3 H).

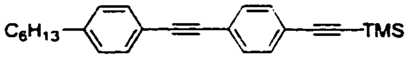


1-*n*-Hexyl-4-(trimethylsilylethynyl)benzene (14, AMR-I-266, 275). See the general procedure for the Pd/Cu coupling reaction. 4-Bromo-1-*n*-hexylbenzene (7.23 g, 30.0 mmol) was coupled to trimethylsilylacetylene (5.94 mL, 42.0 mmol) as described above using copper(I) iodide (0.69 g, 3.6 mmol), bis(triphenylphosphine)palladium(II) chloride (0.84 g, 1.2 mmol), triphenylphosphine (1.57 g, 6.0 mmol), triethylamine (30.36 mL. 300 mmol), and THF (30 mL) in a large oven dried pressure tube equipped with a magnetic stirbar. The reaction was sealed under a N_2 atmosphere and was heated to 85 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and hexanes as the eluent. The reaction afforded 5.26 g (68 % yield) of the desired material. IR (KBr) 2923.1, 2851.3, 2158.2, 1923.1, 1507.7, 1461.5, 1405.1, 1246.2, 1220.5, 861.5, 835.9, 753.8, 600.0 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ

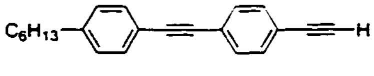
7.35 (d, J=8.0 Hz, 2 H), 7.07 (d, J=8.1 Hz, 2 H), 2.56 (t, J=7.7 Hz, 2 H), 1.62-1.50 (m, 2 H), 1.28 (br s, 8 H), 0.86 (br t, 3 H), 0.22 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.48, 131.75, 128.18, 120.17, 105.36, 93.15, 35.95, 31.76, 31.24, 28.95, 22.68, 14.18, 0.17. HRMS calcd $C_{17}H_{26}Si$: 258.1804. Found: 258.1793.



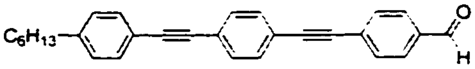
1-*n*-Hexyl-4-(ethynyl)benzene (AMR-I-270, II-6). See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. 1-*n*-Hexyl-4-(trimethylsilylethynyl)benzene (0.18 g, 0.7 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (0.48 g, 3.5 mmol), methanol (10 mL), and methylene chloride (10 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.



1-(4′-(*n*-Hexyl)-1′-(ethynyl)phenyl)-4-(trimethylsilylethynyl)benzene (15, AMR-I-271, II-7). See the general procedure for the Pd/Cu coupling reaction. 1-*n*-Hexyl-4-(ethynyl)benzene (3.30 g, 17.73 mmol) was coupled with 1-bromo-4-(trimethylsilylethynyl)benzene (4.82 g, 19.05 mmol) as described above using copper(I) iodide (0.41 g, 2.13 mmol), bis(triphenylphosphine)palladium(II) chloride (0.62 g, 0.89 mmol), triphenylphosphine (0.93 g, 3.55 mmol), triethylamine (8.63 mL, 62.06 mmol), and THF (75 mL) in an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar. The reaction mixture was heated to reflux for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and hexanes as the eluent. R_f (product): 0.30. The reaction afforded 5.06 g (76 % yield over two steps) of the desired product from 1-*n*-Hexyl-4-(trimethylsilylethynyl)benzene. IR (KBr) 3128.2, 2953.8, 2851.3, 2143.6, 1384.6, 1241.0, 1117.9, 866.7, 835.9, 759.0 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 6 H), 7.14 (d, *J*=8.1 Hz, 2 H), 2.60 (t, *J*=7.7 Hz, 2 H), 1.60 (br p, *J*=7.1 Hz, 2 H), 1.38-1.22 (m, 8H), 1.92-0.80 (m, 3 H), 0.25 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.42, 131.59, 131.52, 131.04, 128.24, 123.35, 122.41, 119.84, 104.49, 95.88, 91.39, 88.21, 35.84, 31.60, 31.11, 28.84, 22.52, 14.03, 0.10. HRMS calcd $C_{25}H_{30}Si$: 358.2117. Found: 358.2109.

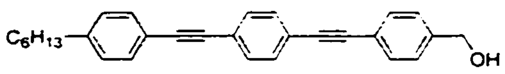


1-(4′-(*n*-Hexyl)-1′-(ethynyl)phenyl)-4-(ethynyl)benzene (AMR-II-11). See the general procedure for the deprotection of a trimethylsilyl-protected alkyne. 1-(4′-(*n*-Hexyl)-1′-(ethynyl)phenyl)-4-(trimethylsilylethynyl)benzene (2.69 g, 7.51 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (5.19 g, 37.53 mmol), methanol (50 mL), and methylene chloride (50 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.



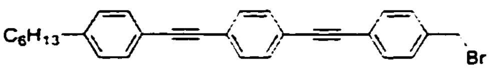
4-(4'-((4''-*n*-Hexyl)-phenylethynyl)-1'-(ethynyl)phenyl)benzaldehyde (16, AMR-II-12). See the general procedure for the Pd/Cu coupling reaction. 1-(4'-(*n*-Hexyl)-1'-(ethynyl)phenyl)-4-(ethynyl)benzene (2.07 g, 7.32 mmol) was coupled to 4-bromobenzaldehyde (1.81 g, 9.76 mmol) as described above using copper(I) iodide (0.17 g, 0.90 mmol), bis(triphenylphosphine)palladium(II) chloride (0.32 g, 0.45 mmol), triphenylphosphine (0.47 g, 1.80 mmol), triethylamine (15.66 mL, 112.65 mmol), and THF (100 mL) in an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar. The reaction mixture was heated to reflux for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride/hexanes (1:1) as the eluent. R_f (product): 0.26. The reaction afforded 2.40 g (81% yield over two steps) of the desired product from 1-(4'-(*n*-Hexyl)-1'-(ethynyl)phenyl)-4-(trimethylsilylethynyl)benzene. IR (KBr) 3148.7, 2923.1, 2851.3, 2205.1, 1697.4, 1594.9, 1517.9, 1384.6, 1302.6, 1205.1, 1159.0, 1117.9, 830.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1 H), 7.86 (d, *J*=8.4 Hz, 2 H), 7.66 (d, *J*=8.5 Hz, 2

H), 7.51 (s, 4 H), 7.43 (d, *J*=8.2 Hz, 2 H), 7.16 (d, *J*=8.2 Hz, 2 H), 2.60 (t, *J*=7.7 Hz, 2 H), 1.64-1.52 (m, 2 H), 1.38-1.24 (m, 8 H), 0.87 (t, *J*=6.6 Hz, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.92, 143.55, 135.26, 131.83, 131.42, 131.28, 129.31, 129.11, 128.25, 123.95, 121.73, 119.76, 92.96, 91.85, 89.95, 88.13, 35.83, 31.58, 31.08, 28.82, 22.50, 13.99. HRMS calcd $C_{29}H_{26}O$: 390.1984. Found: 390.1978.



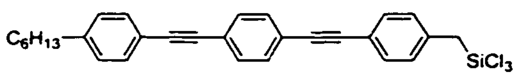
4-(4'-((4''-*n*-Hexyl)-phenylethynyl)-1'-(ethynyl)phenyl)benzyl alcohol (AMR-II-13) To an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar was added 4-(4'-(phenylethynyl)-1'-(ethynyl)-2',5'-diethylphenyl)benzaldehyde (01.30 g, 3.33 mmol) under a N_2 atmosphere. Methylene chloride (75mL) and ethanol (50 mL) were added and the reaction mixture was cooled to 0 °C. Sodium borohydride (0.18 g, 4.66 mmol) was added slowly and the resultant reaction mixture was allowed to for 30 min then was refluxed for 30 min. Upon completion of the reaction, the reaction mixture was quenched with water. The organic layer was diluted with methylene chloride and washed with water (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo. The desired material was purified by multiple hexane washes to afford 1.14 g (87 % yield) of the desired compound. IR (KBr) 3200.0, 2953.8, 2256.4, 1769.2, 1717.9, 1635.9, 1384.6, 1184.6, 1061.5, 1000.0, 9288.2, 835.9, 467.1 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J*=8.5 Hz, 2 H), 7.50 (s, 4 H), 7.45 (d, *J*=8.2 Hz, 2 H), 7.36 (d, *J*=8.2 Hz, 2 H), 7.17 (d, *J*=8.4

Hz, 2 H), 4.73 (s, 2 H), 2.62 (t, J=7.5 Hz, 2 H), 1.65-1.48 (m, 2 H), 1.31 (br s, 8 H), 0.90-0.80 (m, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.72, 141.15, 131.79, 131.52, 131.49, 131.46, 128.50, 126.84, 123.36, 122.78, 122.31, 120.09, 91.54, 90.92, 89.24, 88.46, 64.98, 35.93, 31.68, 31.19, 28.91, 22.59, 14.09. HRMS calcd $C_{29}H_{28}O$: 392.2140. Found: 392.2134.



4-(4'-((4''-*n*-Hexyl)phenylethynyl)-1'-(ethynyl)phenyl)benzyl bromide (17, AMR-II-23, 48, 53). To an oven dried round bottom flask equipped with a West condenser and a magnetic stirbar was added 4-(4'-((4''-*n*-hexyl)phenylethynyl)-1'-(ethynyl)phenyl)benzyl alcohol (0.20 g, 0.51 mmol). The vessel was capped under a N_2 atmosphere, THF (10 mL) were added. Pyridine (0.20 mL, 2.55 mmol) and mesyl chloride (0.06 mL, 0.77 mmol) was added and the resultant mixture was allowed to stir at ambient temperature for 4 h. Sodium bromide (0.35 g, 2.70 mmol) and acetone (5 mL) were added to the reaction mixture. The reaction mixture was then allowed to reflux for 12 h. Upon completion of the reaction, the reaction mixture was then quenched with water. The organic layer was diluted with methylene chloride and washed with water (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo. ^{1}H NMR showed mostly benzyl chloride; therefore, the material was placed in an oven dried round bottom flask equipped with a stirbar and a West condenser. Sodium bromide (0.14 g, 1.35 mmol) and acetone (5 mL) were added and allowed to heat to reflux for 12 h.

Upon completion of the reaction, the reaction mixture was then quenched with water. The organic layer was diluted with methylene chloride and washed with water (3×). The combined aqueous layers were extracted with methylene chloride (2×). The combined organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. No further purification was needed. The reaction afforded 0.16 g (70 % yield) of the desired product. IR (KBr) 3122.2, 2922.2, 2855.6, 1383.3, 1116.7, 833.3, 600.0, 522.2, 450.0 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.58-7.52 (m, 6 H), 7.46 (d, *J*=8.3 Hz, 2 H), 7.42 (d, *J*=8.4 Hz, 2 H), 7.21 (d, *J*=8.1 Hz, 2 H), 4.54 (s, 2 H), 2.64 (t, *J*=7.7 Hz, 2 H), 1.68-1.46 (m, 2 H), 1.40-1.26 (m, 8 H), 0.90 (t, *J*=6.8 Hz, 3 H). ^{13}C NMR (400 MHz, CD_2Cl_2) δ 141.40, 135.01, 134.76, 134.65, 134.56, 134.54, 132.29, 131.70, 129.91, 126.65, 125.76, 123.08, 94.74, 93.69, 92.98, 91.41, 39.14, 36.41, 34.98, 34.54, 32.23, 25.91, 17.17. HRMS calcd $C_{29}H_{27}Br$: 454.1296. Found: 454.1302.



4-(4'-((4''-*n*-Hexyl)phenylethynyl)-1'-(ethynyl)phenyl)benzyl bromide (18, AMR-II-41, 53, 63). To a flame dried 100 mL round bottom flask equipped with a magnetic stirbar solids 4-(4'-((4''-*n*-Hexyl)phenylethynyl)-1'-(ethynyl)phenyl)benzyl bromide (0.11 g, 0.24 mmol) and copper iodide (0.01 g, 0.01 mmol) were added and air removed and nitrogen backfilled (3×). The solids were dissolved in methylene chloride (10 mL) and cooled to 0 °C for 5 min. Then triethylamine (0.10 mL, 0.93 mmol) followed by freshly distilled trichlorosilane (0.10 mL, 0.93 mmol) were added. The reaction mixture was allowed to sitr at room temperature for 2 d. The solvents in the reaction mixture were removed in vacuo. Solid material was dissolved in diethylether and transferred via syringe filtration with celite to another dry flask. Solvent removed in vacuo. Material determined to be insoluble in numerous solvents and the extreme reactivity of the trichlorosilane derivative did not allow for characterization.

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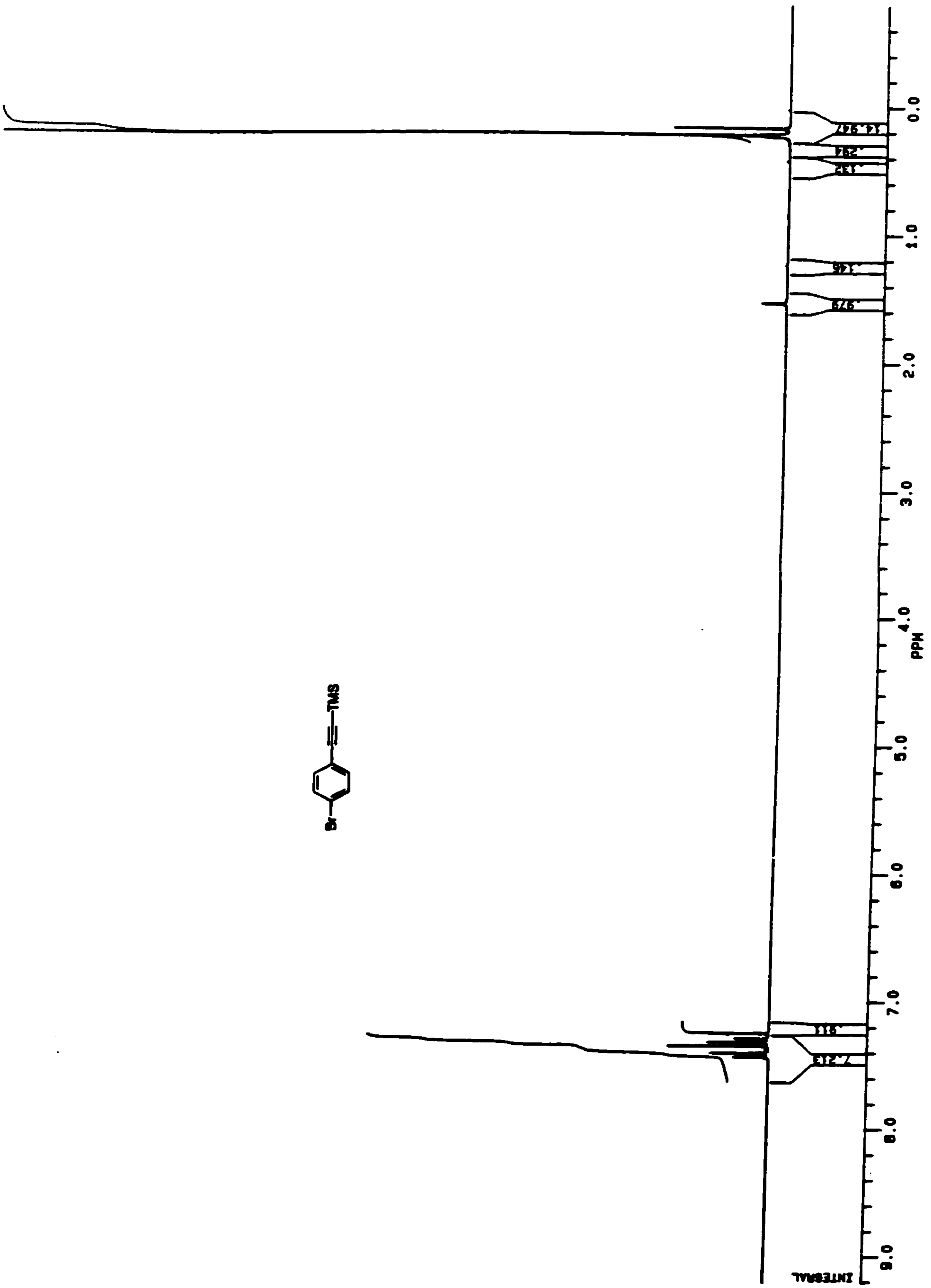
Spectral Section for

Chapter 3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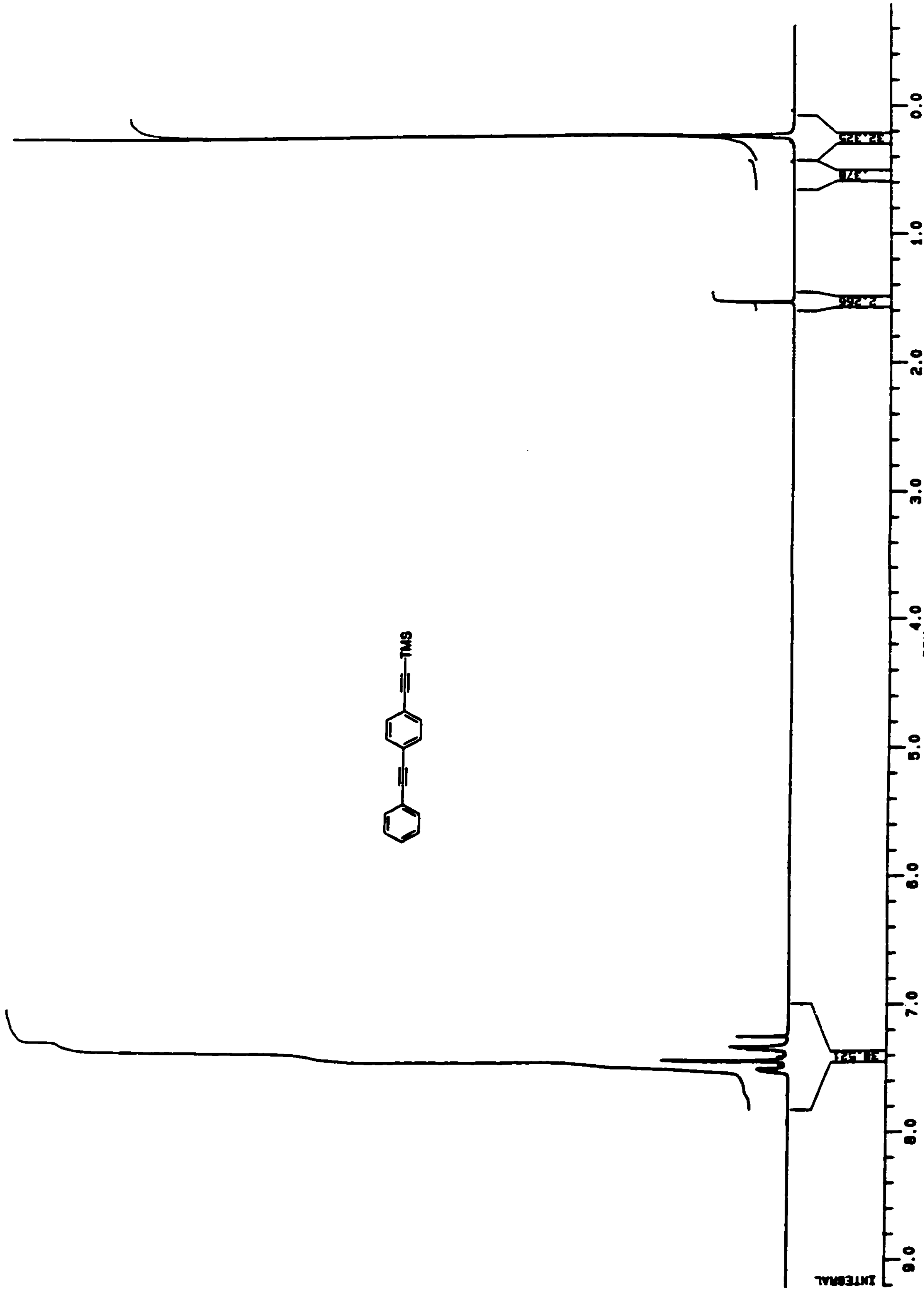
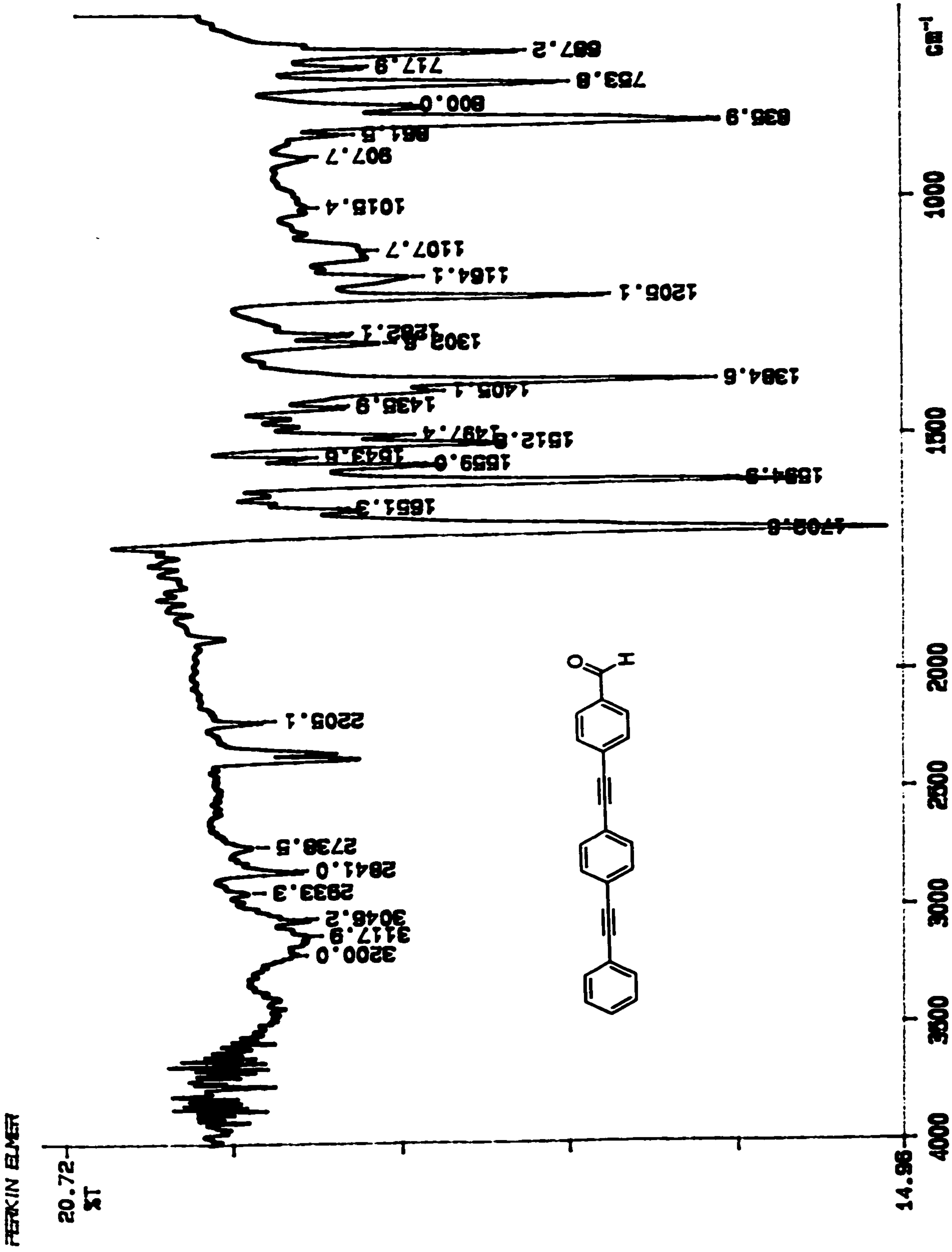
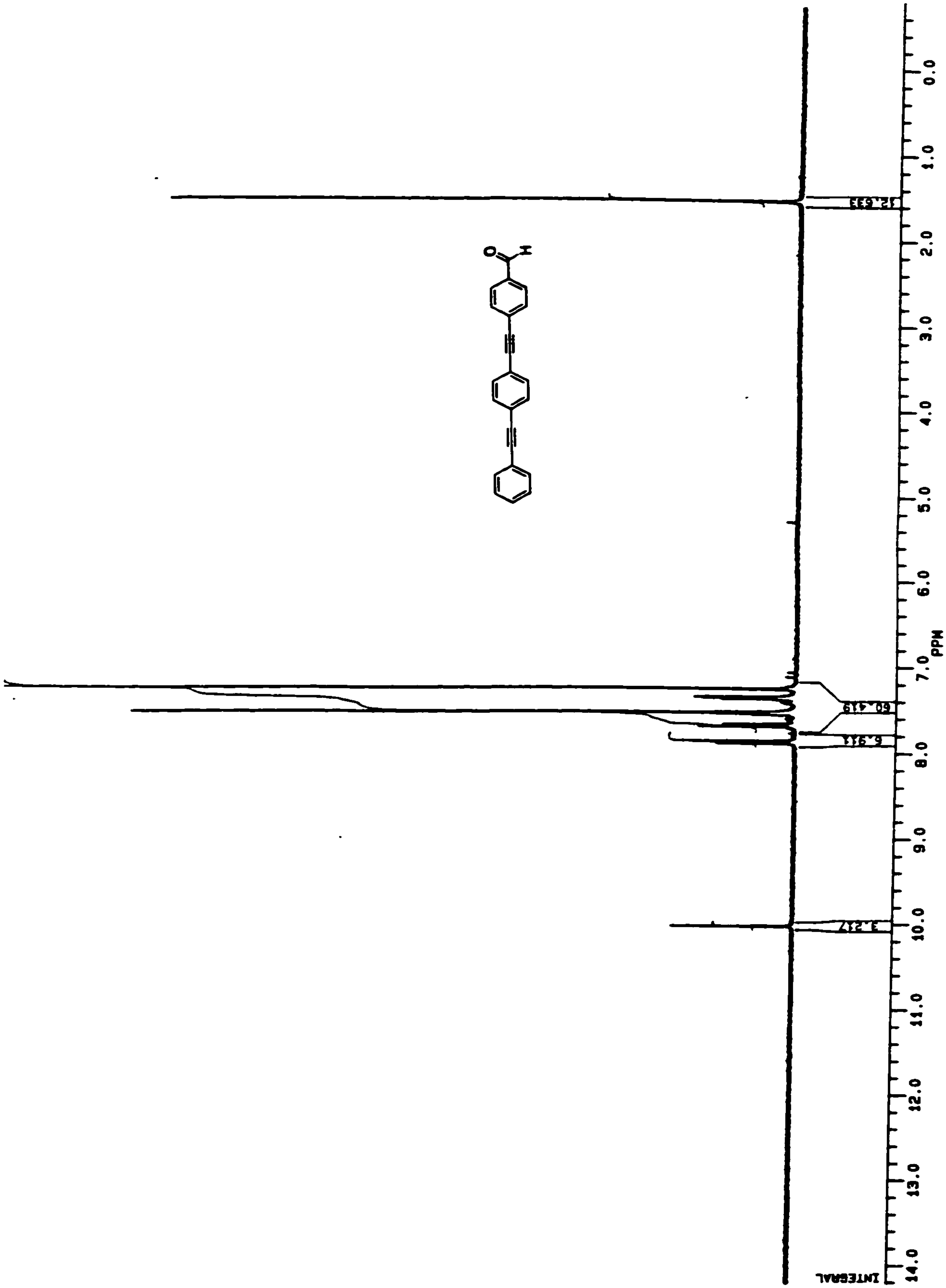
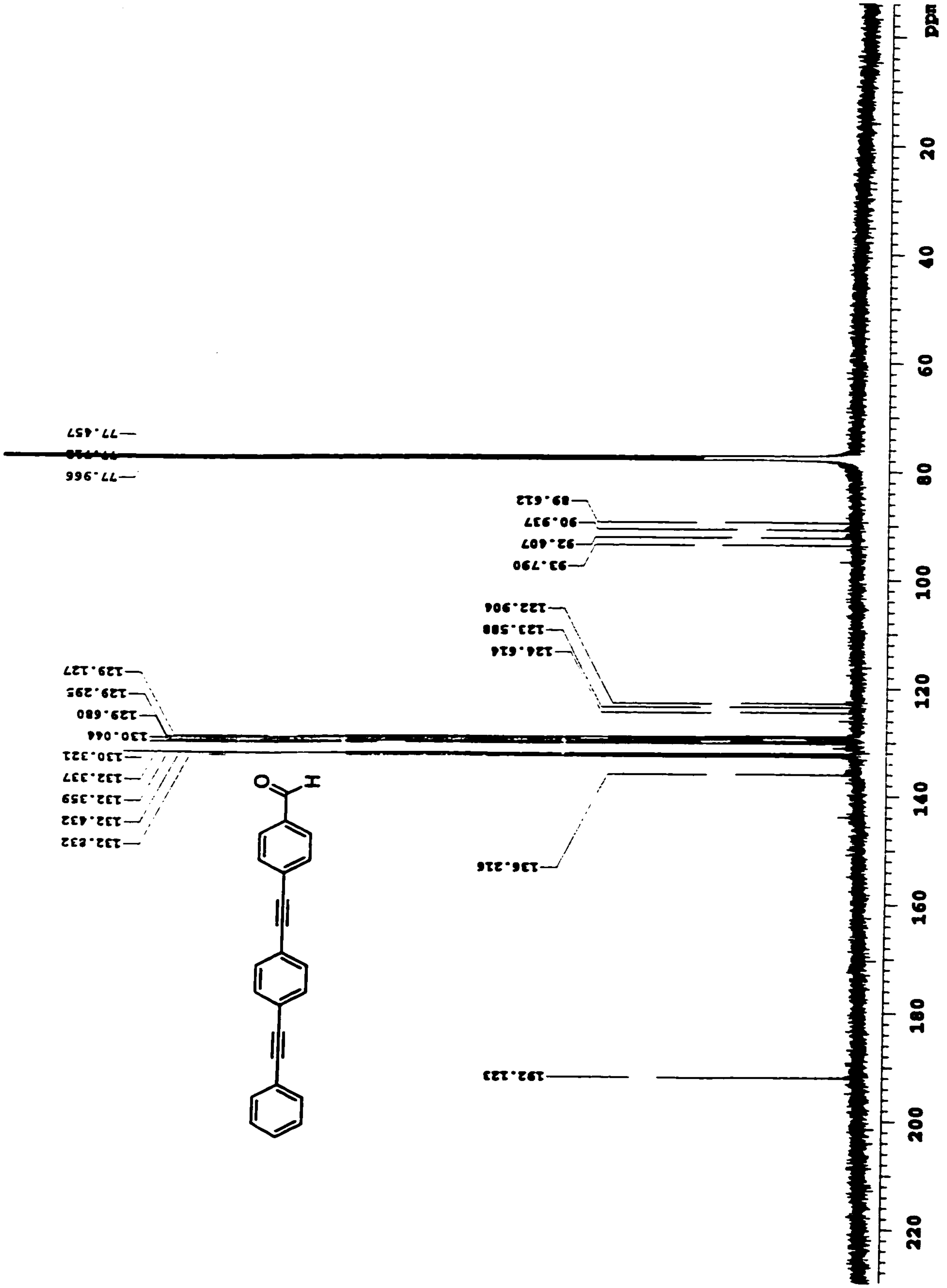
8.0
9.0

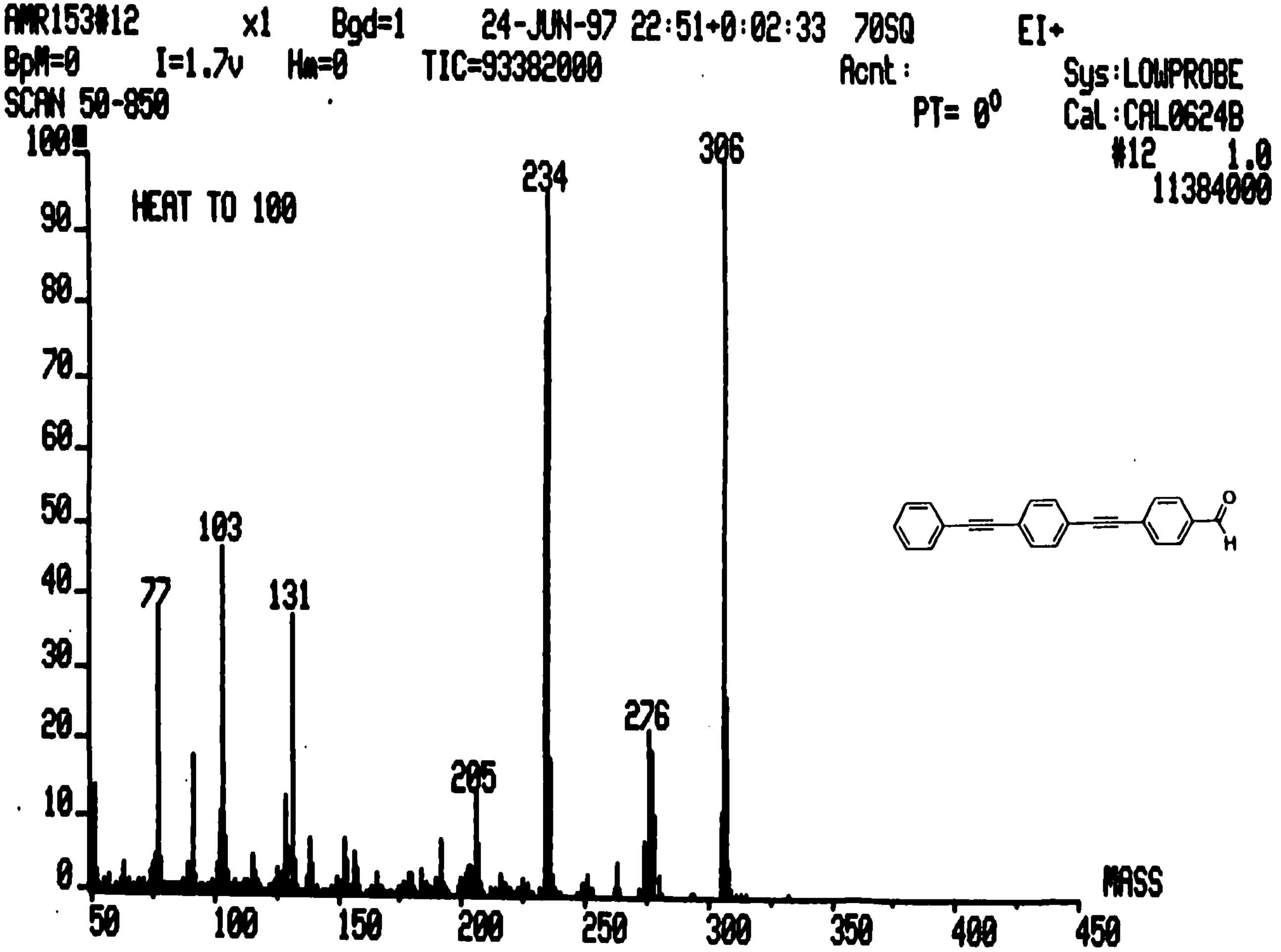

TMS
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
INTEGRAL
32.325
.378
2.266
38.521


PERKIN ELMER
20.72
%T
14.96
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3200.0
3117.9
3048.2
2933.3
2841.0
2738.5
2205.1
1702.6
1651.3
1594.9
1559.0
1543.6
1512.8
1497.4
1435.9
1405.1
1384.6
1302.6
1282.1
1205.1
1164.1
1107.7
1015.4
907.7
861.5
835.9
800.0
753.8
717.9
687.2
H
O



0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
PPM
8.0
9.0
10.0
11.0
12.0
13.0
14.0
INTEGRAL
12.633
60.419
6.913
3.217
O
H


ppm
20
40
60
80
100
120
140
160
180
200
220
77.457
77.966
89.613
90.937
92.607
93.790
122.906
123.588
124.614
129.127
129.295
129.680
130.046
130.331
132.337
132.359
132.432
132.832
136.216
192.133
H
O

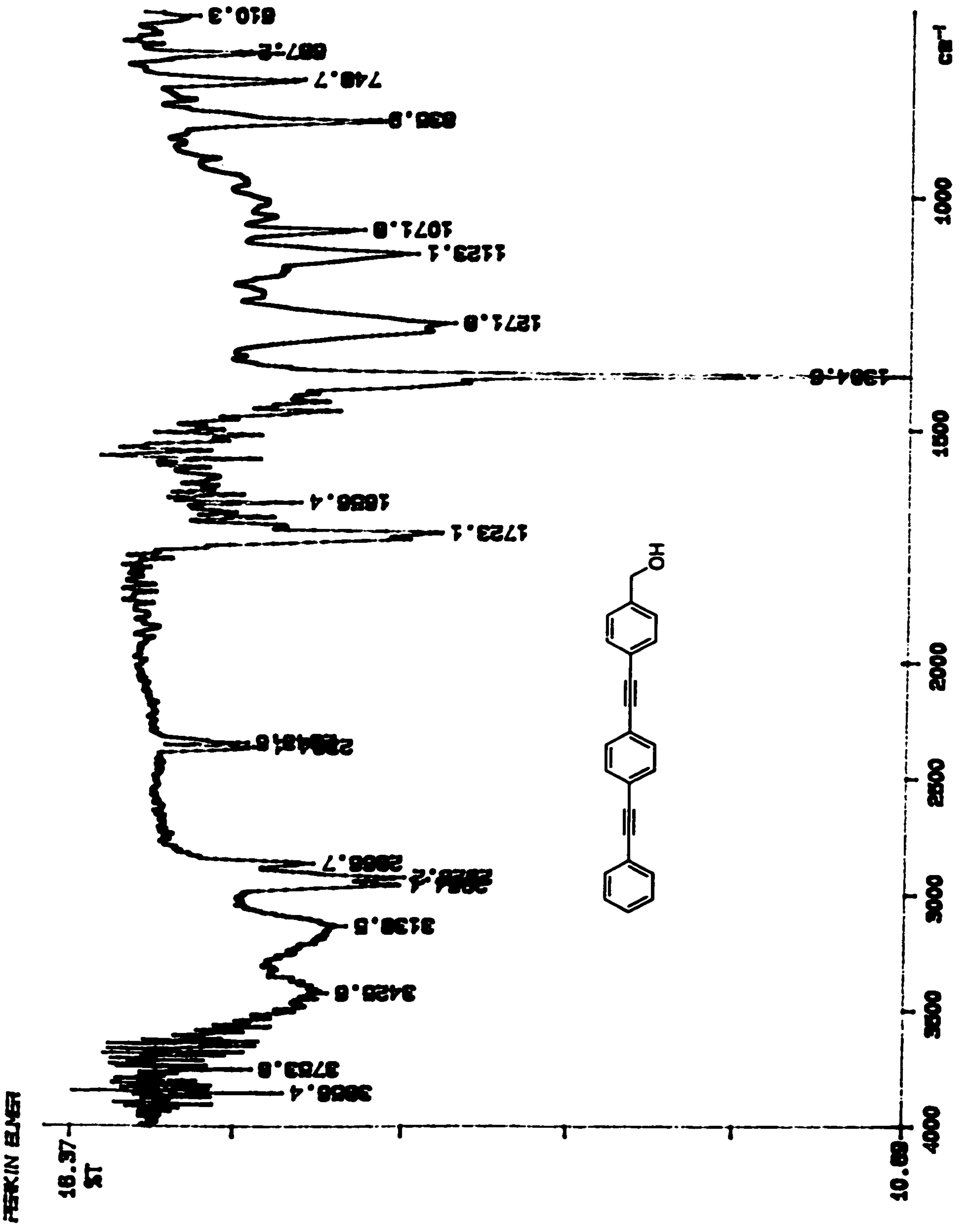


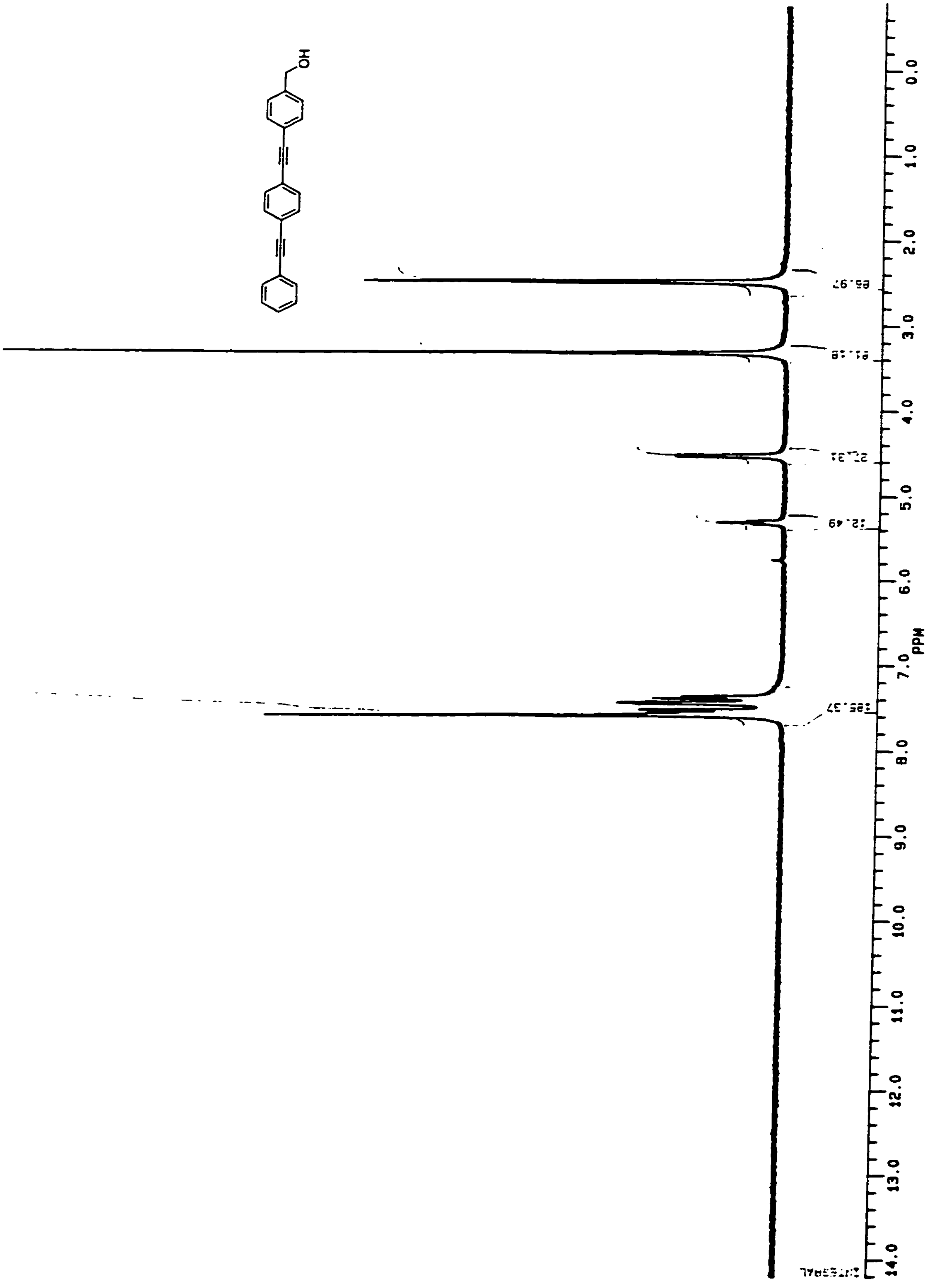
H: Res 7/18

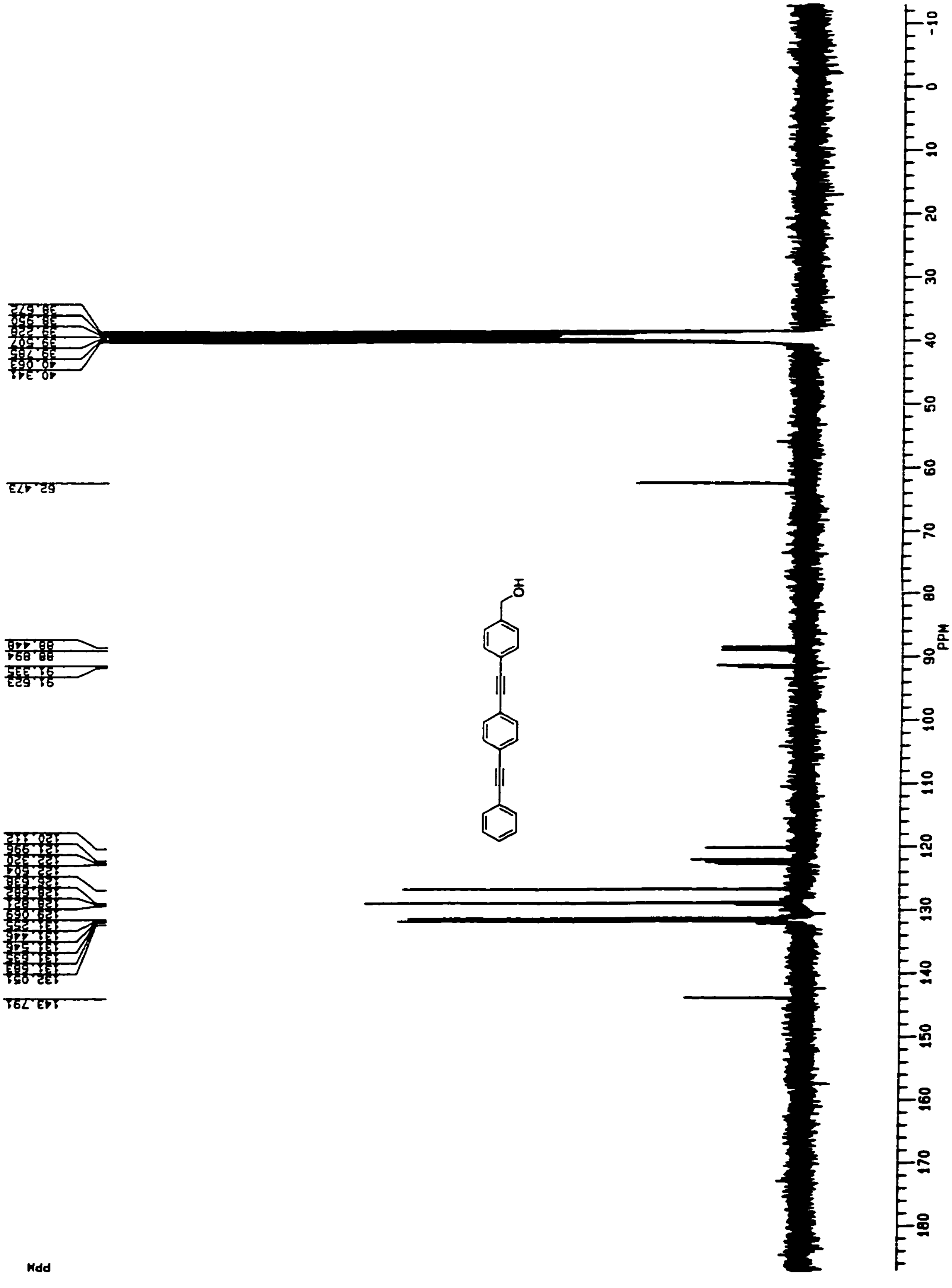
obs mass = 306.1037

$C_{23}H_{14}O$ = 306.1044

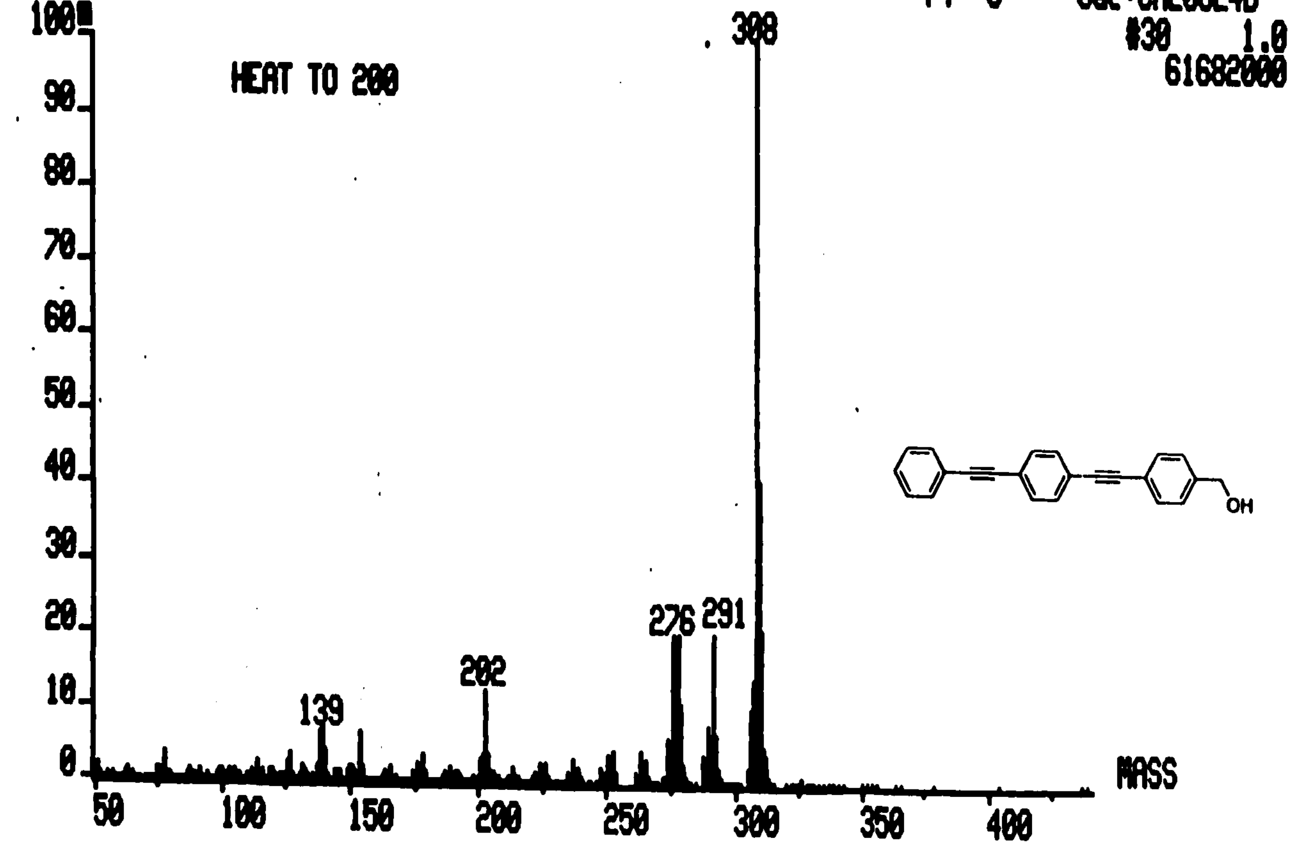
E = 2.3 ppm


PERKIN ELMER
16.37
%T
10.88
4000
3500
3000
2500
2000
1500
1000
cm-1
610.3
697.2
748.7
835.9
1071.8
1123.1
1271.8
1384.6
1656.4
1723.1
2284.6
2868.7
2923.2
2954.4
3138.5
3425.6
3753.8
3858.4
HO


OH
86.97
81.18
25.31
12.49
185.37
INTEGRAL
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0


38.672
38.950
39.228
39.507
39.785
40.063
40.341
62.473
88.448
88.894
91.335
91.623
120.112
121.996
122.320
122.604
126.618
128.584
128.874
129.059
131.225
131.446
131.547
131.635
131.683
132.051
143.791
PPM
OH
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
PPM

```
AMR159#30      x1    Bgd=21    24-JUN-97 22:59+0:06:16  70SQ        EI+
BpM=0     I=9.4v   Hm=0     TIC=321492992              Acnt:         Sys:LOWPROBE
SCAN 50-850                                                  PT= 0⁰    Cal:CAL0624B
                                                                        #30     1.0
                                                                          61682000
```



H: Res 7/18

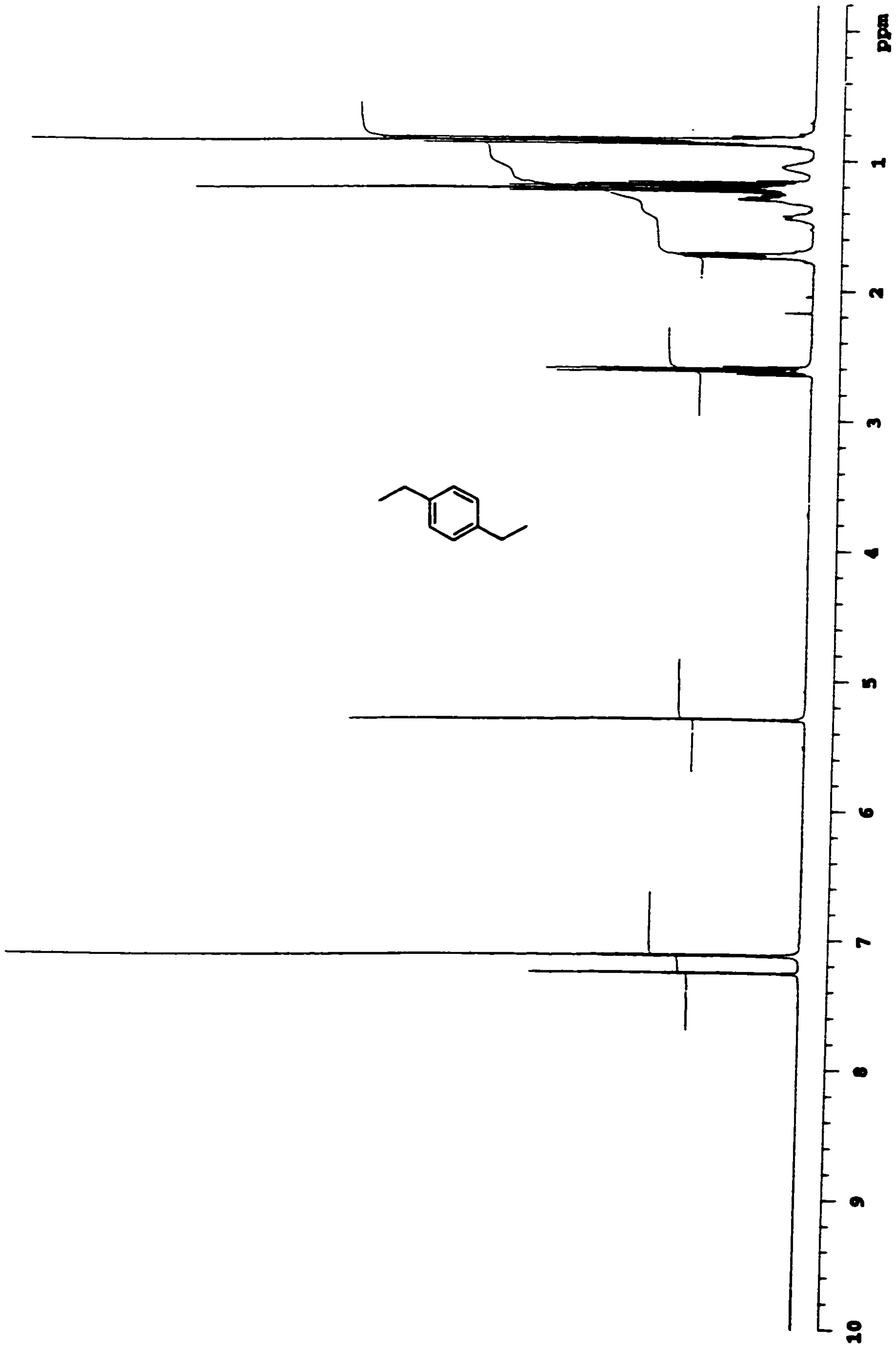
obs mass = 30~~8.11~~83

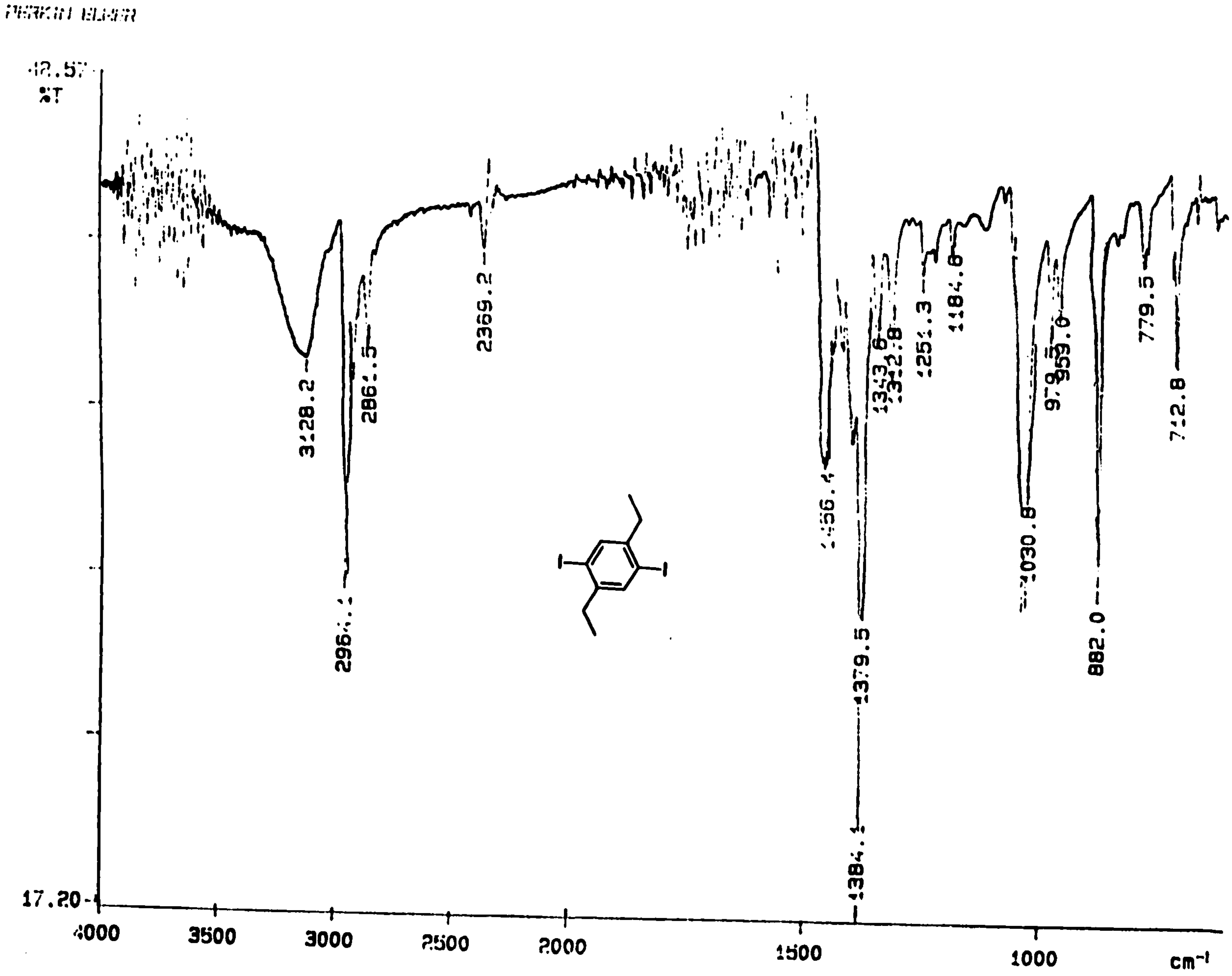
$C_{23}H_{16}O$ = 308.1201

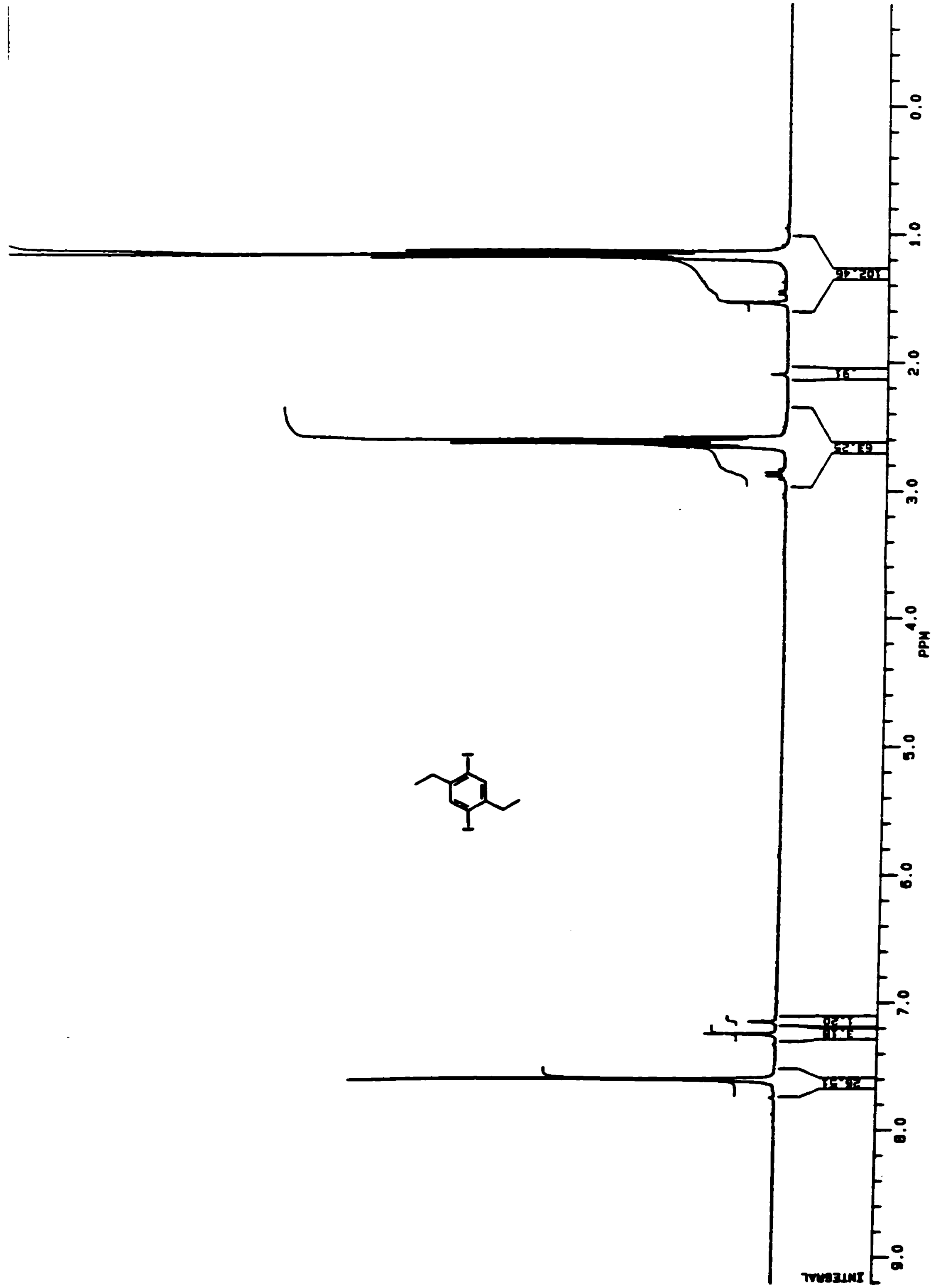
E = 5.~~8~~ ppm

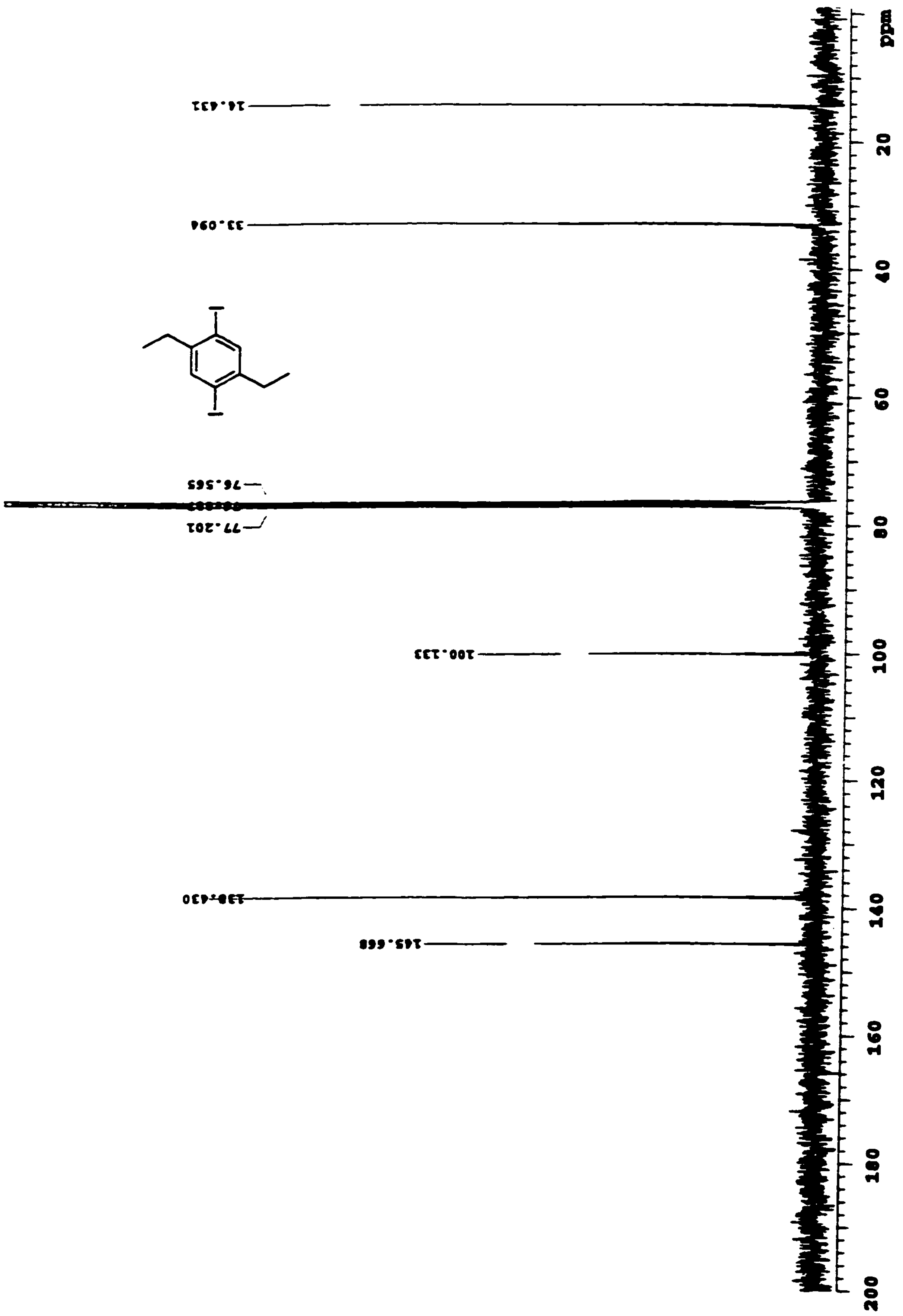
try 2 308.1212

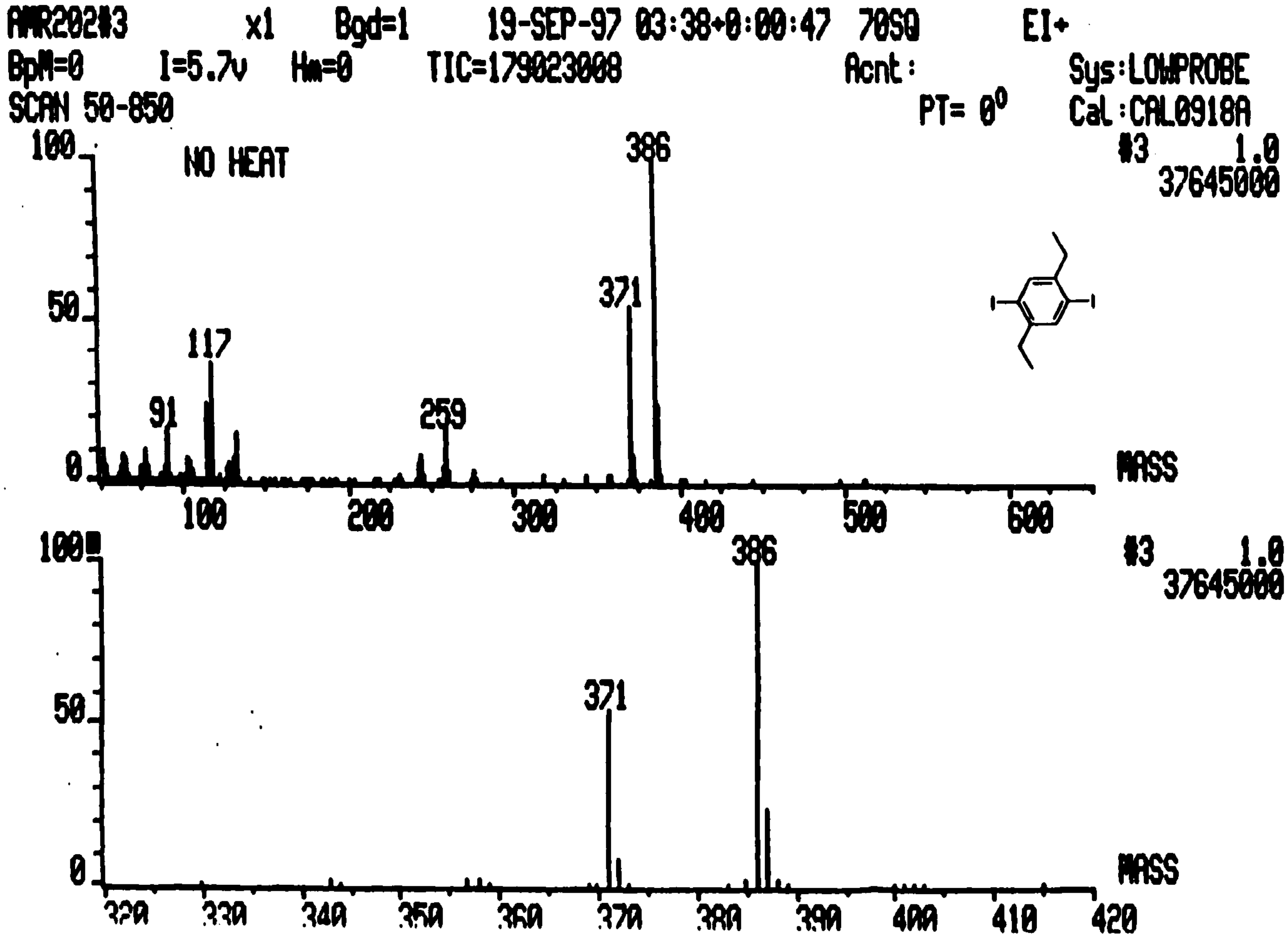
E = 3.6


ppm
1
2
3
4
5
6
7
8
9
10


PERKIN ELMER
42.57
%T
17.20
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3128.2
2964.1
2861.5
2369.2
1456.4
1384.1
1379.5
1343.6
1312.8
1254.3
1184.8
1030.8
979.5
959.0
882.0
779.5
742.8


102.45
.91
63.25
1.20
1.18
26.51
INTEGRAL
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0

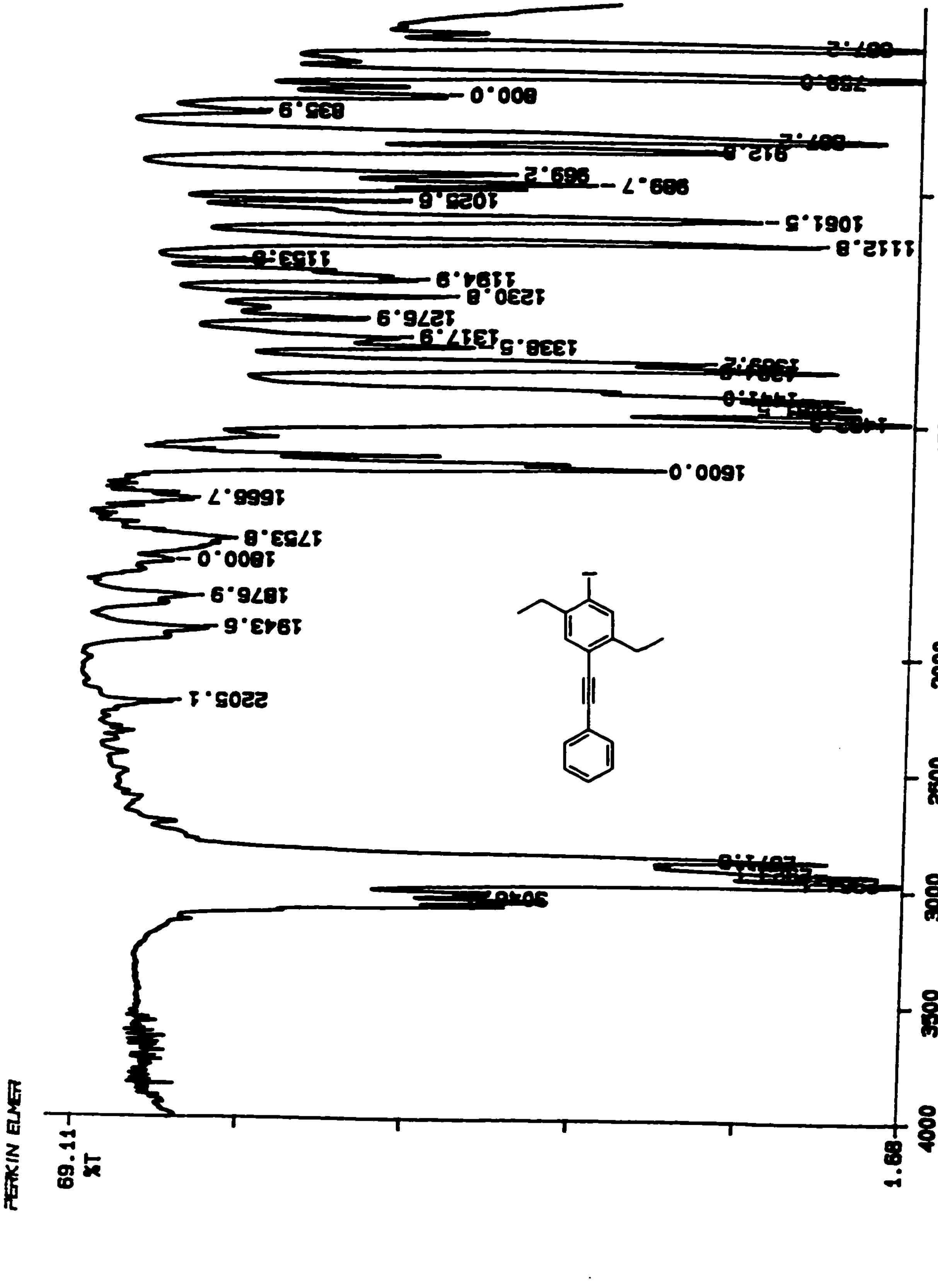

14.431
33.094
76.565
77.201
100.133
138.430
145.668
ppm
20
40
60
80
100
120
140
160
180
200

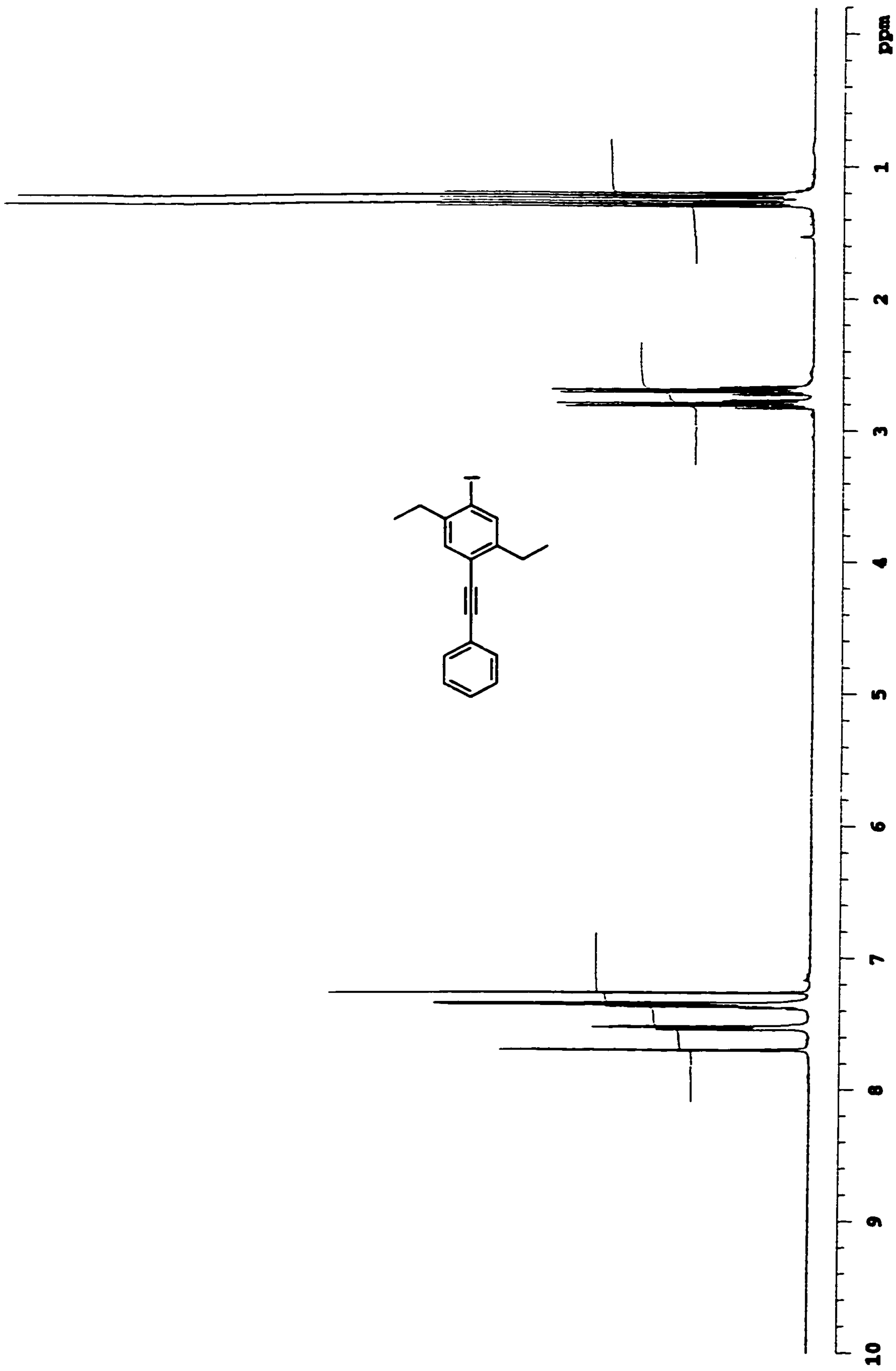


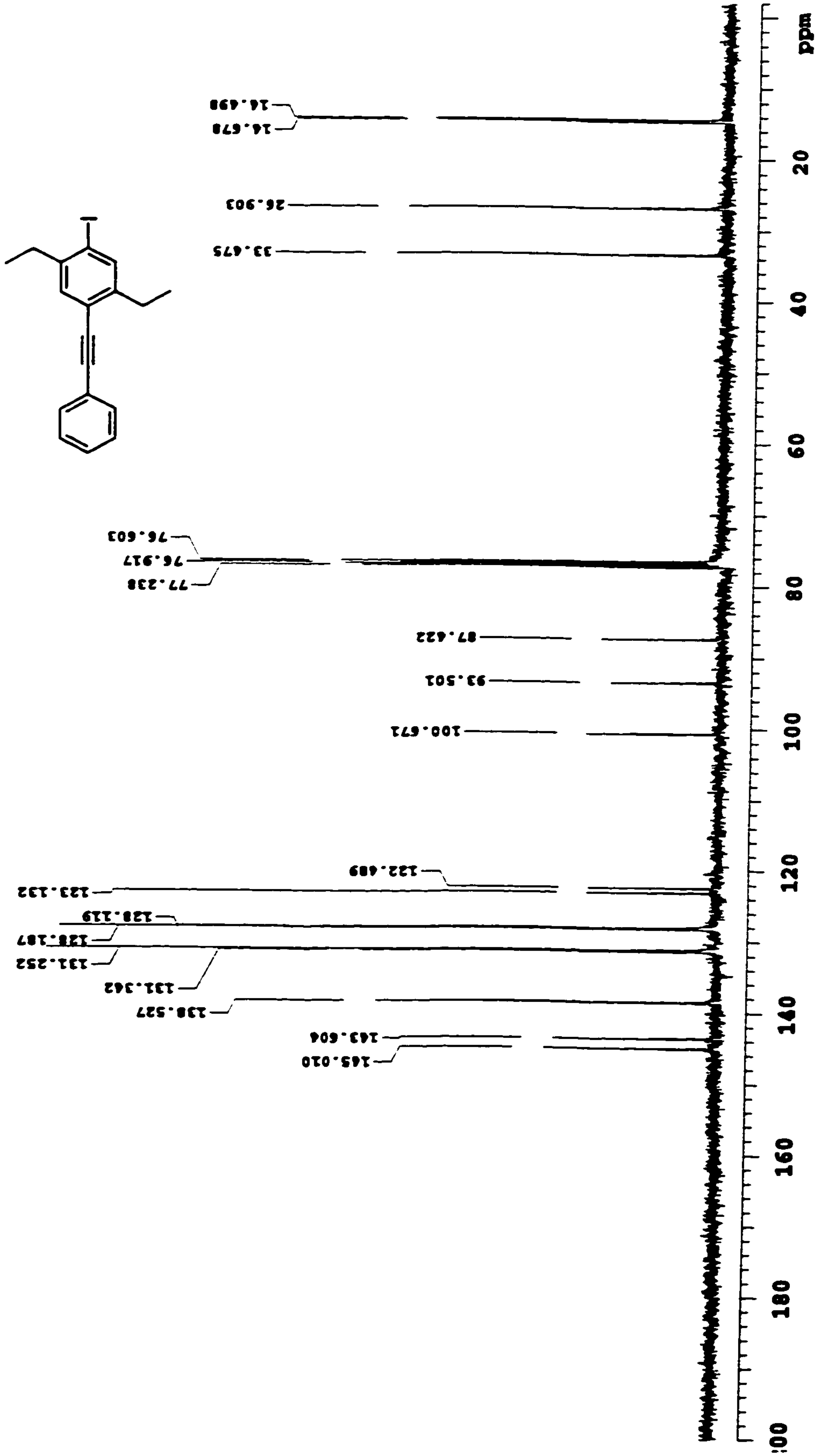
Accurate Mass
1/23

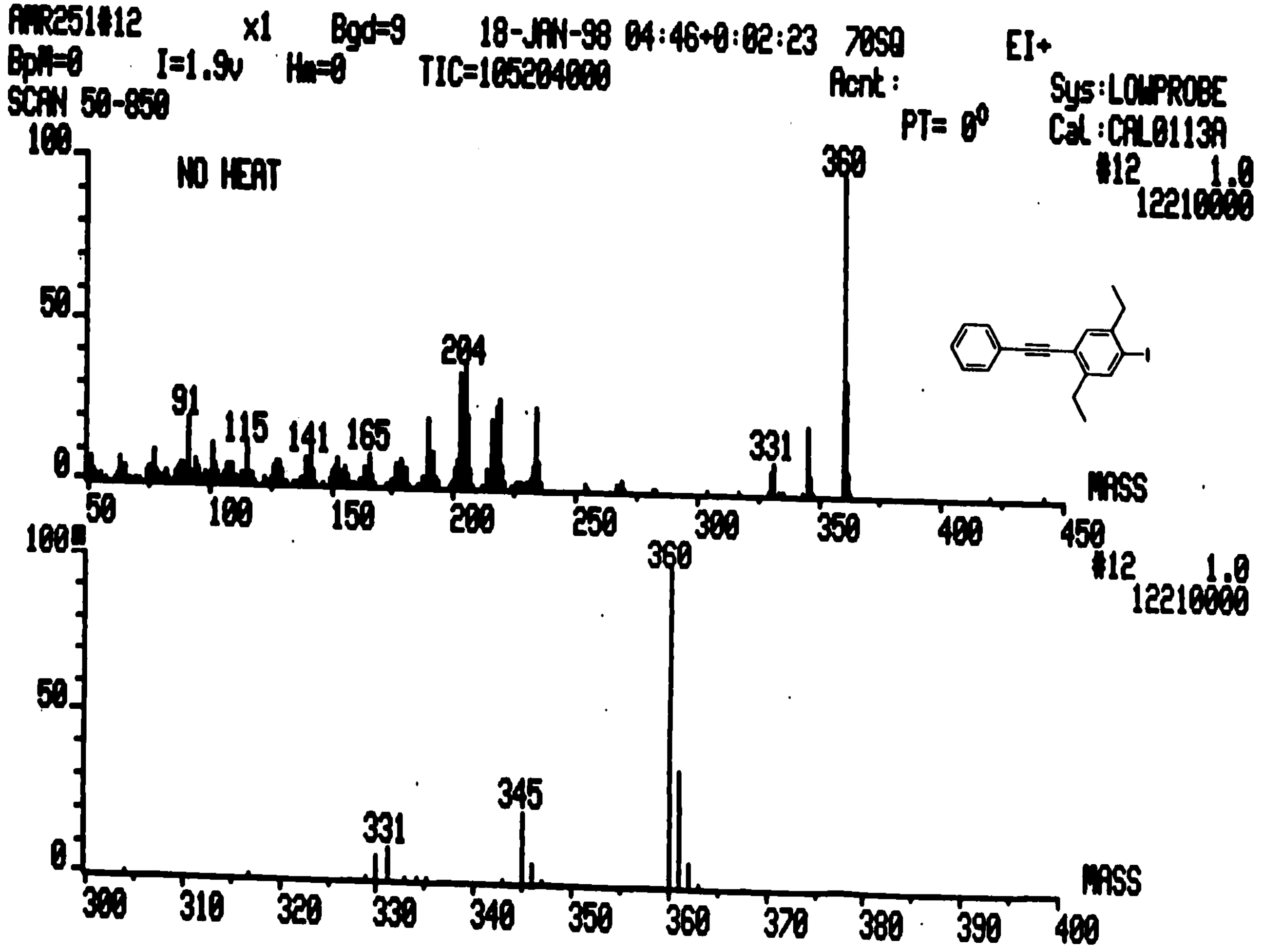
observ. mass = 385.9027
calc mass = 385.9029
$C_{10}H_{12}I_2$

Error 0.5 ppm


PERKIN ELMER
69.11
%T
1.68
4000
3500
3000
2500
2000
1500
1000
cm-1
2205.1
1943.6
1876.9
1800.0
1753.8
1666.7
1600.0
1441.0
1384.6
1369.2
1338.5
1317.9
1276.9
1230.8
1194.9
1153.6
1112.8
1061.5
1025.6
989.7
969.2
912.8
897.2
835.9
800.0
758.0
687.2


ppm
1
2
3
4
5
6
7
8
9
10
I

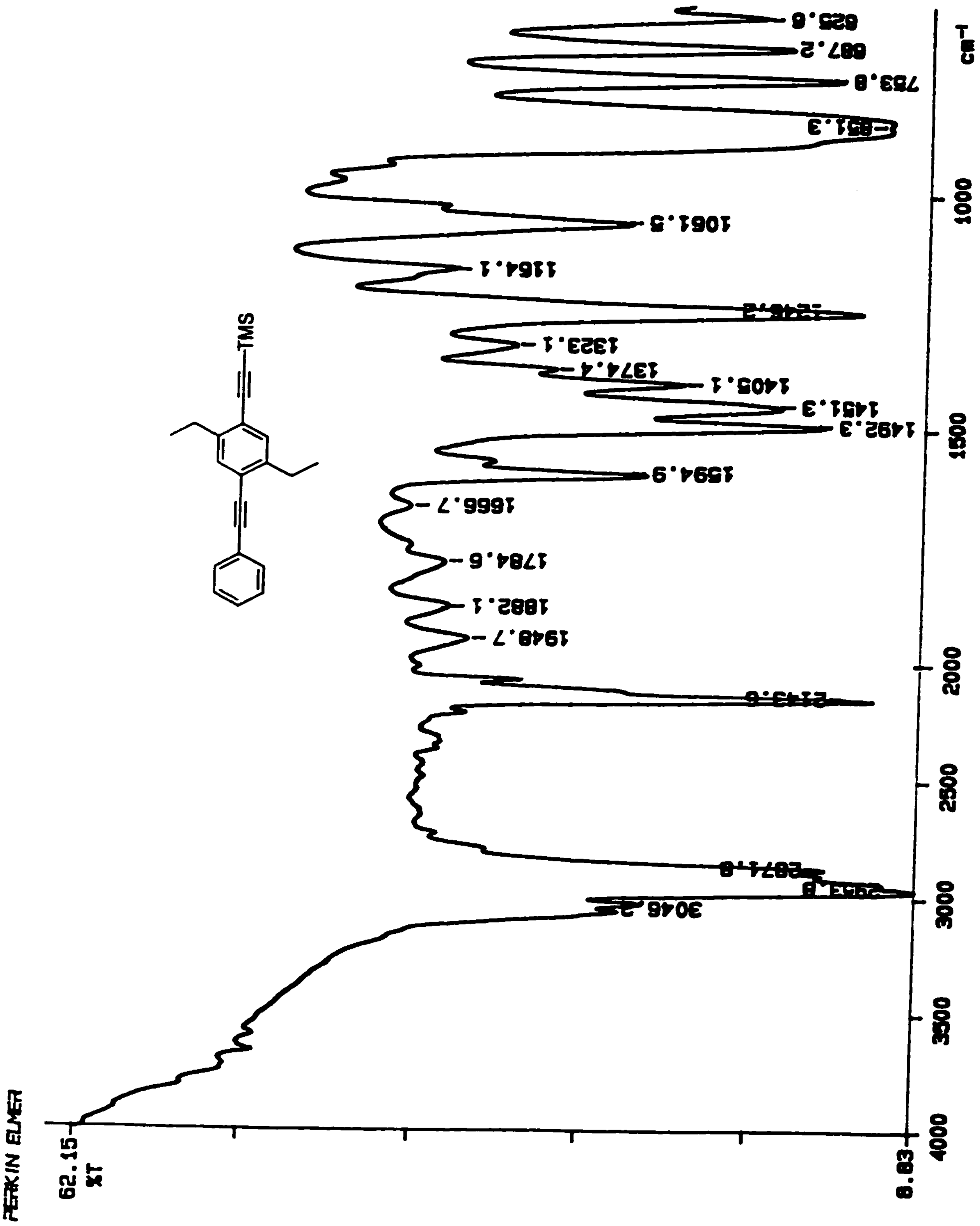

14.498
14.678
26.903
33.675
76.603
76.917
77.238
87.422
93.501
100.671
122.489
123.132
128.119
128.187
131.252
131.342
138.527
143.604
145.010
ppm
20
40
60
80
100
120
140
160
180
200

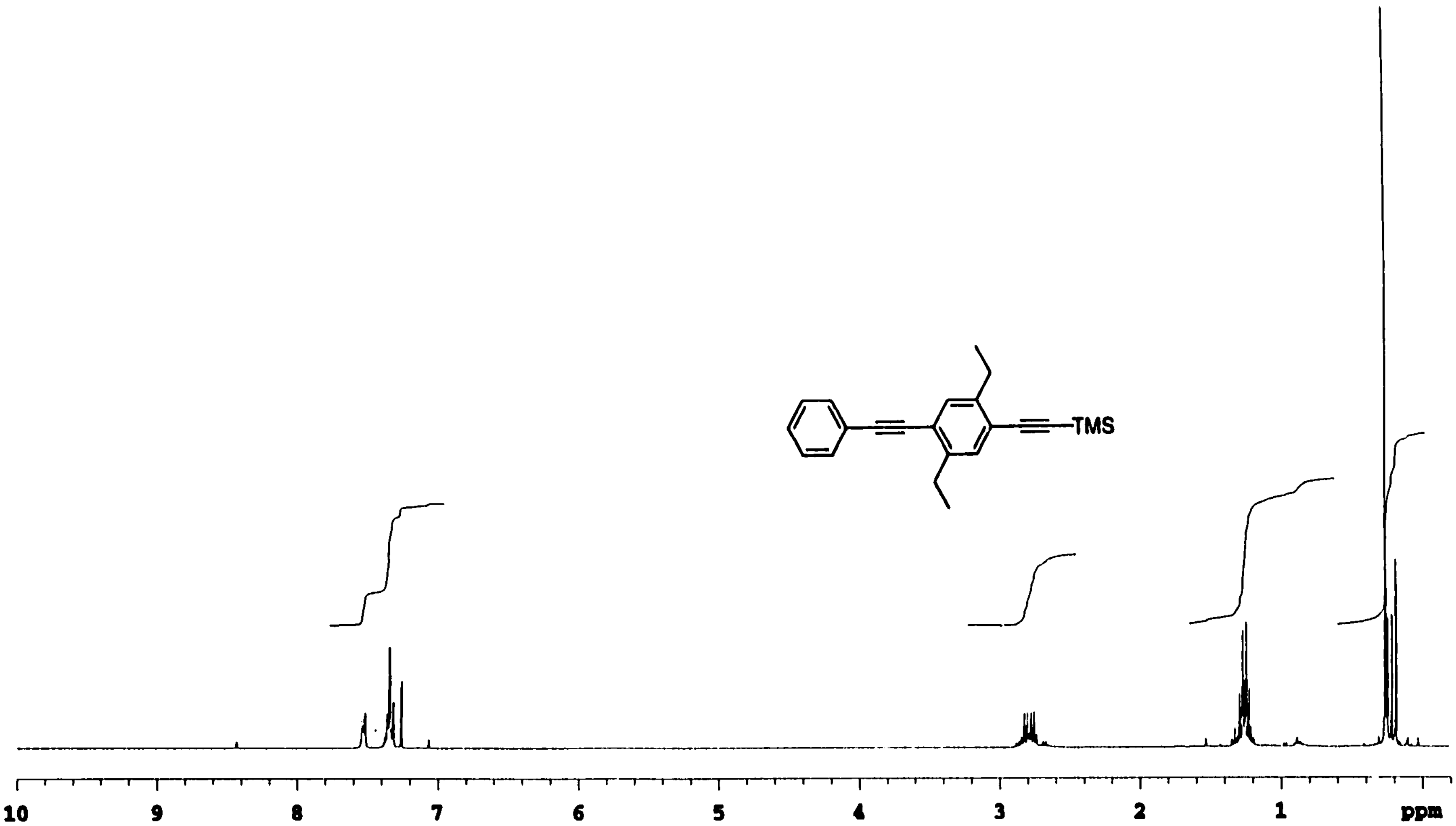


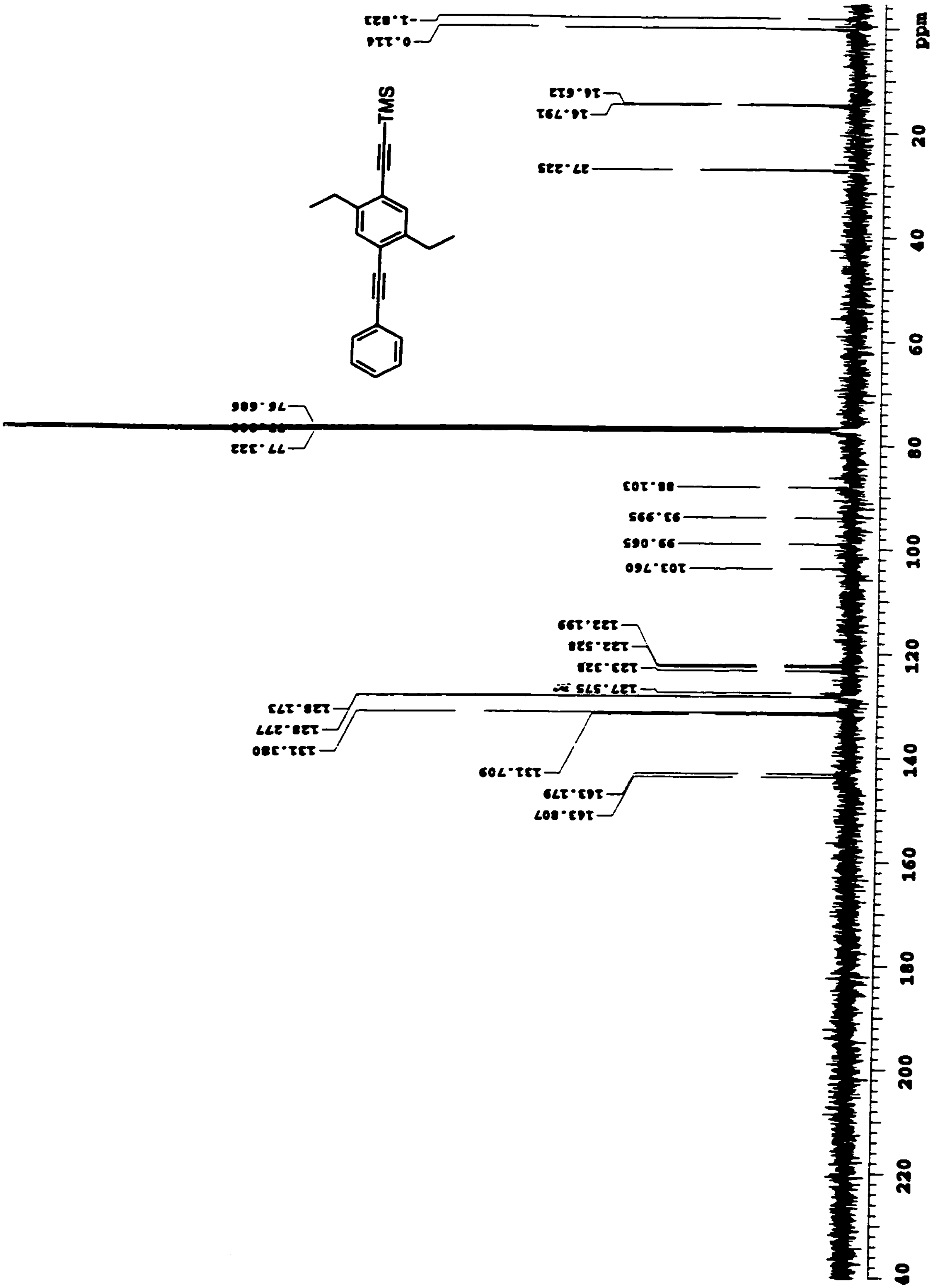
Exact Mass
1/27

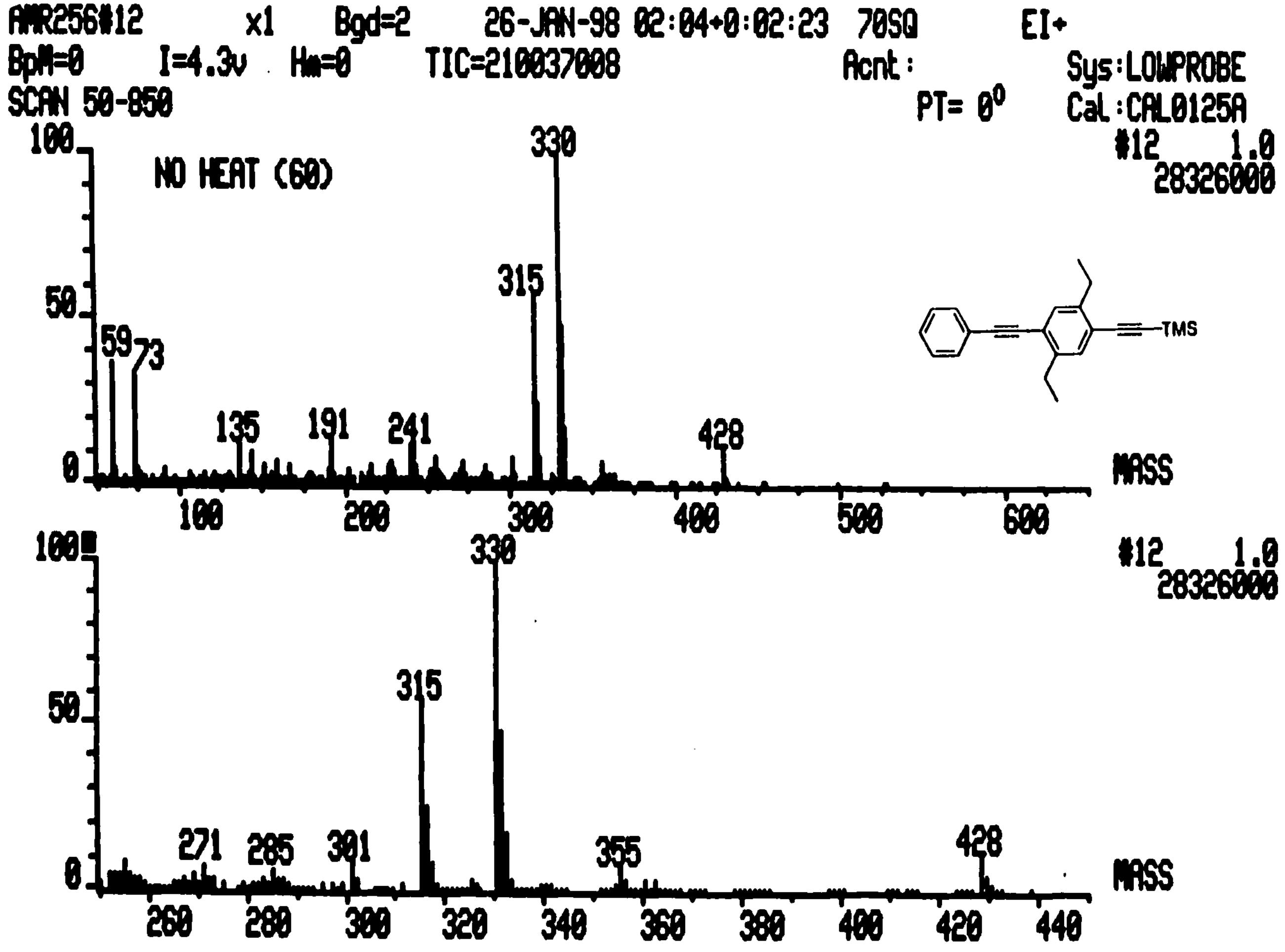
obsv. mass = 360.0375
Calc mass = 360.0375
$C_{18}H_{17}I$

Error = 0 ppm


PERKIN ELMER
62.15
%T
8.83
4000
3500
3000
2500
2000
1500
1000
cm-1
3046.2
2953.8
2874.8
2143.6
1948.7
1882.1
1784.6
1666.7
1594.9
1492.3
1451.3
1405.1
1374.4
1323.1
1246.2
1164.1
1061.5
851.3
753.8
687.2
625.6
TMS


TMS
10
9
8
7
6
5
4
3
2
1
ppm


TMS
-1.833
0.114
14.613
14.791
27.225
76.686
77.000
77.333
88.103
93.995
99.065
103.760
122.199
122.528
123.328
127.575
128.173
128.277
131.380
131.709
143.179
143.807
ppm
20
40
60
80
100
120
140
160
180
200
220
40

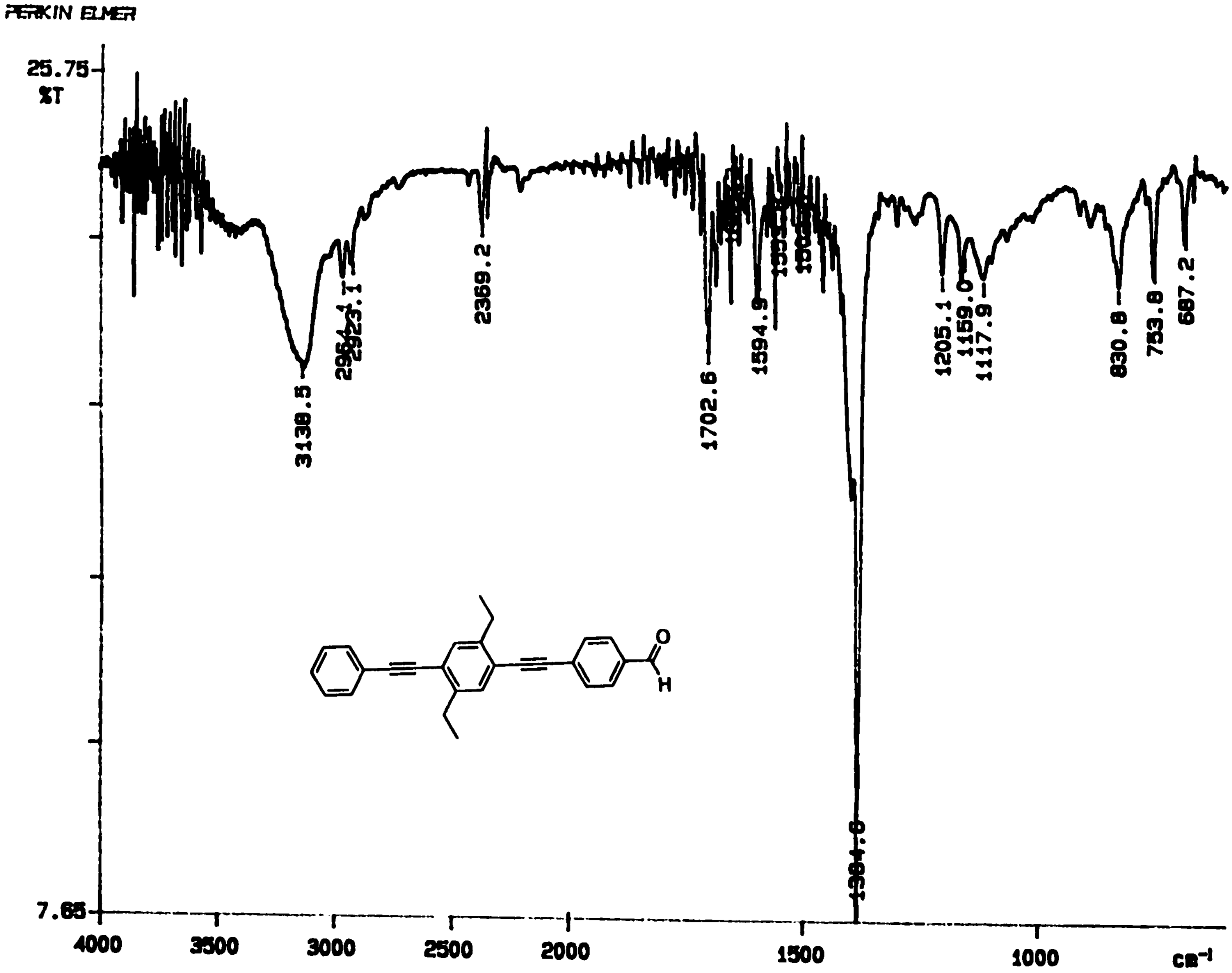


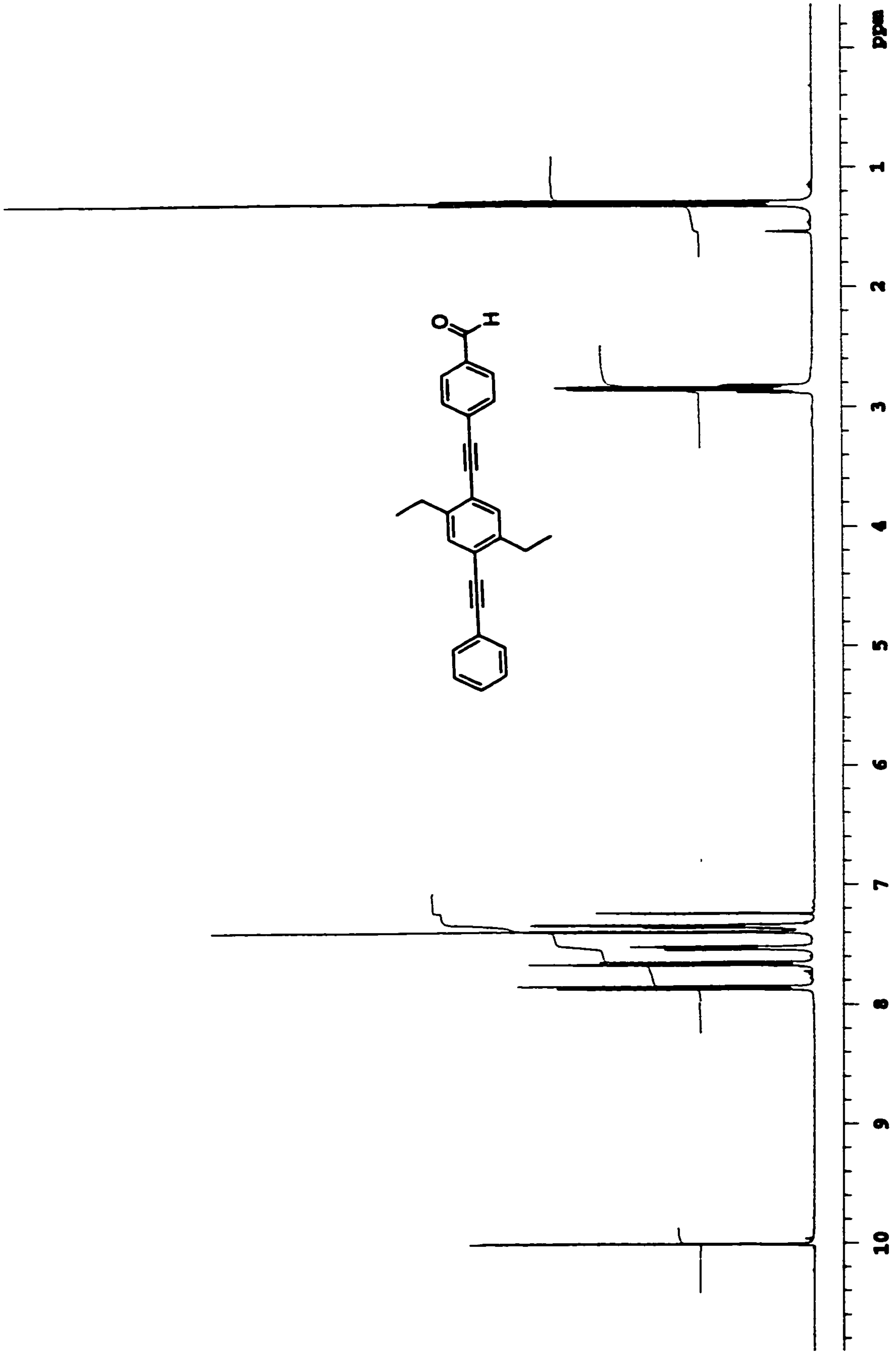
H. Res 1/24

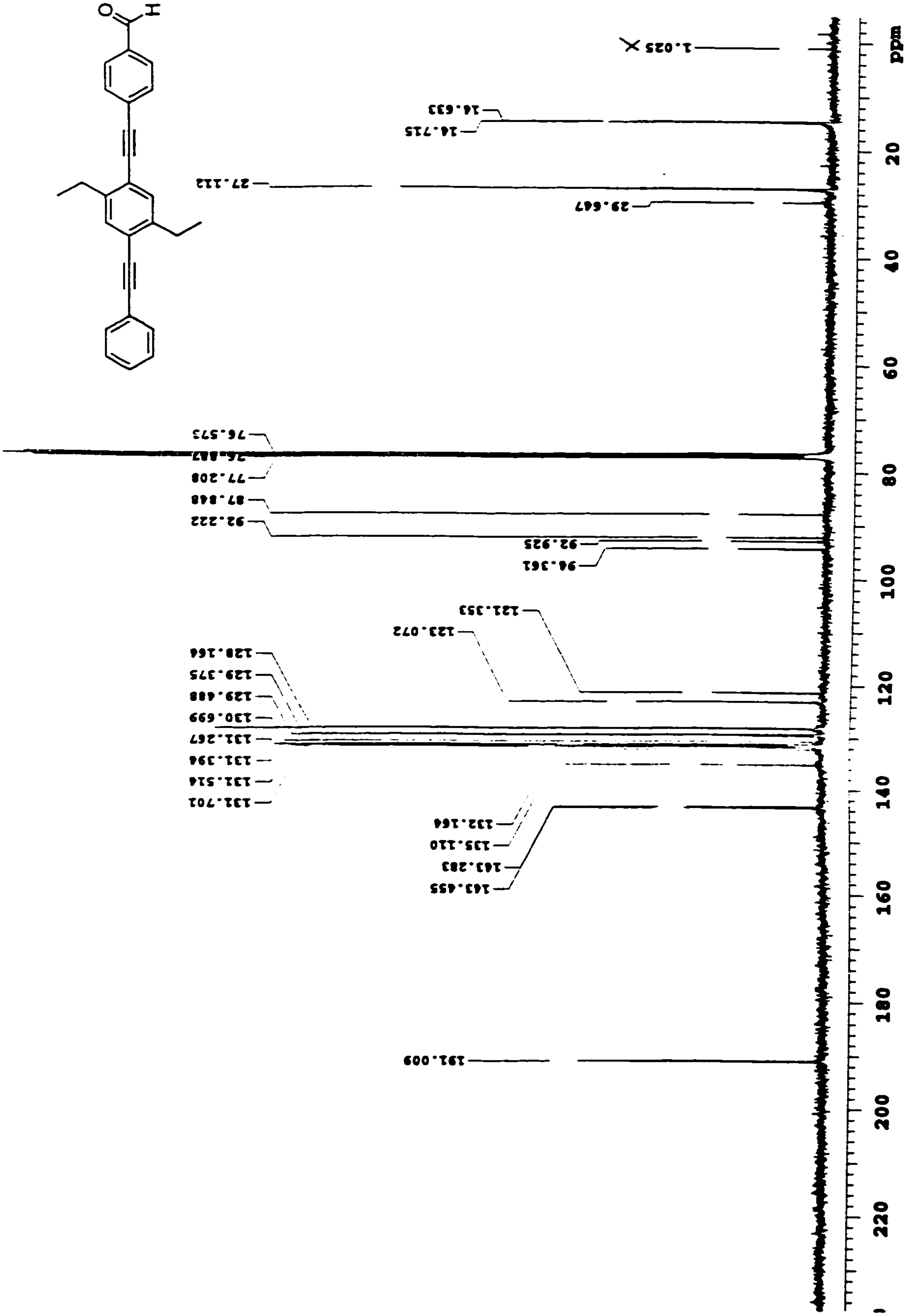
obs mass = 330.1807

$C_{23}H_{26}Si$ = 330.1804

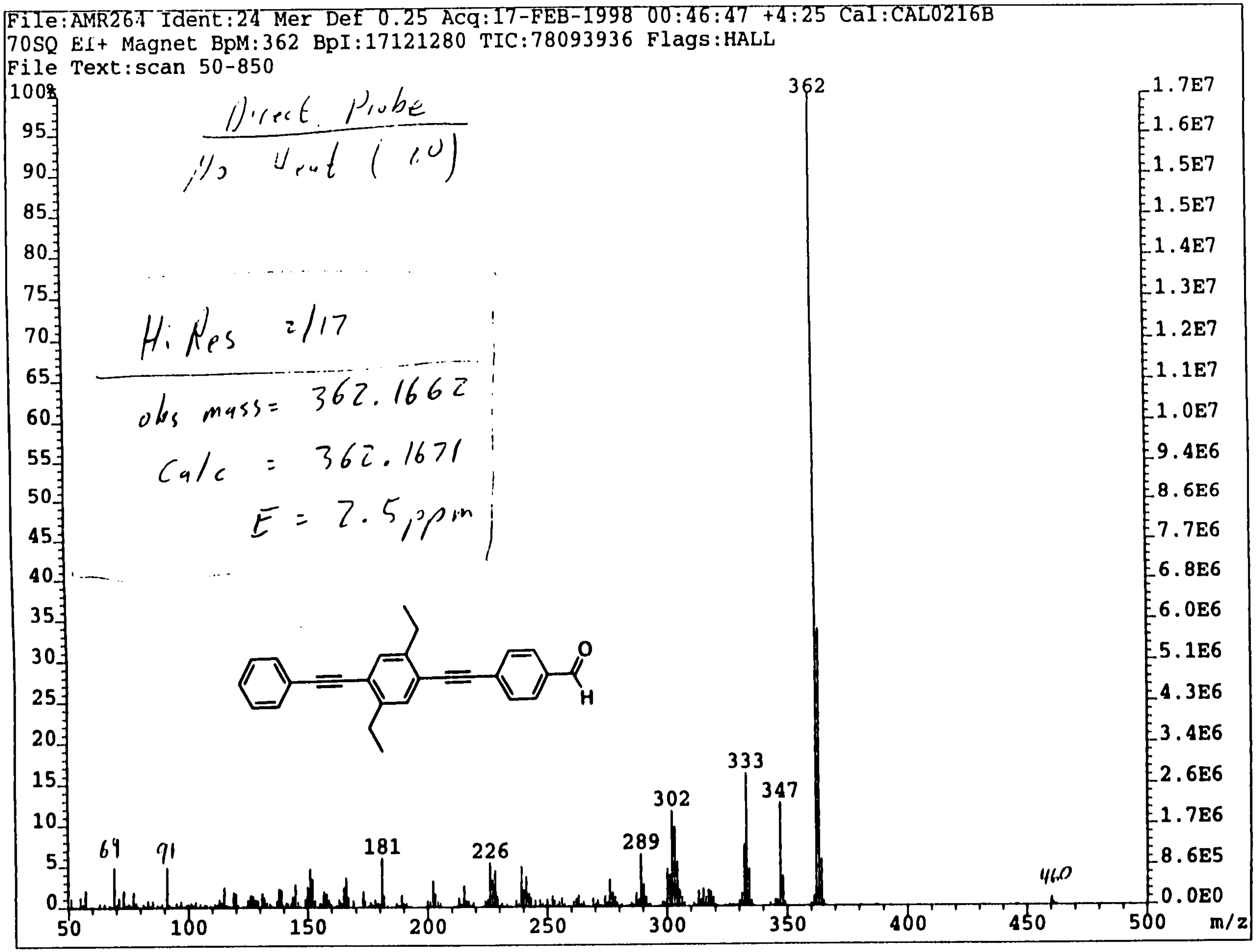
E = 0.9 ppm


PERKIN ELMER
25.75
%T
7.65
4000
3500
3000
2500
2000
1500
1000
cm-1
3138.5
2964.4
2923.1
2369.2
1702.6
1594.9
1384.6
1205.1
1159.0
1117.9
830.8
753.8
687.2
O
H


ppm
1
2
3
4
5
6
7
8
9
10
O
H


O
H
1.025
14.633
14.715
27.113
29.647
76.573
76.887
77.208
87.848
92.222
92.925
94.361
121.353
123.072
128.164
129.375
129.488
130.699
131.267
131.394
131.514
131.701
132.164
135.110
143.283
143.455
191.009
ppm
20
40
60
80
100
120
140
160
180
200
220

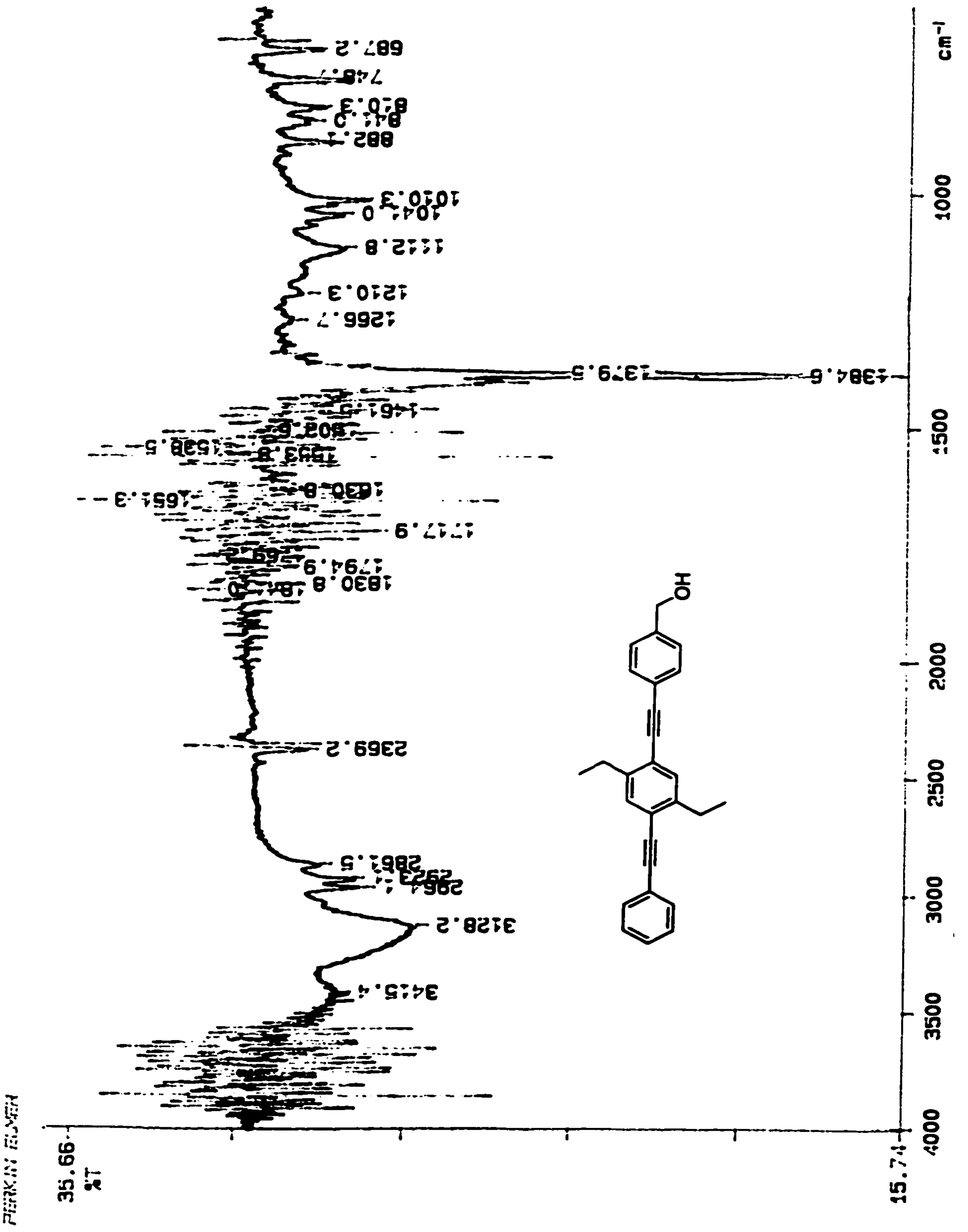
File:AMR264 Ident:24 Mer Def 0.25 Acq:17-FEB-1998 00:46:47 +4:25 Cal:CAL0216B
70SQ EI+ Magnet BpM:362 BpI:17121280 TIC:78093936 Flags:HALL
File Text:scan 50-850

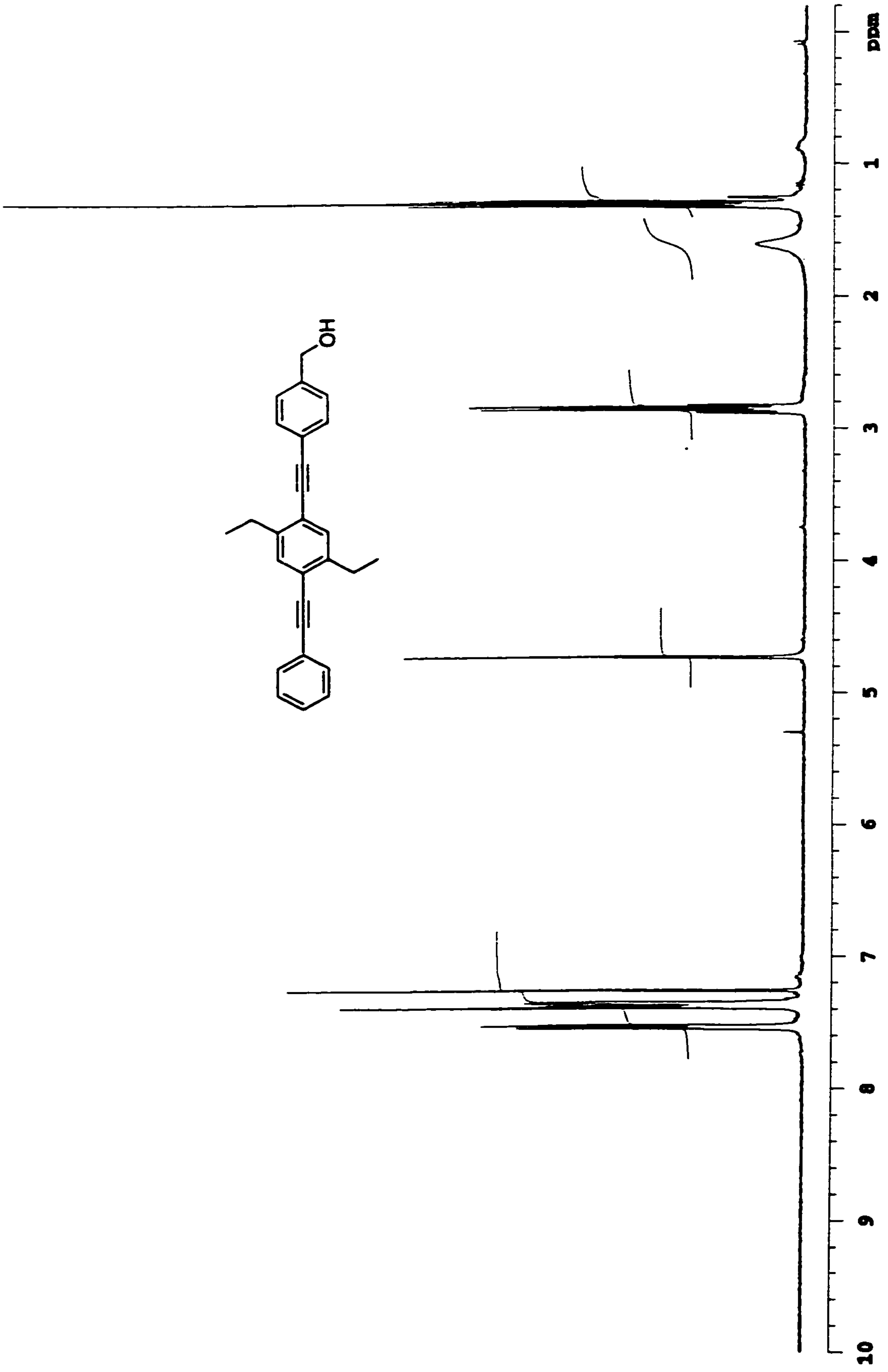


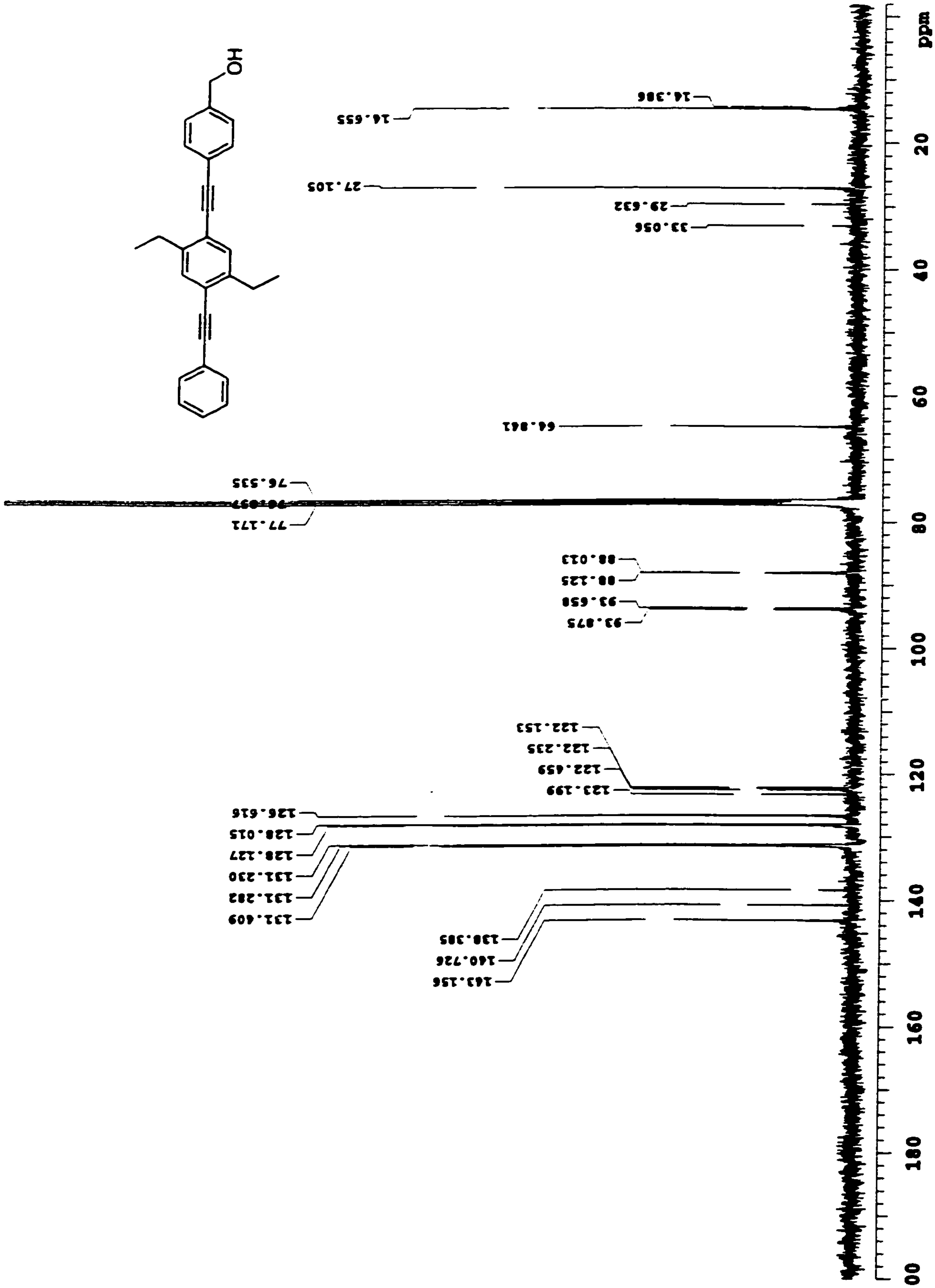
Direct Probe
1/2 Vent (1.0)

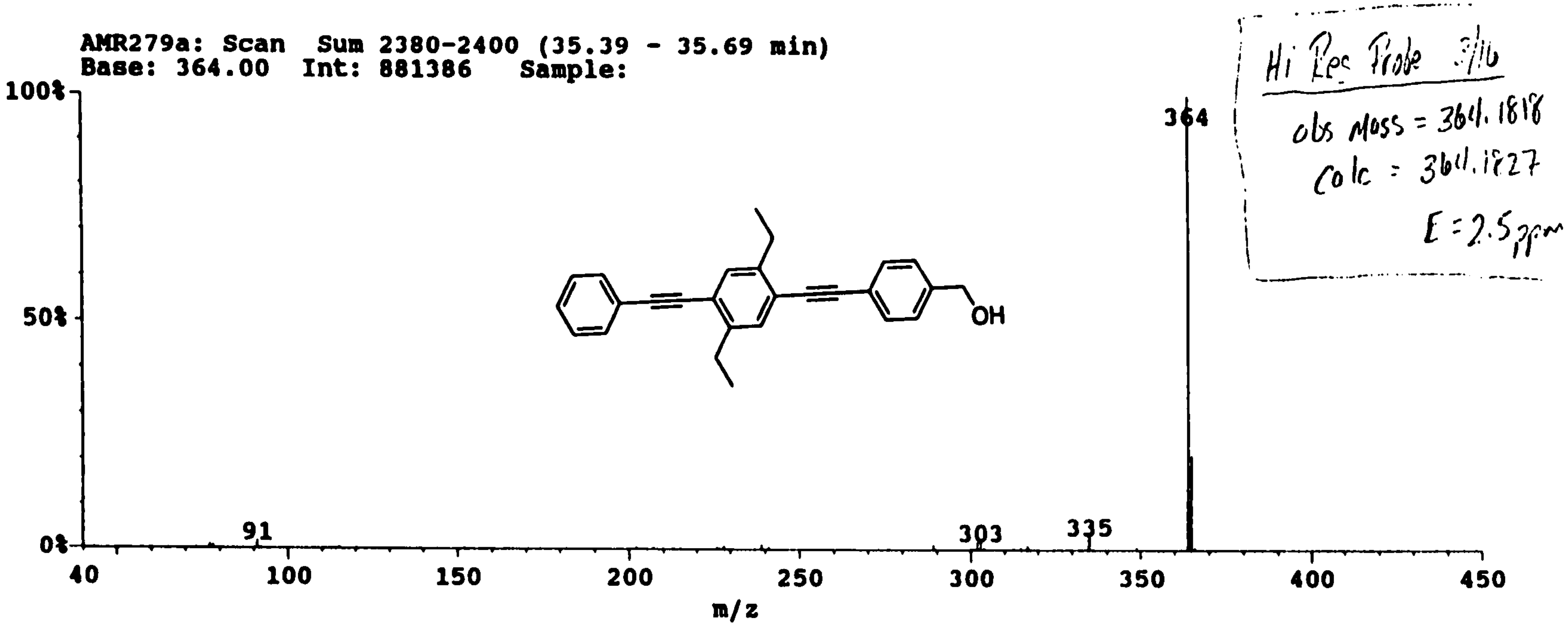
Hi Res 2/17

obs mass = 362.1662
Calc = 362.1671
E = 2.5 ppm

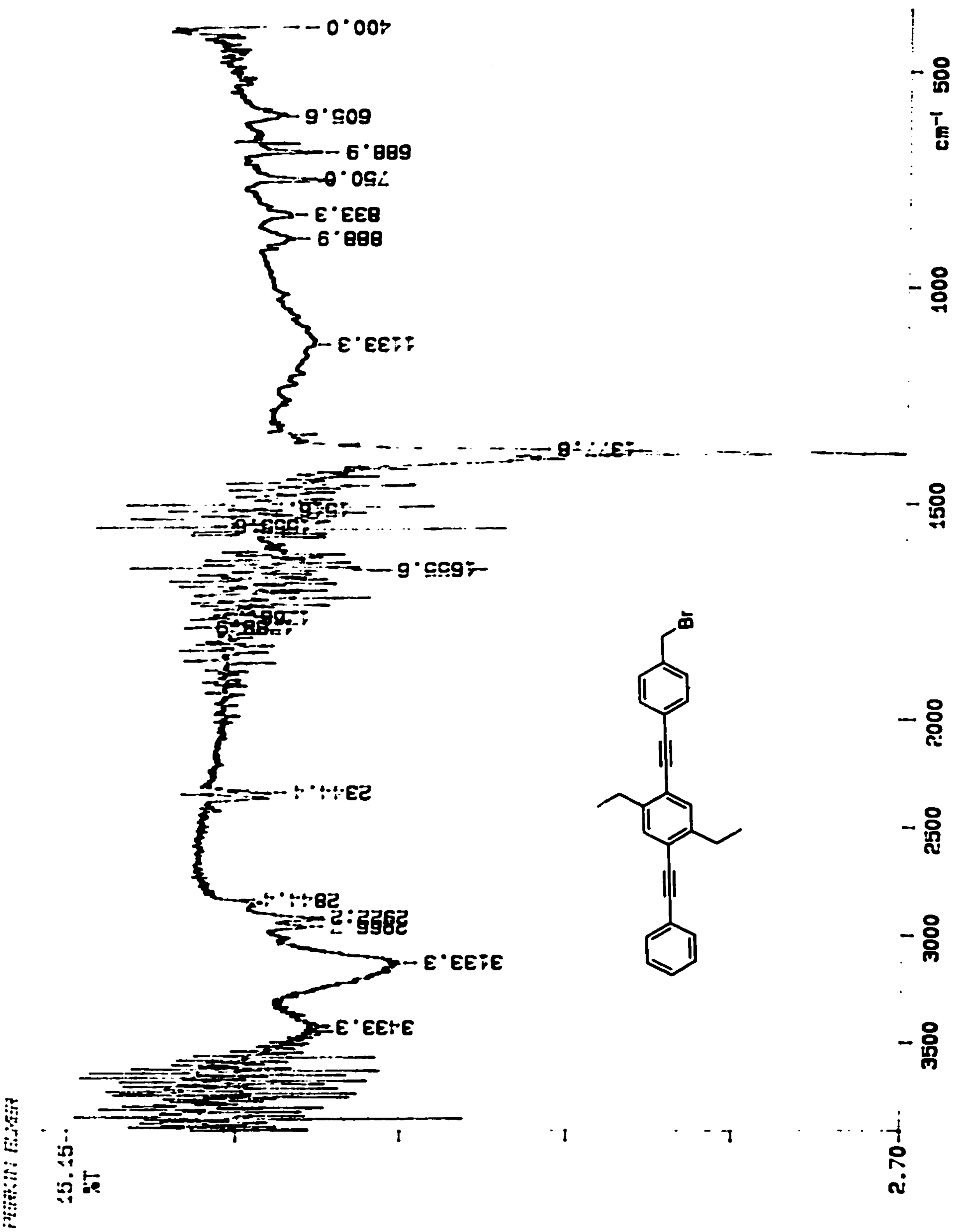

PERKIN ELMER
35.66
%T
15.74
4000
3500
3000
2500
2000
1500
1000
cm-1
3415.4
3128.2
2964.1
2923
2861.5
2369.2
1830.8
1841.0
1794.9
1769.2
1717.9
1651.3
1630.8
1553.8
1538.5
1508.6
1461.5
1384.6
1379.5
1266.7
1210.3
1112.8
1041.0
1010.3
882.1
841.0
810.3
748.7
687.2
OH

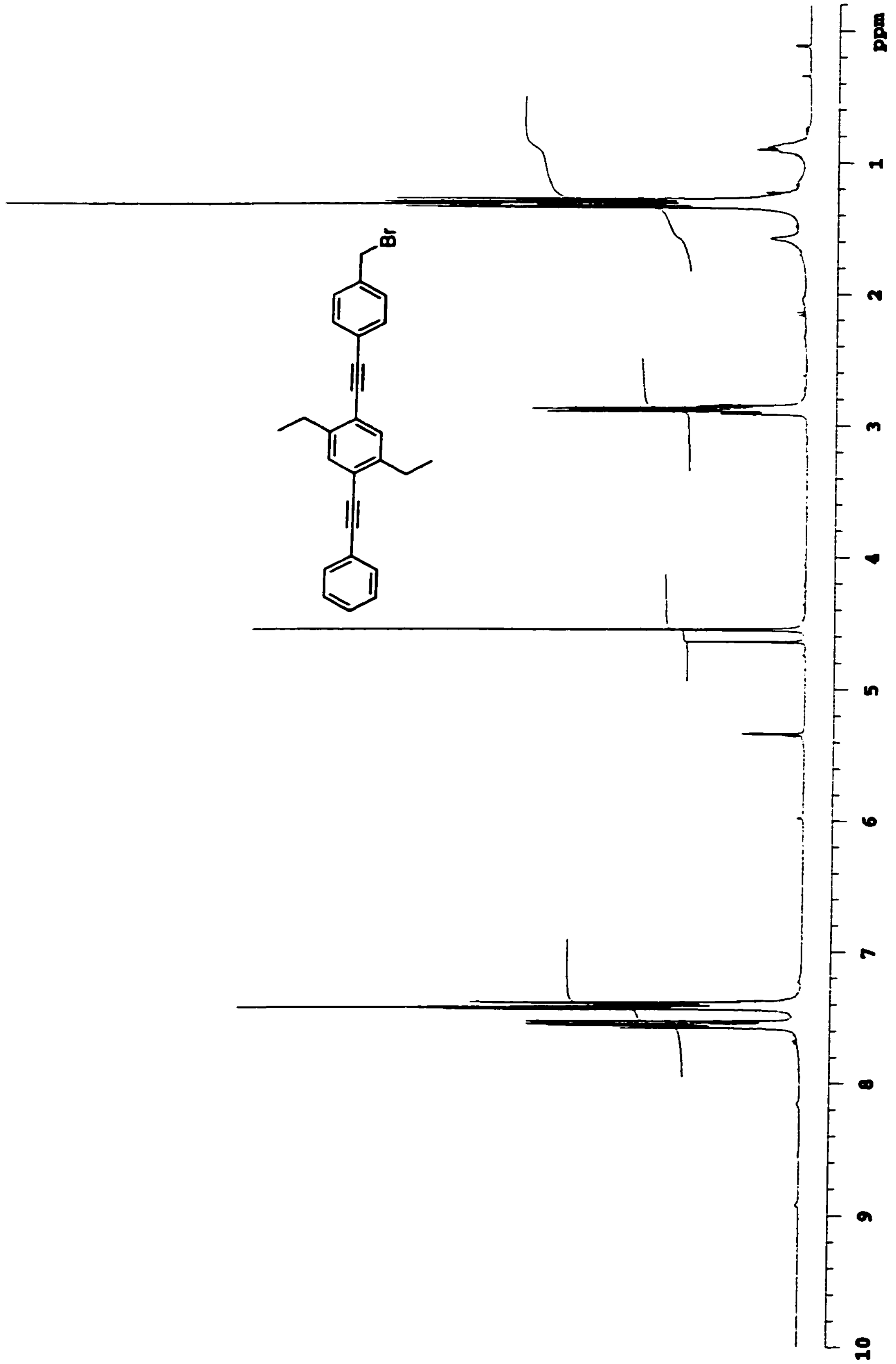

OH
ppm
1
2
3
4
5
6
7
8
9
10

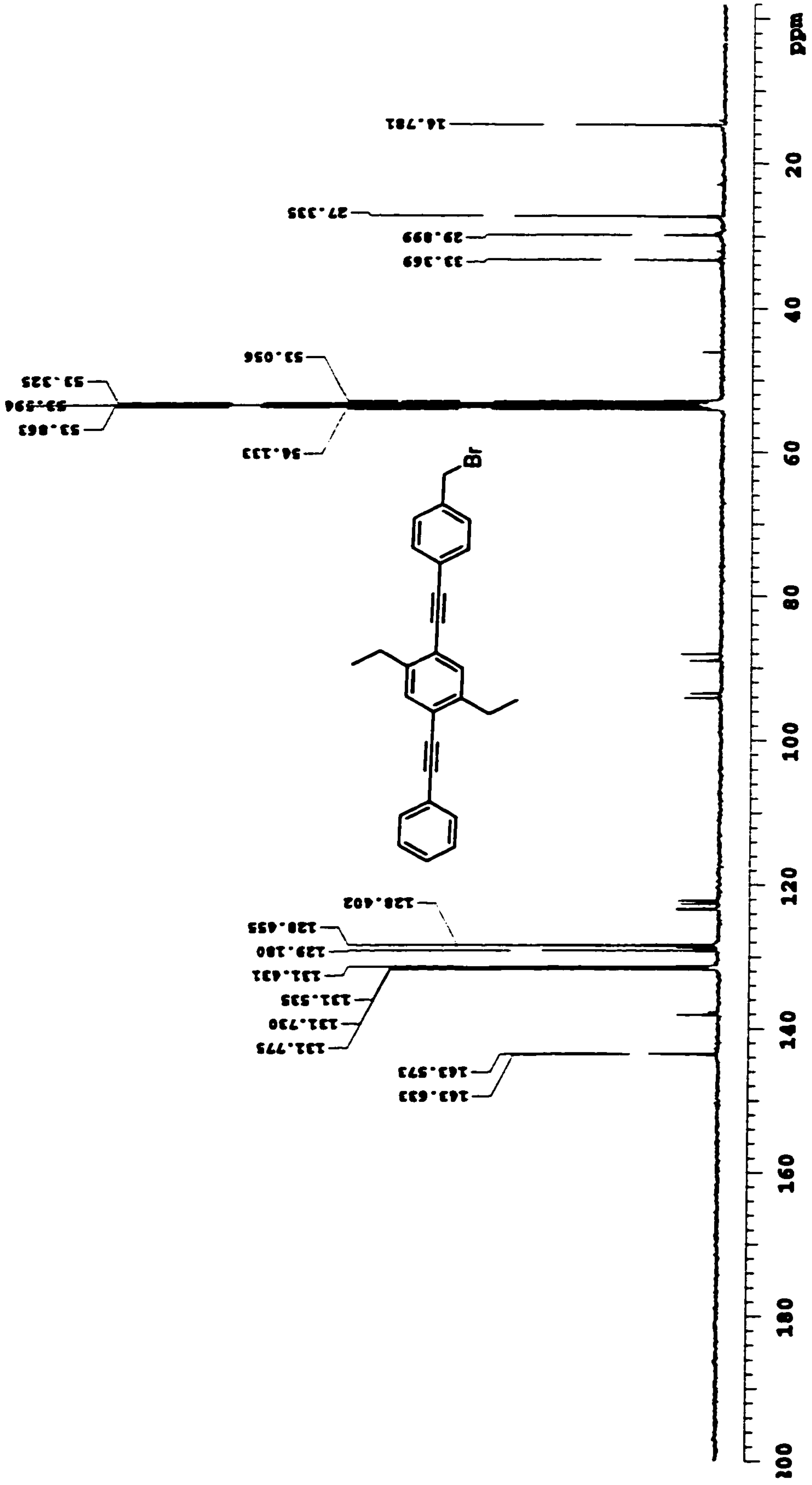

OH
14.386
14.655
27.105
29.632
33.056
64.841
76.535
77.171
88.013
88.125
93.658
93.875
122.153
122.235
122.459
123.199
126.616
128.015
128.127
131.230
131.283
131.409
138.385
140.726
143.156
20
40
60
80
100
120
140
160
180
00
ppm



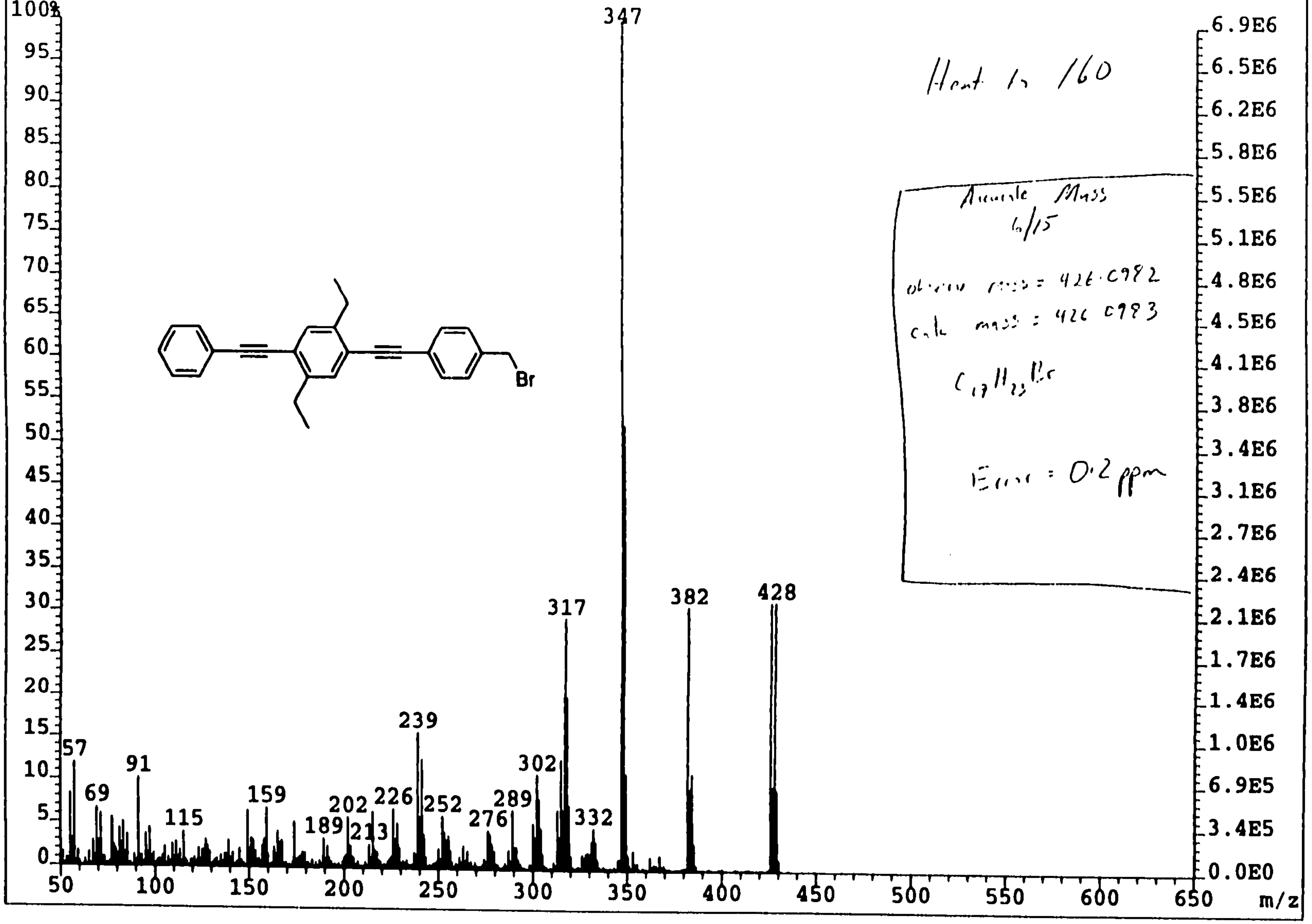
Hi Res Probe 3/16
obs Mass = 364.1818
Calc = 364.1827
E = 2.5 ppm


PERKIN ELMER
25.15
%T
2.70
3500
3000
2500
2000
1500
1000
500
cm-1
400.0
605.6
688.9
750.6
833.3
888.9
1133.3
1377.8
1655.6
2344.4
2844.4
2922.2
2966.7
3133.3
3433.3
Br


Br
ppm
1
2
3
4
5
6
7
8
9
10


14.781
27.335
29.899
33.369
53.056
53.325
53.594
53.863
54.133
Br
128.402
128.455
129.180
131.431
131.535
131.730
131.775
143.573
143.633
ppm
20
40
60
80
100
120
140
160
180
200

File:AMR38 Ident:11_14 Mer Def 0.25 Acq:11-JUN-1998 16:33:19 +2:39 Cal:CAL0611A_1
70SQ EI+ Magnet BpM:347 BpI:6858752 TIC:63175592 Flags:HALL
File Text:scan 50-850

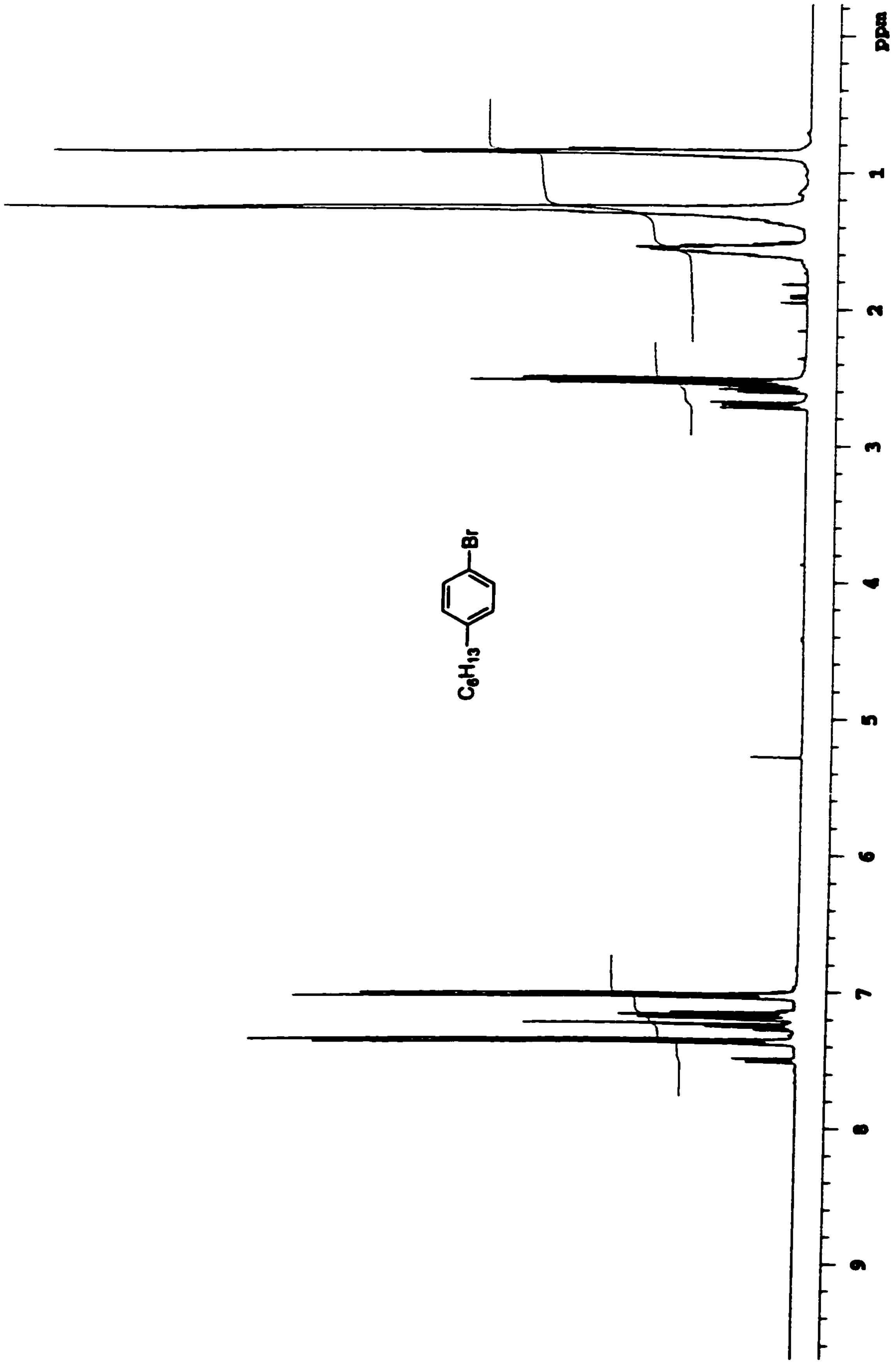


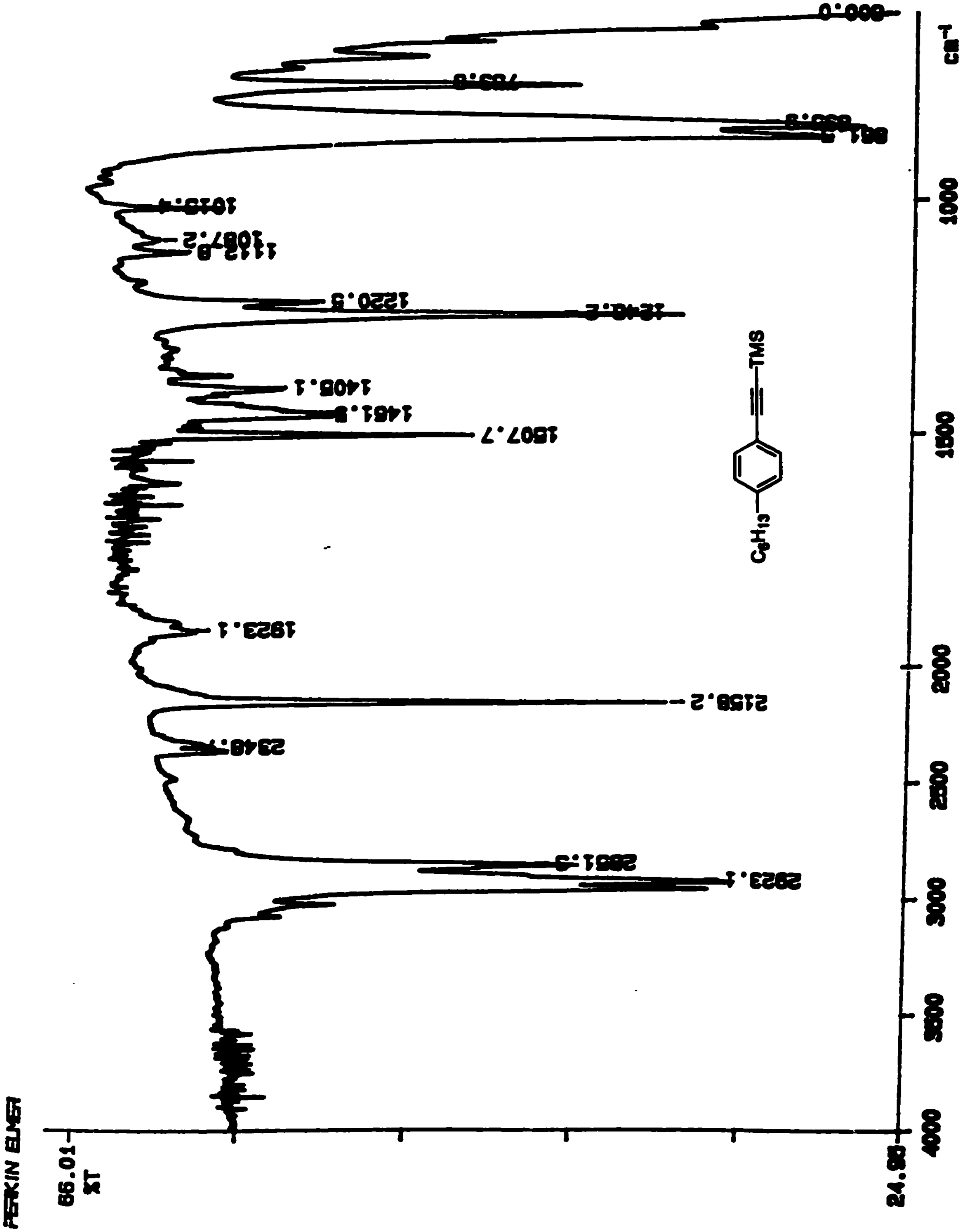
Heat to 160

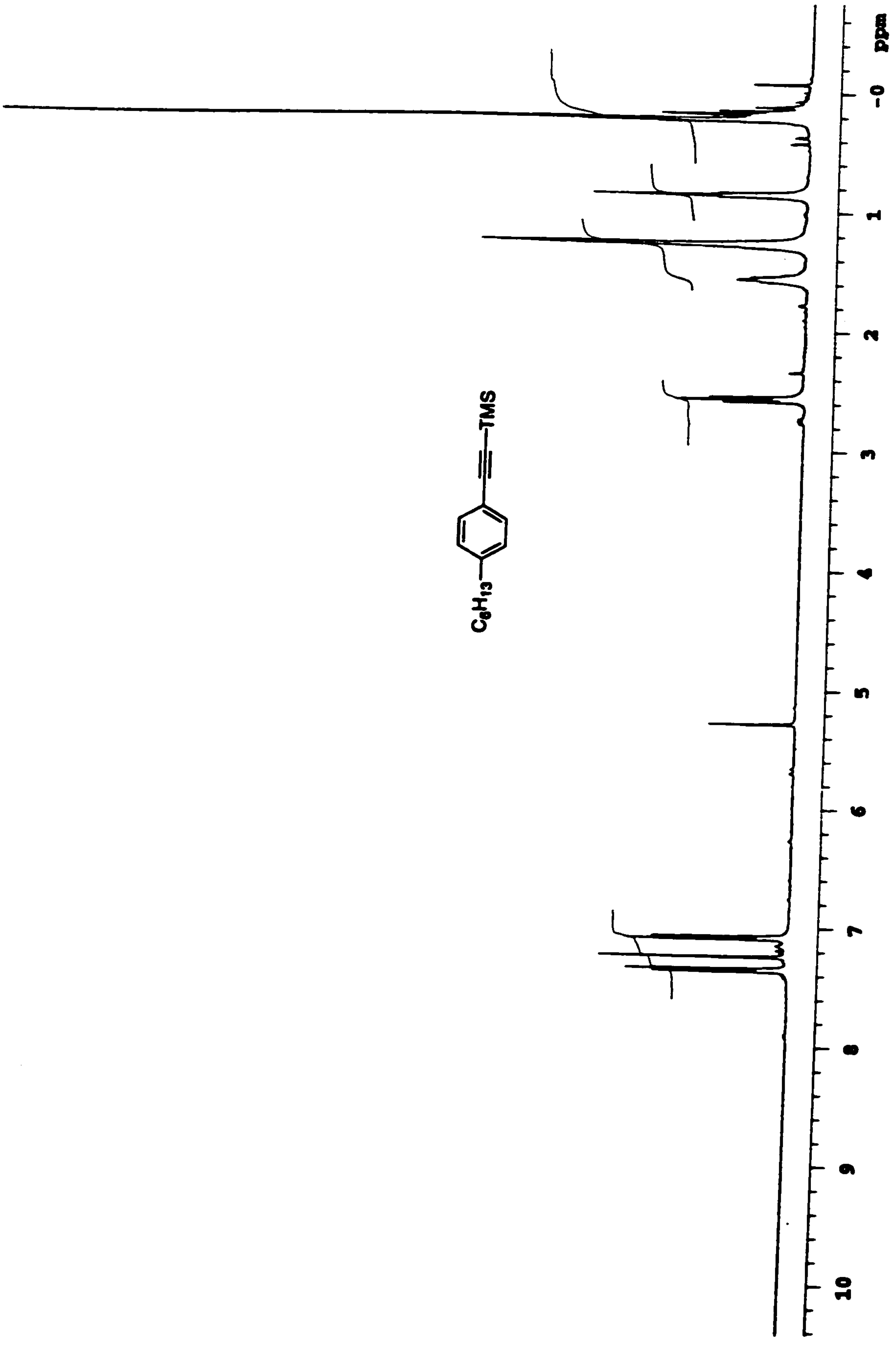
Accurate Mass
6/15

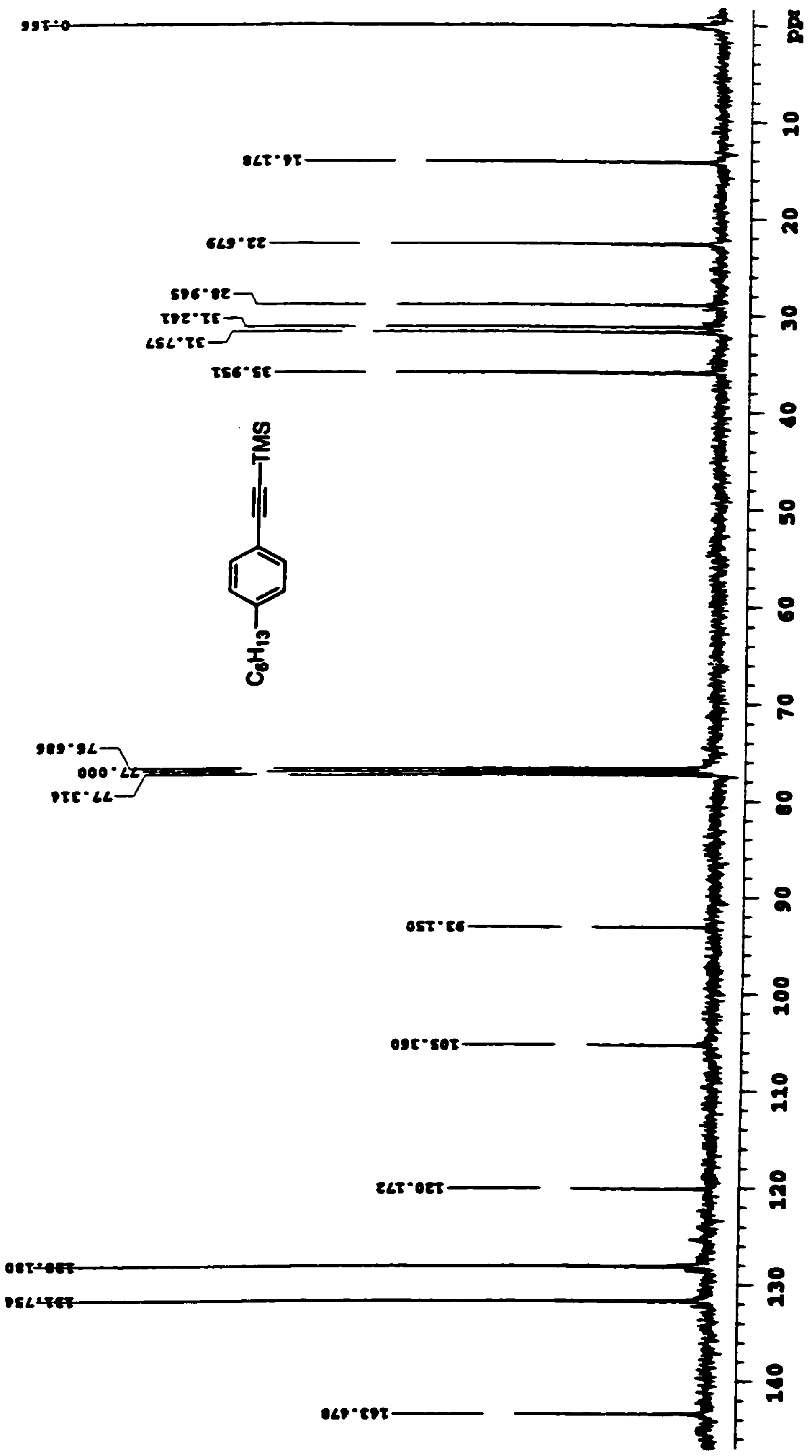
observed mass = 426.0982
calc mass = 426.0983
$C_{27}H_{23}Br$

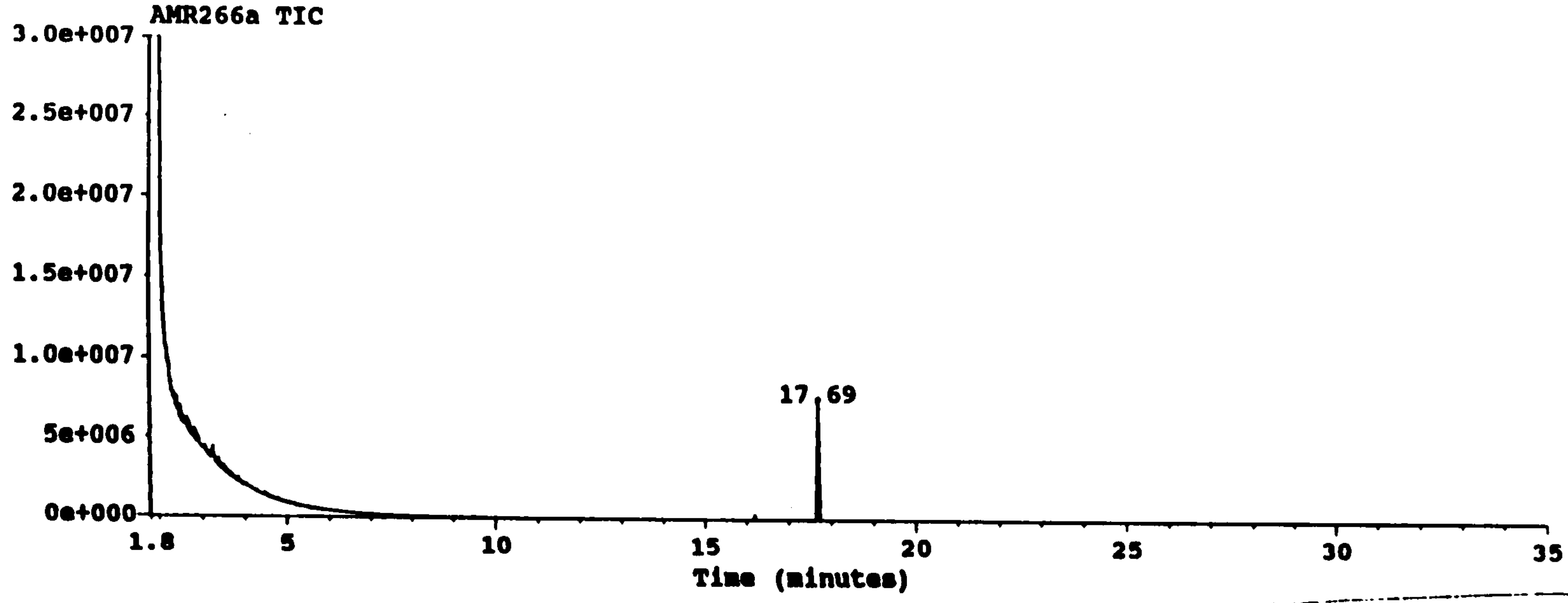
Error = 0.2 ppm

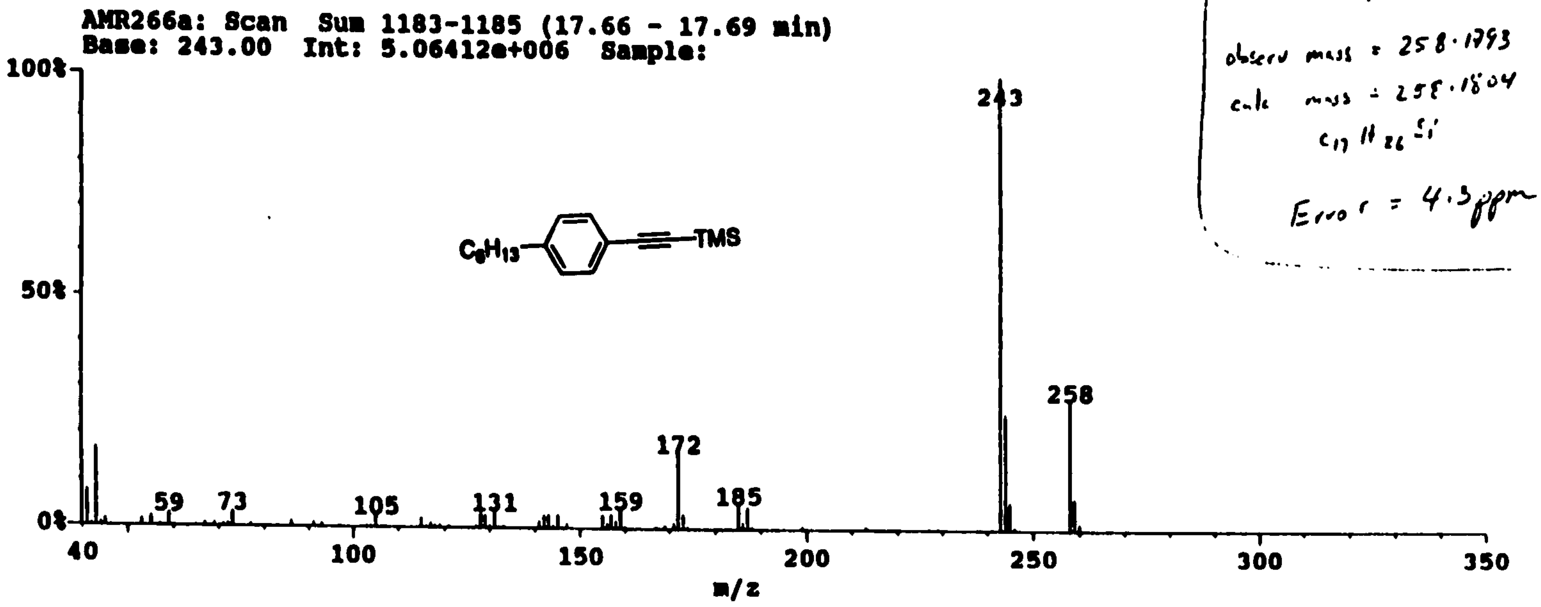

Br
C$_6$H$_{13}$
ppm
1
2
3
4
5
6
7
8
9


PERKIN ELMER
66.01
%T
24.98
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
2923.1
2851.9
2348.7
2158.2
1923.1
1507.7
1461.8
1405.1
1248.2
1220.5
1112.8
1067.2
1019.4
861
830.8
763.8
600.0
C_6H_{13}
TMS


C$_6$H$_{13}$
TMS
ppm
0
1
2
3
4
5
6
7
8
9
10


0.166
14.178
22.679
28.965
31.241
31.757
35.951
76.686
77.000
77.314
93.150
105.360
120.172
128.180
131.754
143.678
C_6H_{13}
TMS
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140


AMR266a TIC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2/18
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calc mass = 258.1804
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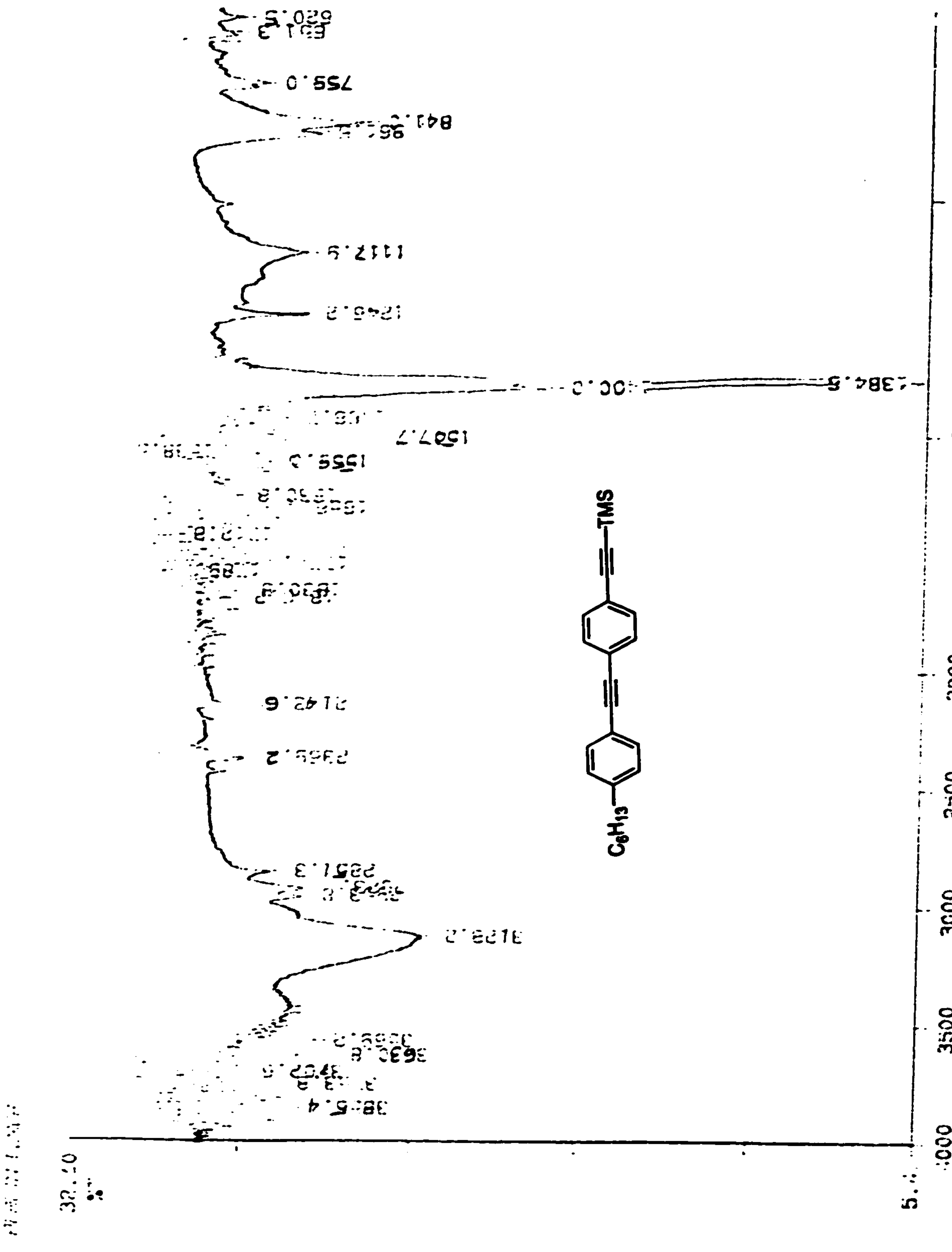
Error = 4.3 ppm


C6H13
TMS
620.5
691.3
755.0
841.0
1112.6
1246.2
1400.0
1384.5
1507.7
1555.0
2142.6
2365.2
2851.3
3129.2
3630.8
3885.4
32.10
5.0
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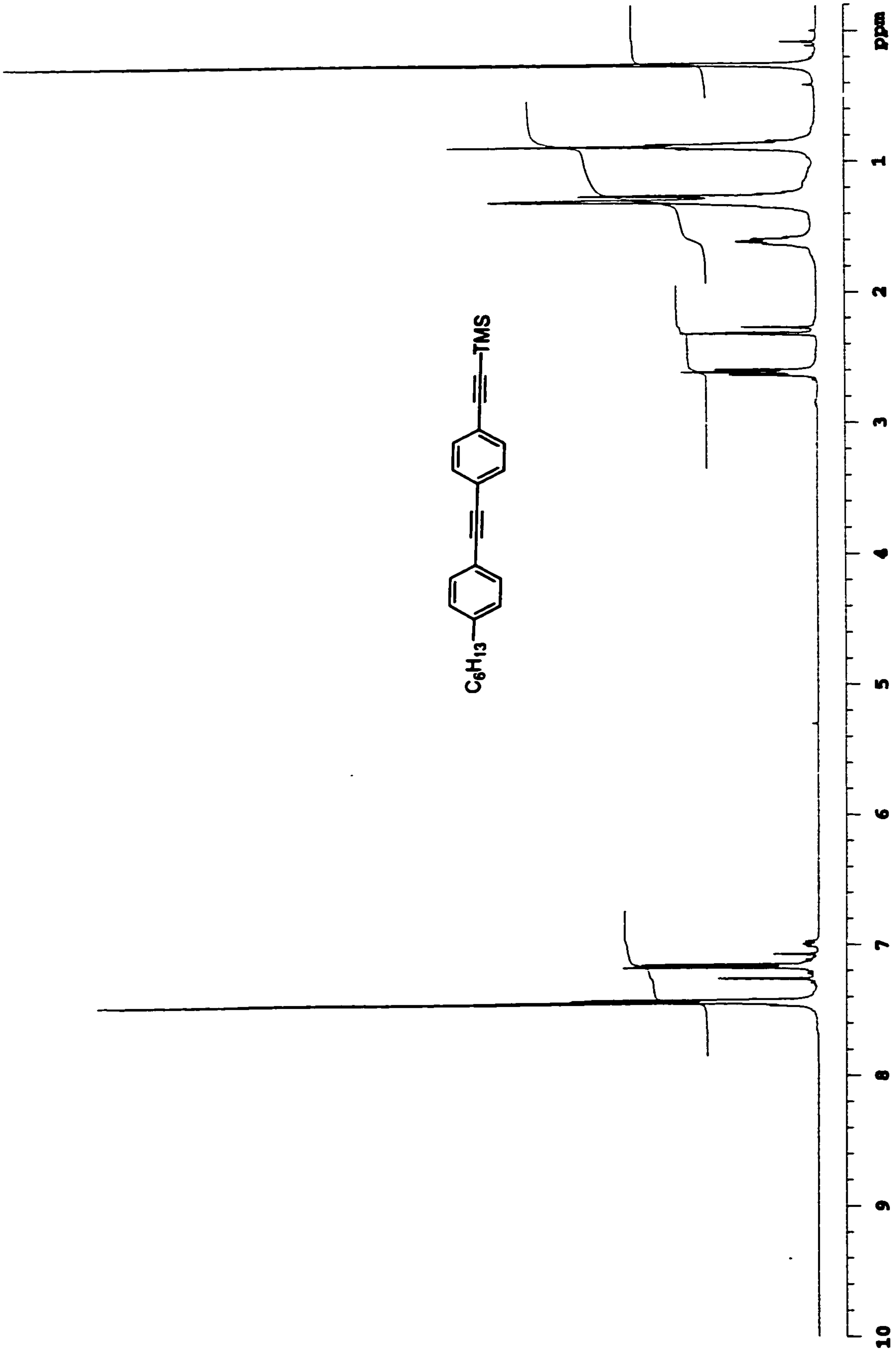
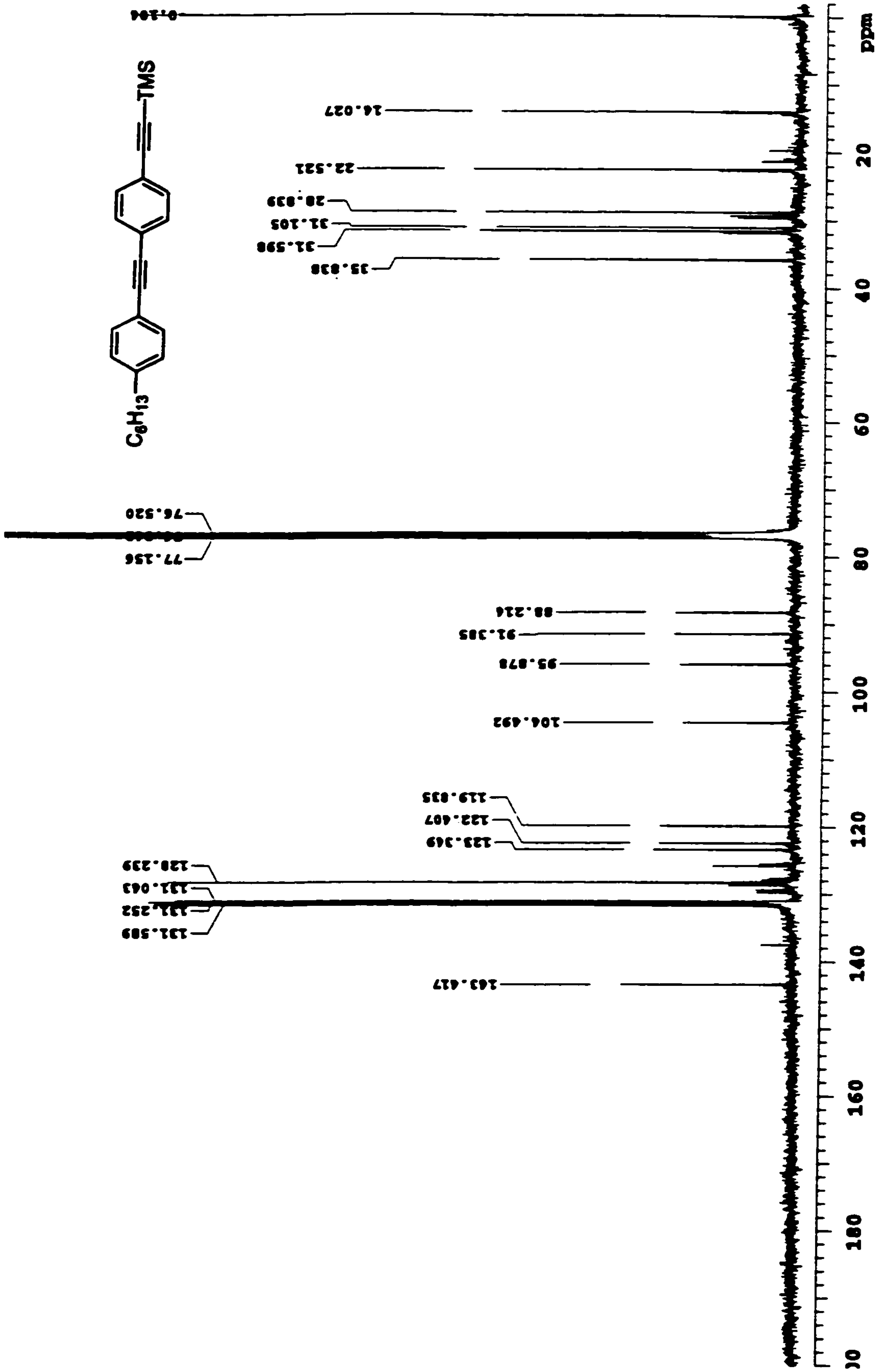
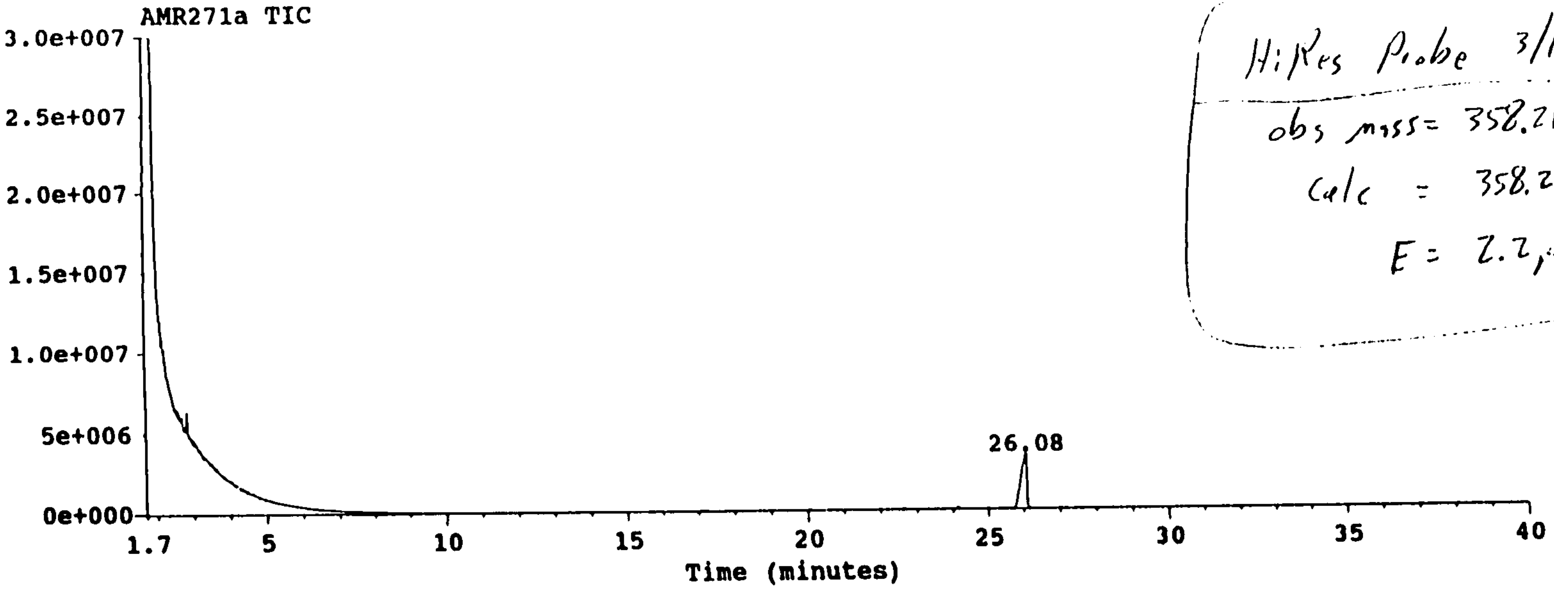
3500
3000
2500
2000
1500
1000
cm-1


C6H13
TMS
ppm
1
2
3
4
5
6
7
8
9
10


C$_6$H$_{13}$
TMS
0.104
14.027
22.531
28.839
31.105
31.598
35.838
76.520
77.156
88.214
91.385
95.878
104.493
119.835
122.407
123.369
128.239
131.043
131.252
131.589
143.417
ppm
20
40
60
80
100
120
140
160
180



HiRes Probe 3/16
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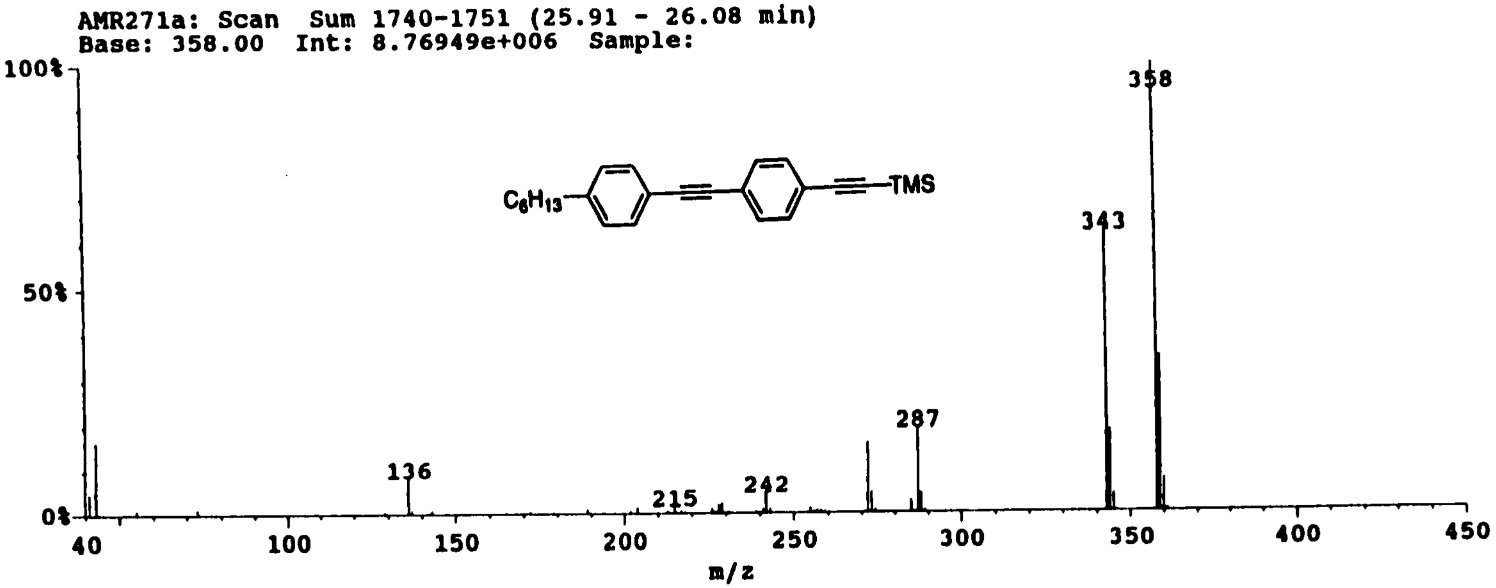
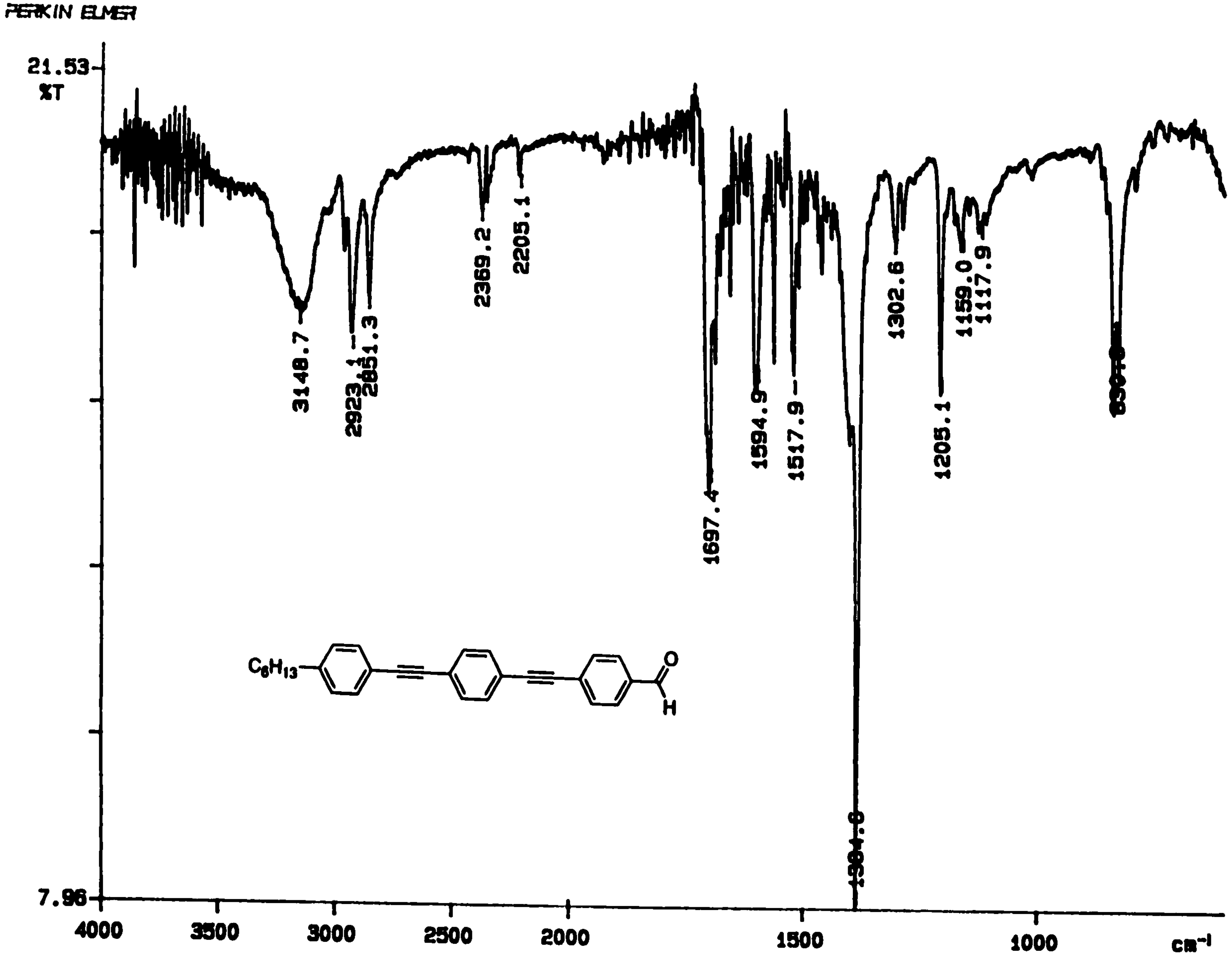
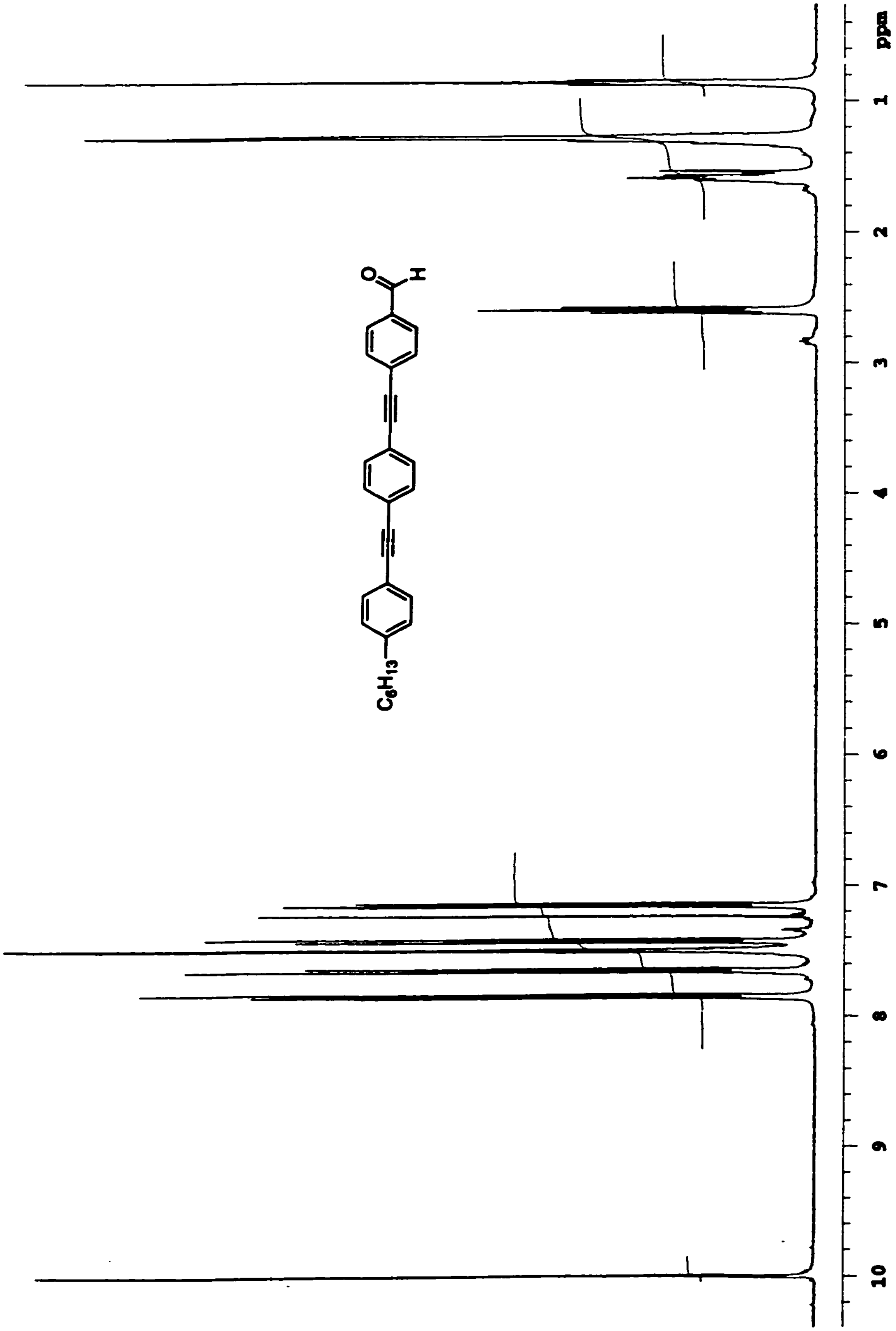
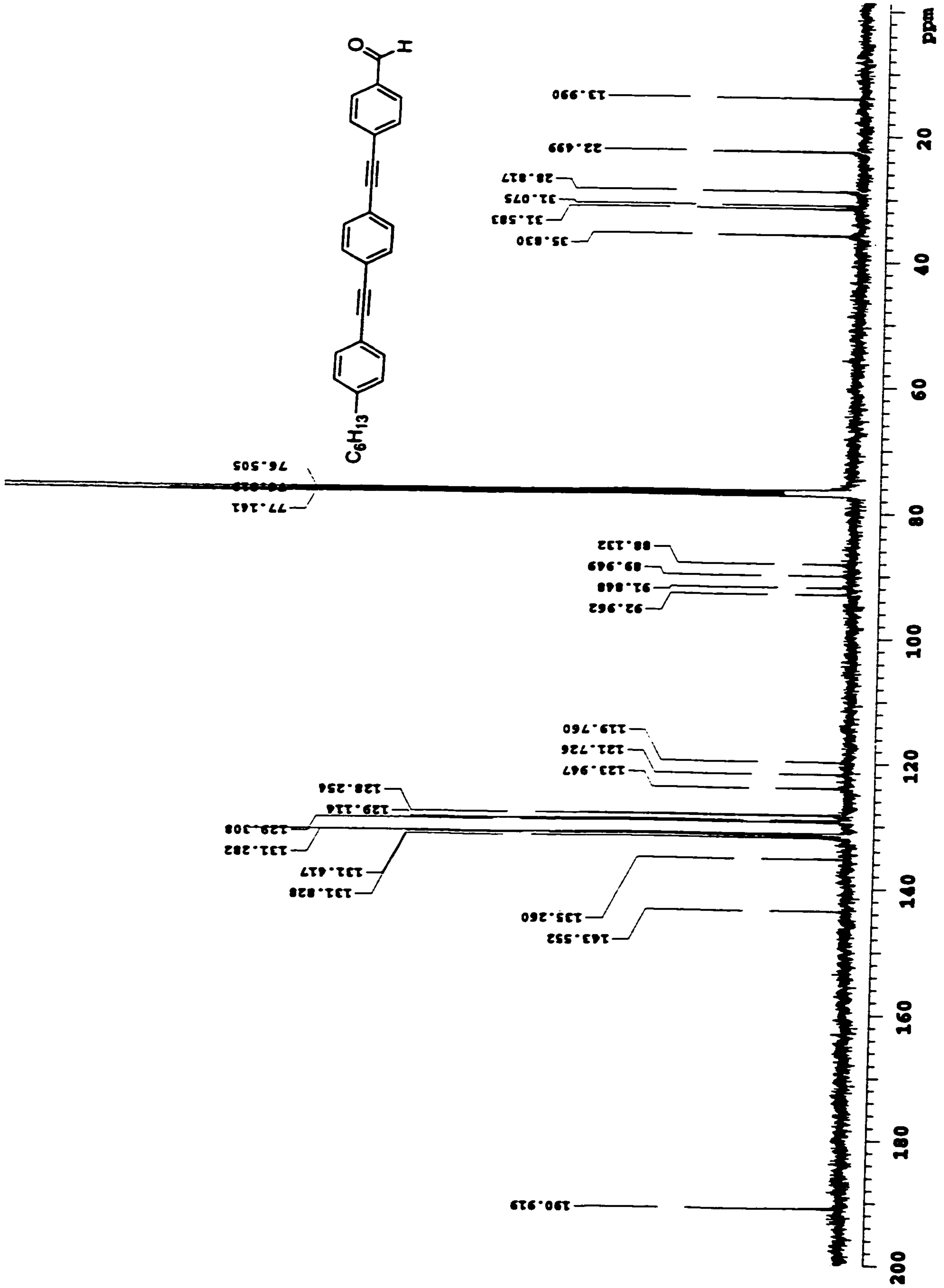
Calc = 358.2117
E = 2.2 ppm

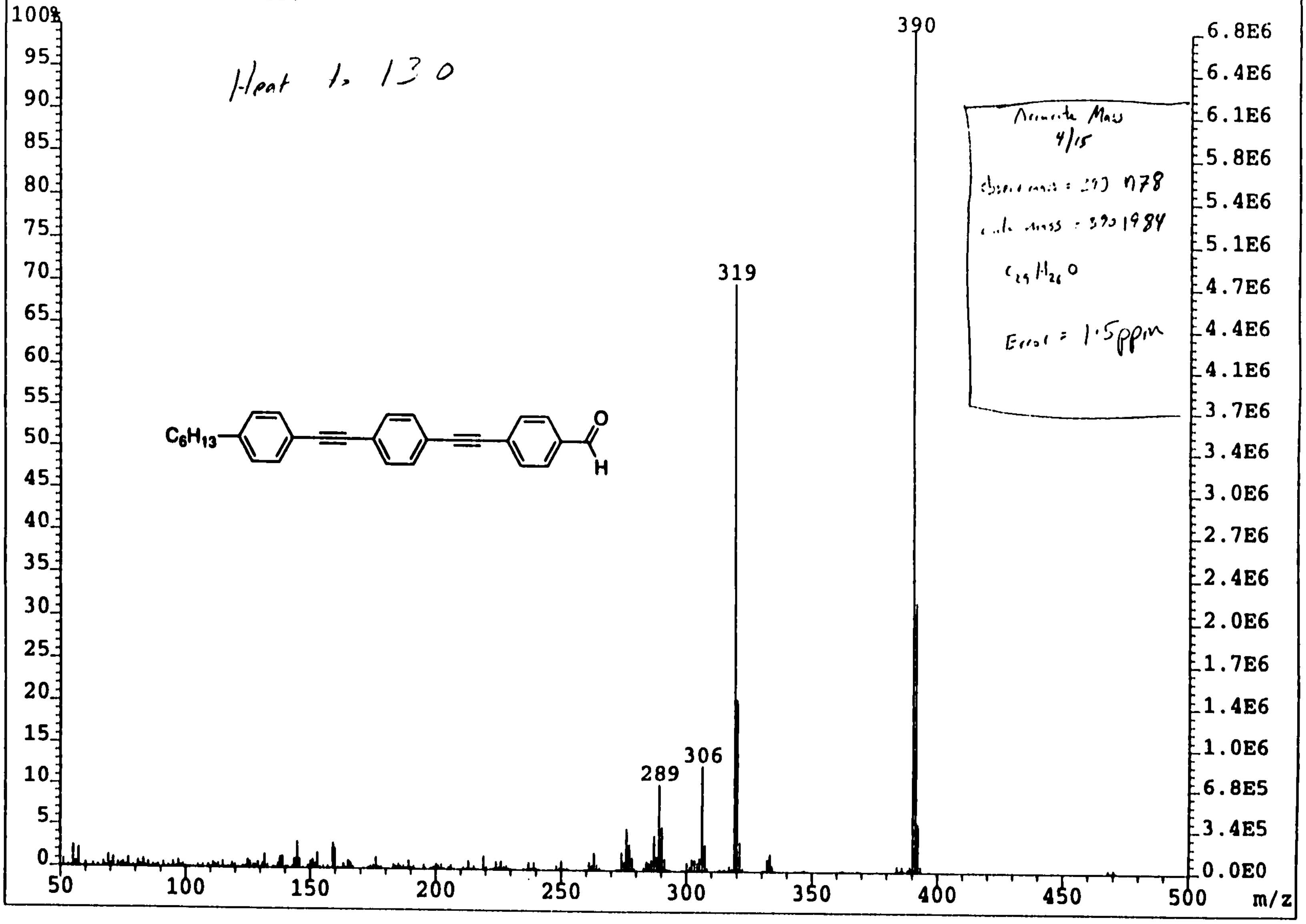



PERKIN ELMER
21.53
%T
7.96
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3148.7
2923.1
2851.3
2369.2
2205.1
1697.4
1594.9
1517.9
1384.8
1302.6
1205.1
1159.0
1117.9
830.8
C_6H_{13}
O
H


C6H13
O
H
ppm
1
2
3
4
5
6
7
8
9
10


C$_6$H$_{13}$
O
H
13.990
22.499
28.817
31.075
31.583
35.830
76.505
77.141
88.132
89.949
91.848
92.962
119.760
121.726
123.967
128.254
129.114
129.308
131.282
131.417
131.828
135.260
143.552
190.919
ppm
20
40
60
80
100
120
140
160
180
200

File:AMRI2 Ident:13_18 Mer Def 0.25 Acq:30-MAR-1998 14:58:19 +3:14 Cal:CAL0330A_1
70SQ EI+ Magnet BpM:390 BpI:6765739 TIC:27936038 Flags:HALL
File Text: scan 50-850



Heat 1, 130

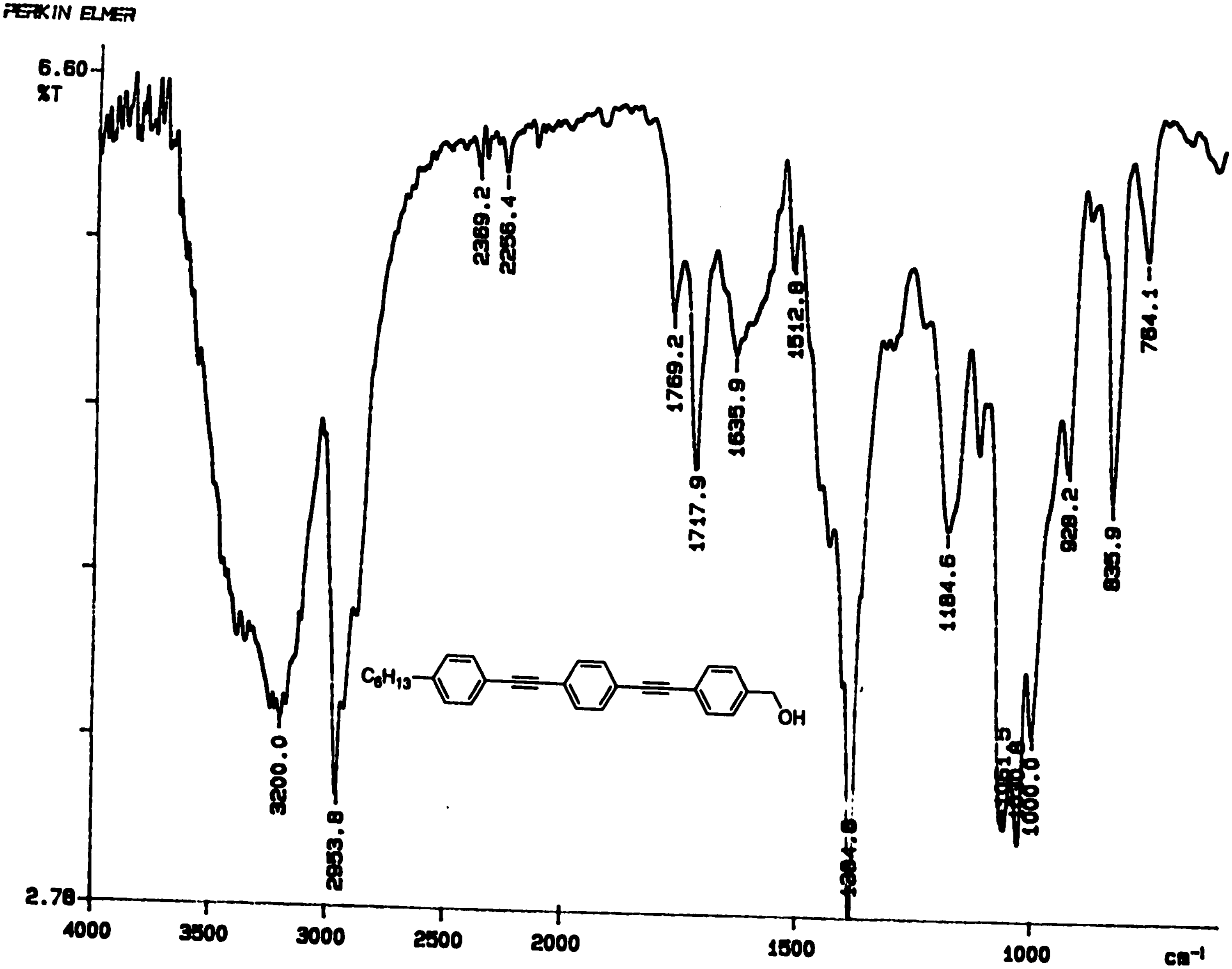
Accurate Mass
4/15

observed mass = 390 1978

calc mass = 390 1984

$C_{29}H_{26}O$

Error = 1.5ppm


PERKIN ELMER
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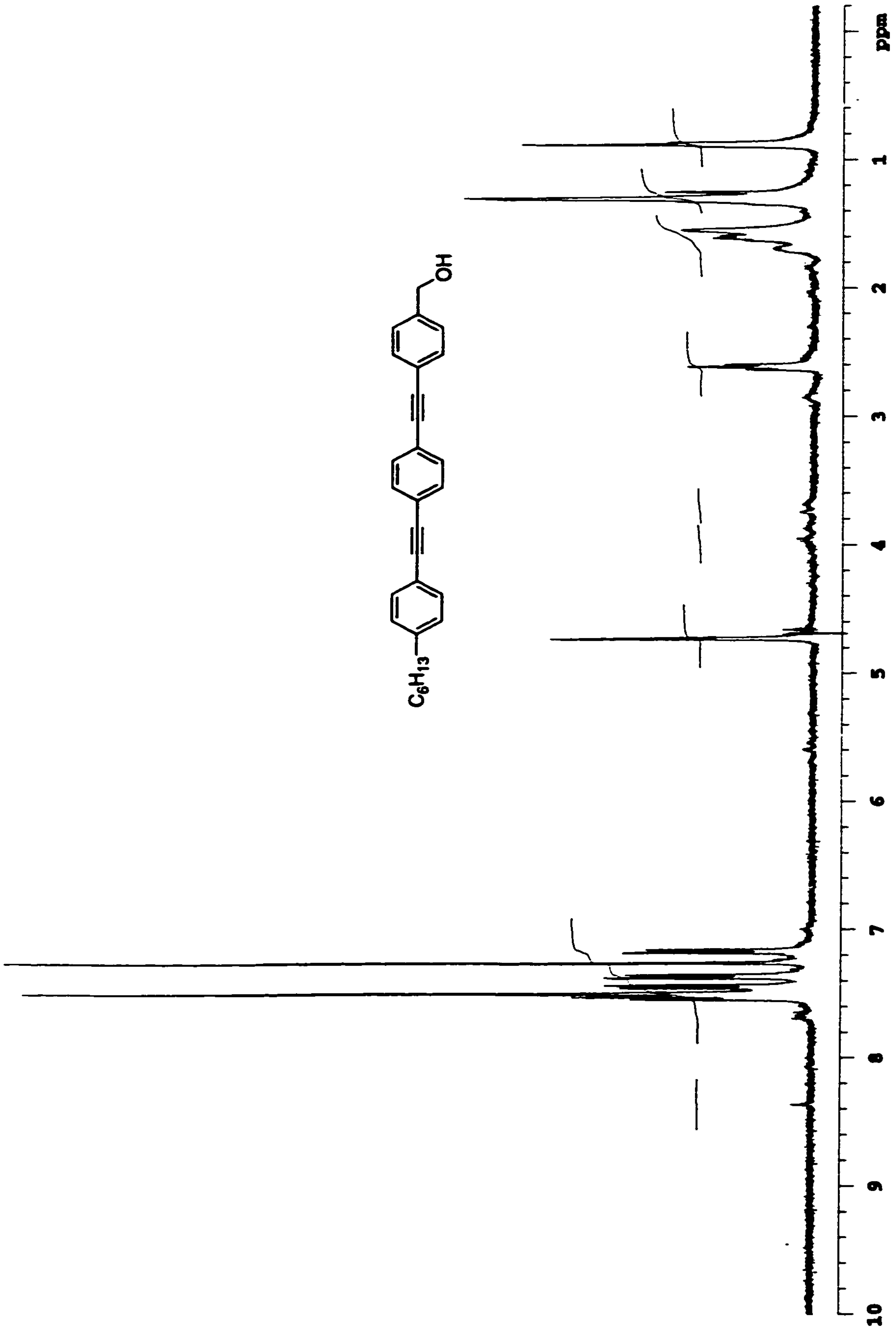
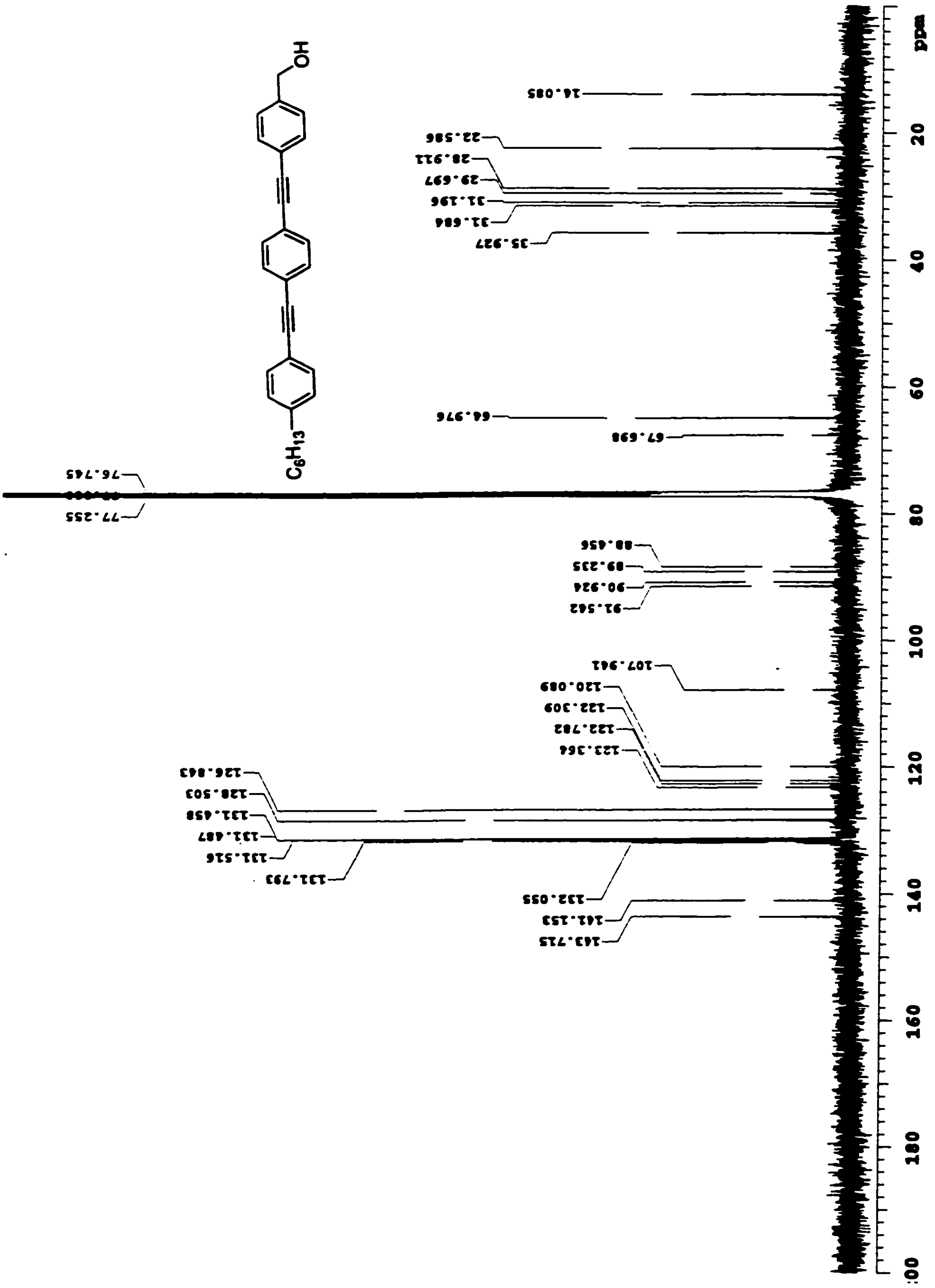
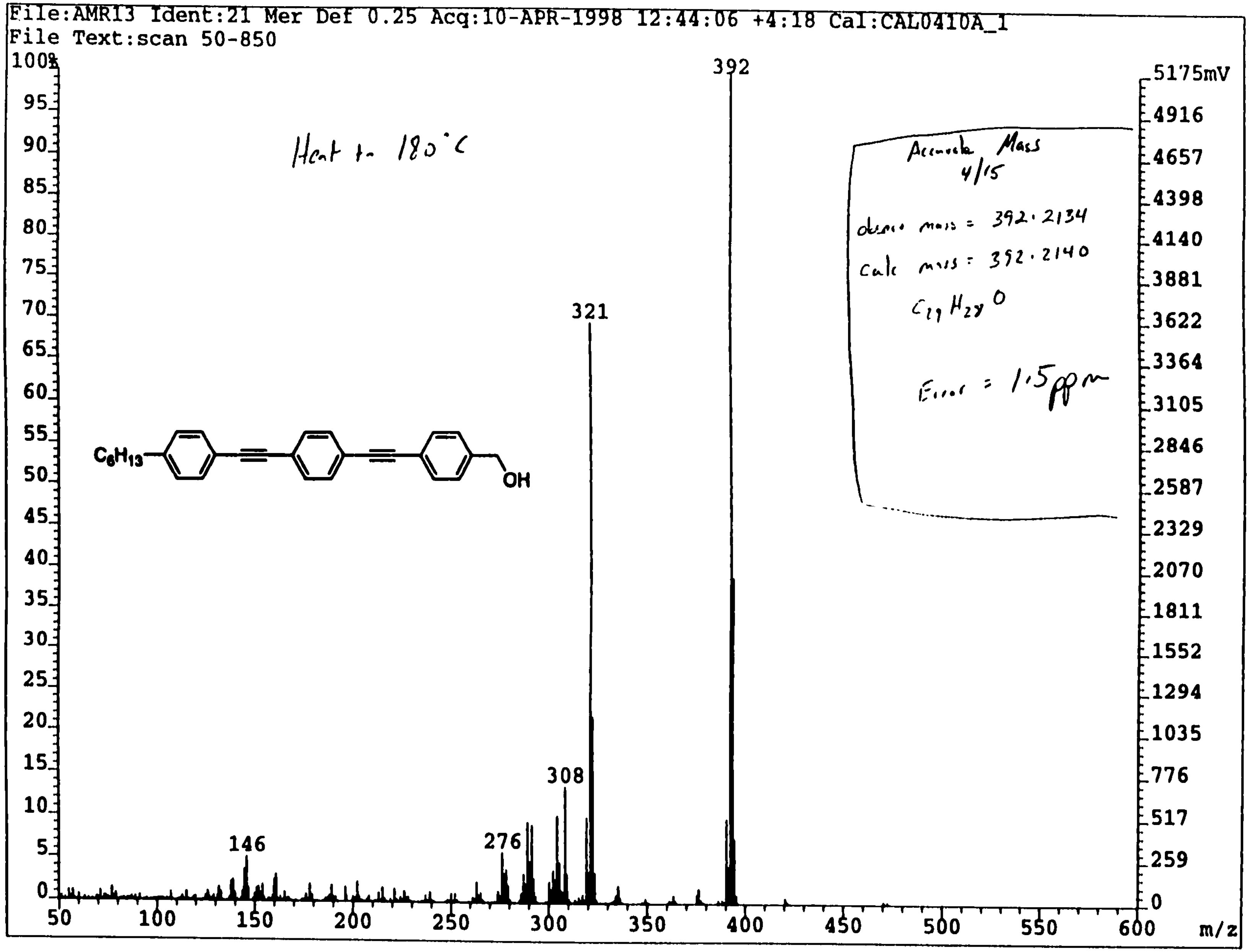
%T
2.78
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3200.0
2953.8
2369.2
2256.4
1769.2
1717.9
1635.9
1512.8
1384.8
1184.6
1061.5
1000.0
928.2
835.9
784.1
C6H13
OH


C$_6$H$_{13}$
OH
ppm
1
2
3
4
5
6
7
8
9
10


HO
C6H13
14.085
22.586
28.911
29.697
31.196
31.684
35.927
64.976
67.698
76.745
77.255
88.456
89.235
90.924
91.562
107.961
120.089
122.309
122.782
123.364
126.843
128.503
131.458
131.487
131.516
131.793
132.055
141.153
143.715
ppm
20
40
60
80
100
120
140
160
180
00


File:AMR13 Ident:21 Mer Def 0.25 Acq:10-APR-1998 12:44:06 +4:18 Cal:CAL0410A_1
File Text:scan 50-850

Heat to 180°C

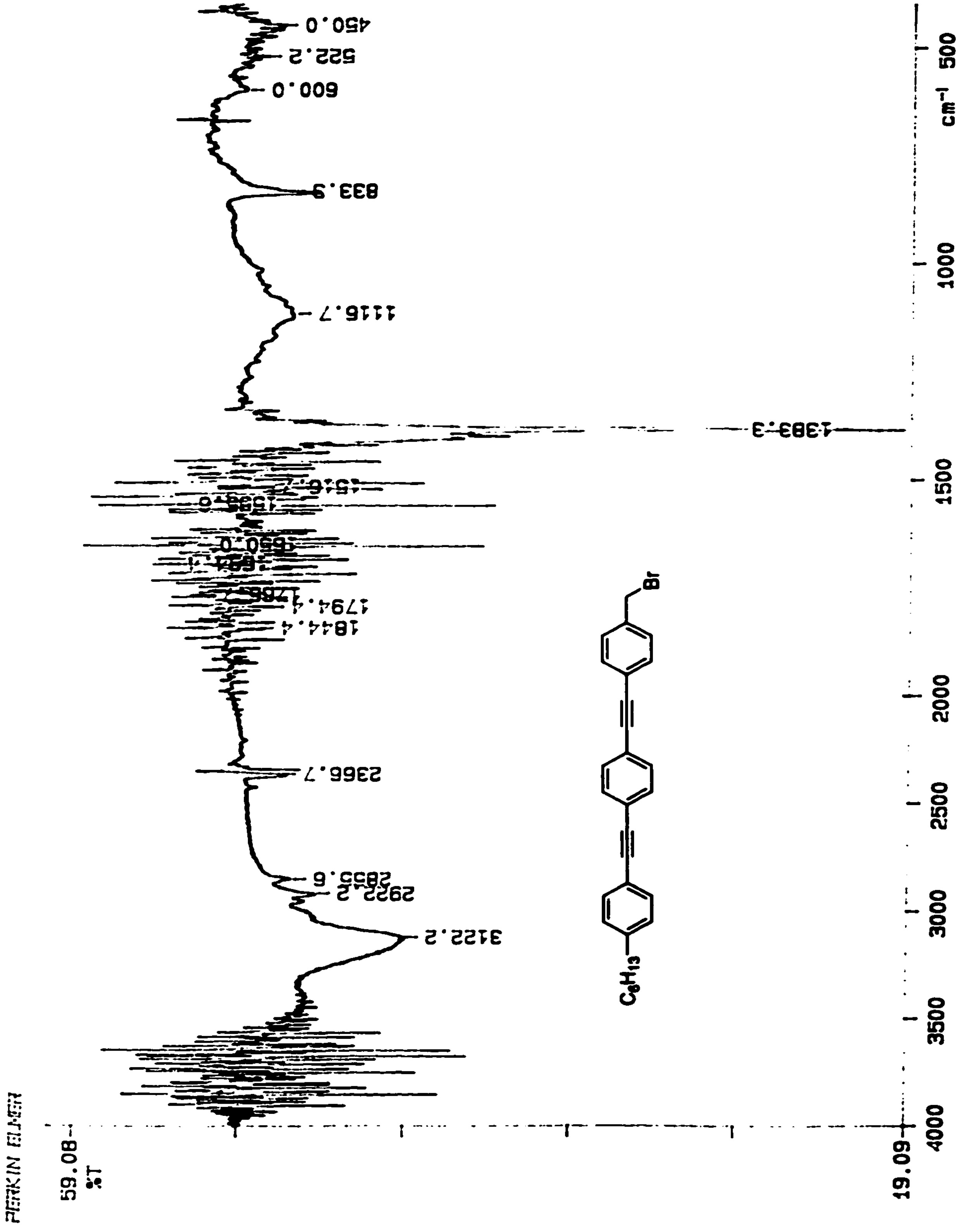
Accurate Mass
4/15

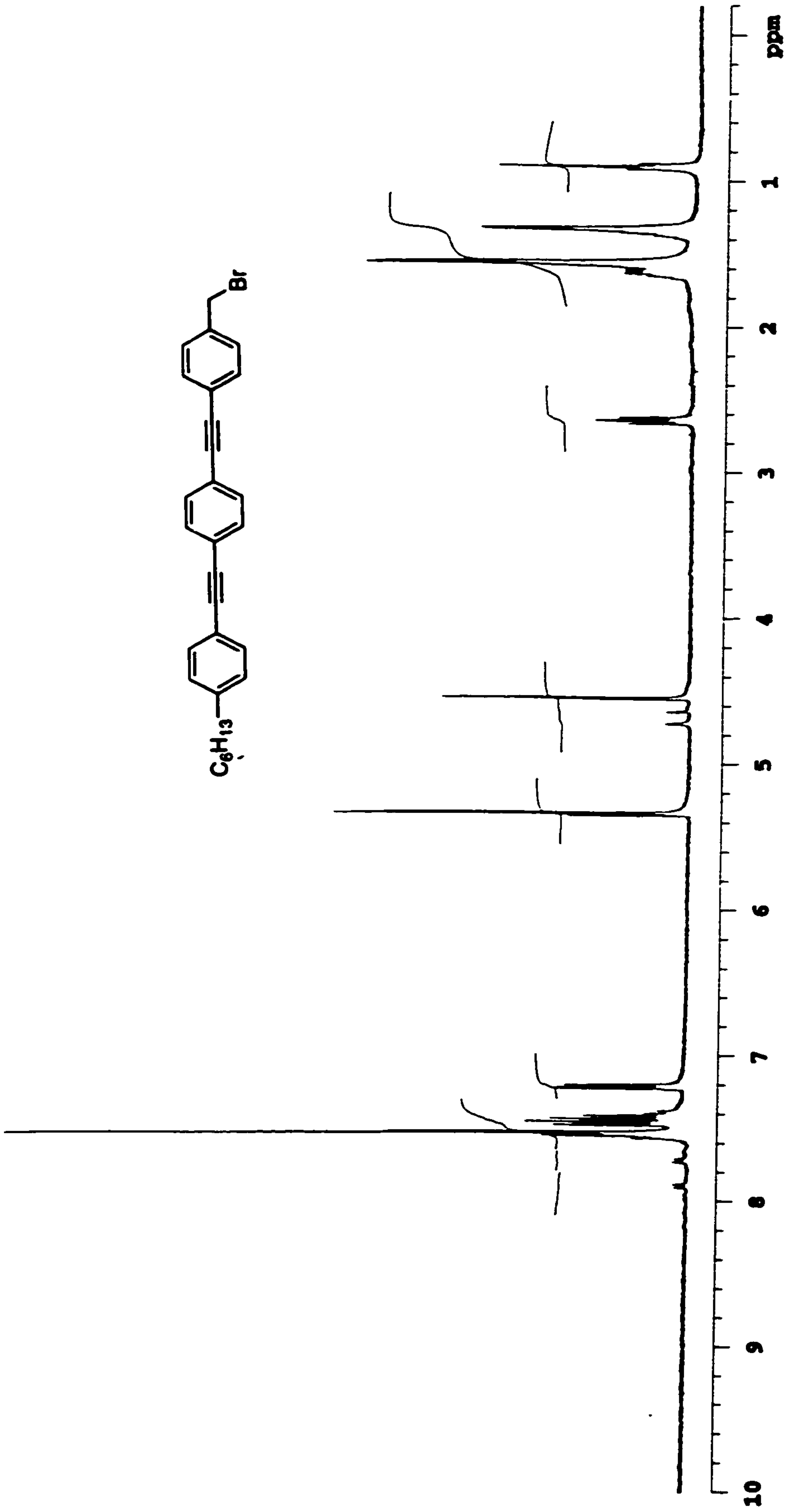
observ mass = 392.2134

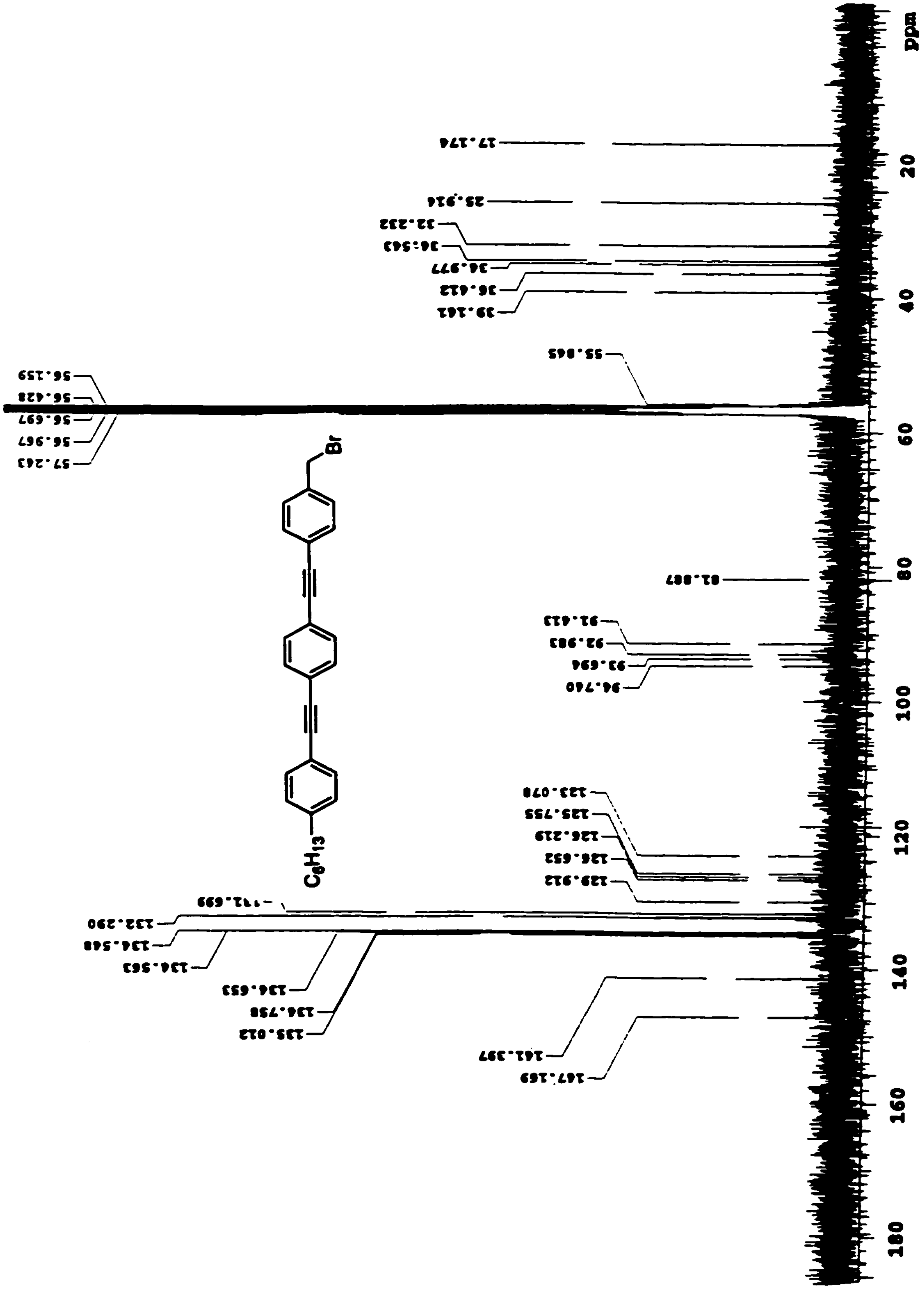
Calc mass = 392.2140

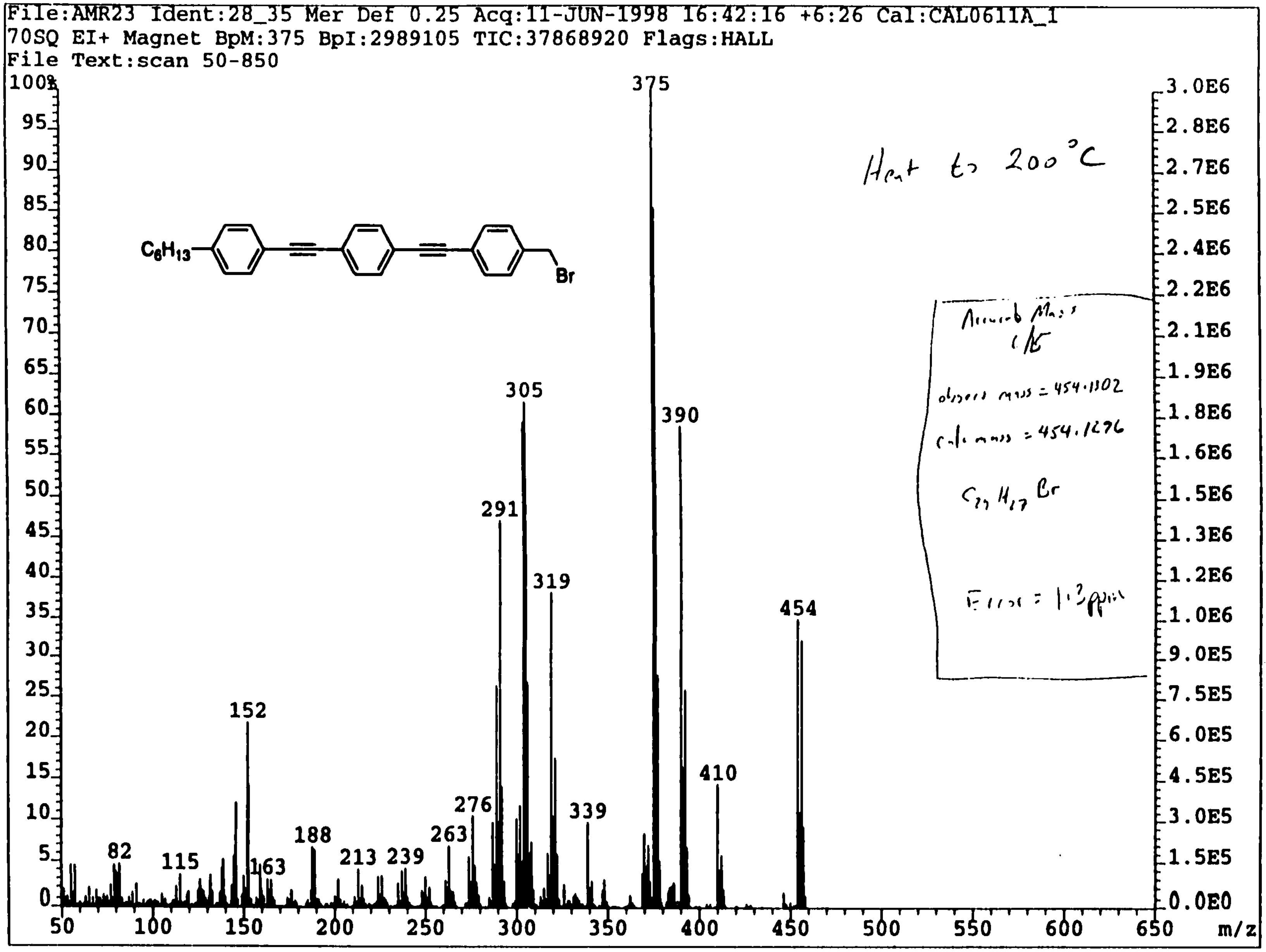
$C_{29}H_{28}O$

Error = 1.5 ppm


PERKIN ELMER
59.08
%T
19.09
4000
3500
3000
2500
2000
1500
1000
500
cm⁻¹
3122.2
2922.2
2855.6
2366.7
1844.4
1794.4
1786.7
1684.1
1650.0
1598.0
1516.7
1383.3
1116.7
833.9
600.0
522.2
450.0
C6H13
Br


C6H13
Br
ppm
1
2
3
4
5
6
7
8
9
10


ppm
20
40
60
80
100
120
140
160
180
17.174
25.914
32.233
34.543
34.977
36.412
39.141
55.865
56.159
56.428
56.697
56.967
57.243
81.887
91.413
92.983
93.694
94.740
123.078
125.755
126.219
126.653
129.913
131.699
132.290
134.548
134.563
134.653
134.758
135.012
141.397
147.169
Br
C_6H_{13}



Heat to 200 °C

Accurate Mass
EI

observed mass = 454.1102

calc mass = 454.1276

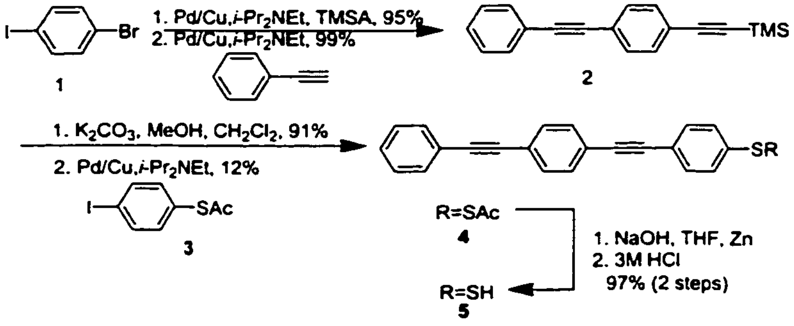
$C_{29}H_{27}Br$

Error = 1.2 ppm

Chapter 4

Preparation of Thiol-Terminated Phenylene-Ethynylene Oligomers for Examination of the Coordination and Structure of a "Molecular Scale Wire" linked to a Triosmium Cluster

Although it has been well-documented that bulk conjugated organic materials can be semiconducting or even conducting when doped,[1] recent studies have shown that oriented thiol-terminated conjugated rigid-rod molecules[2] can conduct electrons through a single, undoped, conjugated molecule, "molecular scale wire", to and from a metallic surface.[3] However, initial studies have indicated the presence of a barrier to electron transfer at the metal-organic interface.[4] A detailed knowledge of the bonding of thiols to metallic surfaces will be crucial to developing an understanding of electron transport mechanisms and the construction of devices involving the metal-organic interfaces. The metal-thiol linkage is usually regarded to be a single metal-sulfur bond with transfer of the hydrogen atom to the metal surface. Therefore, we have undertaken a study to determine the nature of the structures and modes of attachment of several thiol-terminated molecular wires to metal clusters serving as models for metal surfaces.



(1)

Eq 1 describes the synthesis of 4,4′-diphenylethynyl-1-thioacetylbenzene **4** from readily available 1-bromo-4-iodobenzene **1**. The starting material was monocoupled, via the more reactive iodo substituted, to trimethylsilylacetylene using a typical Sonagashura coupling procedure.[5] The reaction proceeded in good yield due to the greater reactivity of the aryl iodide toward coupling. Intermediate **2** was then coupled to phenylacetylene using similar conditions yet higher temperatures to enhance coupling to the aryl bromide. The alkyne was deprotected using potassium carbonate and methanol and then coupled to 1-iodo-4-thioacetylbenzene[6] to form molecular wire **4**. The deprotection of the thioacetate must be preformed under a dry argon or nitrogen environment. Precautions must be taken to exclude water and air, in order to inhibit disulfide formation.

Reaction of the thiol-terminated molecular wire **5** with $Os_3(CO)_{10}(NCMe)_2$ in methylene chloride forms the desired complex in 49% yield.[7] Crystals of **5** reacted with the triosmium complex suitable for X-ray crystallographic analysis were obtained by slow evaporation of solvent from a solution in methylene chloride at 25 °C. An ORTEP diagram of the molecular structure of **5** reacted with the triosmium complex is shown in Figure 1.[8,9]

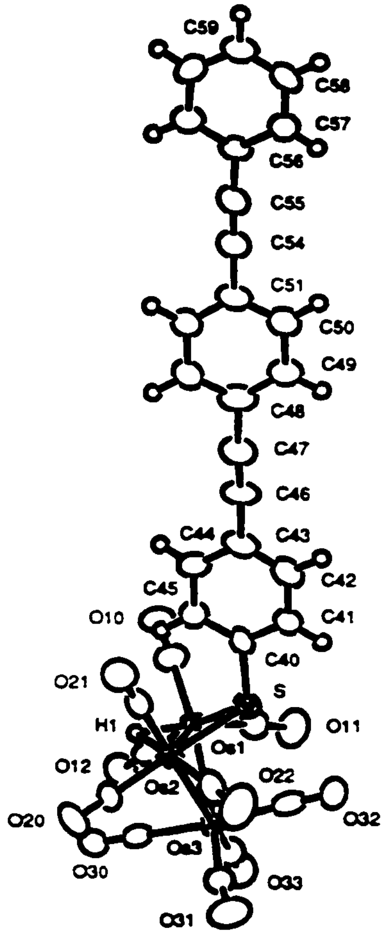
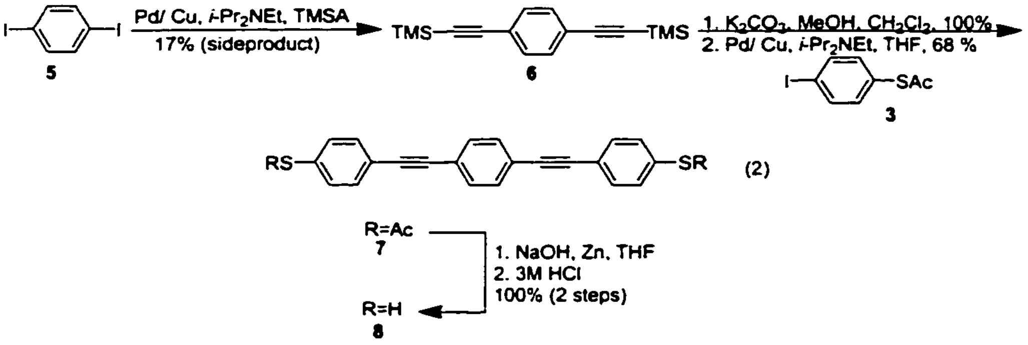

C59
C58
C57
C56
C55
C54
C51
C50
C49
C48
C47
C46
C44
C43
C42
C45
C41
O10
C40
O21
S
H1
O11
Os1
O12
O22
Os2
O20
O32
Os3
O30
O33
O31

Figure 1: An ORTEP diagram of the molecular structure Of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5)$, **5**. Selected interatomic distances (Å) and angles(°) are: Os(1) - Os(2) = 2.8765(8), Os(1) - Os(3) = 2.8565(7), Os(2) - Os(3) = 2.8626(8), Os(1) - S = 2.423(3), Os(2) - S = 2.421(4), Os(1) - H(1) = 1.9(1), Os(2) - H(1) = 1.81(8), S - C(40) = 1.82(1), C(46) - C(47) = 1.16(2), C(54) - C(55) = 1.19(2), S ··· C(59) = 18.27(2); Os(1) - S - C(40) = 113.5(4), Os(2) - S - C(40) = 111.6(5).

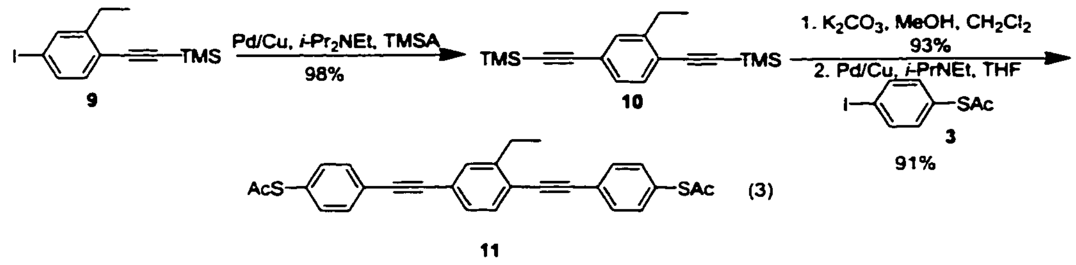
The molecule consists of a linear $SC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ linked to the triosmium cluster by the sulfur atom bridging two of the three-osmium atoms. The reaction has produced cleavage of the thiol sulfur-hydrogen bond and transfer of the hydrogen atom to the osmium cluster to become a hydride ligand. The position of the hydride ligand was located and refined crystallographically. It bridges the Os(1) – Os(2) bond of a triangular cluster of three osmium atom, Os(1) – H(1) = 1.9(1)Å and Os(2) – H(1) = 1.81(8)Å, and exhibits the characteristic high field resonance shift in the ^{1}H NMR spectrum, δ=-17.04. The sulfur atom bridges the same two metal atoms on the other side of the Os_3 plane, Os(1) – S= 2.423(3)Å and Os(2) – S= 2.421(4)Å. These values are similar to those found for other bridging thiolate-triosmium linkages that have been structurally characterized previously.[10] The alkyne C-C bonds are short, C(46)-C(47)=1.16(2)Å, C(54)-C(55)=1.19(2)Å as expected for C-C triple bonds, and the alkyne groups are linear. The sulfur-carbon distance, S-C(40)=1.82(1)Å, is typical of a carbon-sulfur single bond. The overall length of the ligand is an interesting feature. The distance from S to C(59) is 18.27Å. Although the central aryl ring is twisted approximately 10° away from the planes of the two other rings, the three aryl rings are nearly coplanar. This is a feature that would facilitate electron transmission through the π-orbital network.

Studies have shown that bis(phenylethynyl)arenes exhibit strong fluorescence and are effective receptors for chemilumescence processes.[11] Accordingly, we have investigated the UV-vis spectral properties of **5** reacted with the triosmium complex. Compound **5** reacted with the triosmium complex exhibits a single strong UV absorption at 332 nm (ε=48,500 $M^{-1}cm^{-1}$) and a series of emissions at 348 nm, 362 nm, and 377 nm (λ_{ex}=300 nm) which can be attributed to the $SC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ ligand. Although the bonding of thiol-terminated molecular wires to metallic surfaces is often drawn to a single metal atom with loss of the hydride unit,[12] we have now shown that for links to osmium, the metal-thiol (thiolate) interface clearly involves a bridging sulfur atom and a bridging hydride ligand.

The synthesis of phenylene ethynylenes with two thioacetyl moieties have been synthesized. These compounds will enable for molecular scale wires that will perform as interconnects between two devices. Numerous molecular scale wires were synthesized with two active termini for the attachment of the wire to differing devices. Eq 2 shows the formation of a dithiol-terminated phenylene ethynylene. The reaction conditions gave high yields, yet the dithiol was only sparingly soluble in most organic solvents, except acetonitrile. We were not able to attach the dithiol to the triosmium cluster in significant yields. It is believed that the low solubility of the dithiol molecular wire significantly reduced the yield of the osmium complex.

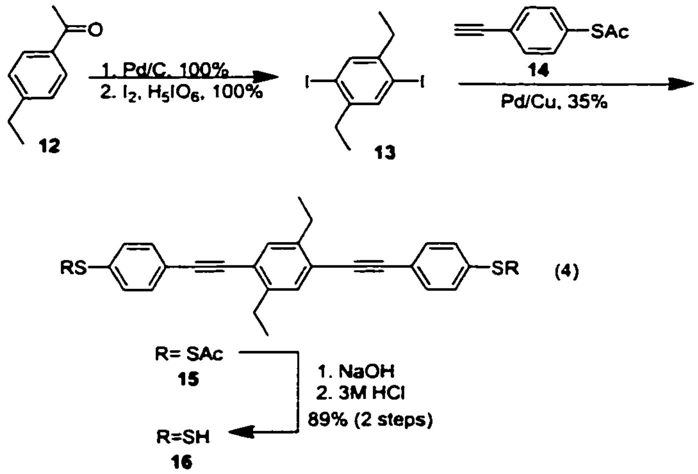

5
Pd/ Cu, i-Pr2NEt, TMSA
17% (sideproduct)
TMS
TMS
6
1. K2CO3, MeOH, CH2Cl2, 100%
2. Pd/ Cu, i-Pr2NEt, THF, 68 %
SAc
3
RS
SR
(2)
R=Ac
7
1. NaOH, Zn, THF
2. 3M HCl
100% (2 steps)
R=H
8

The solubility of unsubstituted compound 7 is moderately low in most organic solvents; therefore, it is necessary to place *n*-alkyl side chain moieties on the phenylene ethynylene oligomers. Although a long alkyl chain is important to retain solubility of a molecular wire in common organic solvents, it also could be sterically problematic for the connection of the wire and the metal probe and increase the difficulty of synthesis.


I
TMS
9
Pd/Cu, i-Pr$_2$NEt, TMSA
98%
TMS
TMS
10
1. K$_2$CO$_3$, MeOH, CH$_2$Cl$_2$
93%
2. Pd/Cu, i-PrNEt, THF
I
SAc
3
91%
AcS
SAc
(3)
11

Intermediate **9** was coupled to trimethylsilylacetylene to afford **10** in high yield. **10** was then deprotected in the presence of potassium carbonate. The dialkyne compound was coupled to alligator clip **3** to afford molecular scale wire **11** in good yield.

To further increase the solubility of the dithiol terminated molecular wire, two ethyl subunits were attached to the central ring. Eq 14 shows the synthesis of this diethyl substituted compound.


O
12
1. Pd/C, 100%
2. I$_2$, H$_5$IO$_6$, 100%
I
I
13
SAc
14
Pd/Cu, 35%
RS
SR
(4)
R= SAc
15
1. NaOH
2. 3M HCl
89% (2 steps)
R=SH
16

4-Ethylacetophenone **12** was reduced to afford 1,4-diethylbenzene followed by cross couplings of 1,4-diiodobenzene **13** with alligator clip 4-thioacetyl-1-ethynylbenzene **14**[15] afforded the rigid rod molecular scale wire **15**. Removal of the acetyl protecting groups with sodium hydroxide in THF/H_2O and rapid workup produced soluble **16** with free thiol ending groups. Disappointly, the molecule was reacted with the triosmium cluster giving no desirable product.

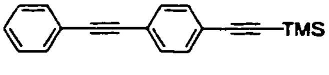
Experimental

General. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. All reagents and starting materials were purchased from Aldrich, Acros, Fischer, Fluka, and Alfa Aesar if not otherwise stated. Alkyllithium reagents were obtained from FMC. Pyridine, methyl iodide, triethylamine, and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Toluene and benzene were distilled over CaH_2. Methylene chloride and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine and *N, N*-diisopropylethylamine was distilled over CaH_2. MeOH was dried over oven dried 3 Å molecular sieves. ^1H NMR spectra were recorded at 300, 400, or 500 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively or at 400 and 500 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively or at 400 MHz on Oxford Instruments 400 MHz NMR using Brüker XWIN NMR processing program. The ^{13}C NMR spectra were recorded at 75, 100, or 125 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively at 100 and 125 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively or at 125 MHz on Oxford Instruments 400 MHz NMR using Brüker XWIN NMR processing program. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0-ppm $CDCl_3$ resonance as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. Gas chromatography experiments were performed on a Hewlett-Packar GC model 5890A equipped with an Alltech column (cat # 932525, serial

9059) 25 m × 0.25 mm D × 0.2 mm. Gravity column chromatography, silica gel plugs, and flash chromatography were preformed using 230-400 mesh silica gel from EM Science. Thin layer chromatography was preformed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Combustion analyses were obtained from Atlantic Microlab, Inc., P. O. Box 2288, Norcross, GA 30091.

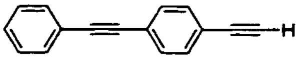
General Procedure for the coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).[5] To an oven dried round bottom flask equipped with a water cooled West condenser or screw capped pressure tube with a magnetic stirbar were added the aryl halide, bis(triphenylphosphine)palladium(II) chloride (3-5 mol % per halide), and copper(I) iodide (6-10 mol % per halide). Triphenylphosphine was used in some reactions to keep the palladium in solution. The vessel was then sealed with a rubber septum under a N_2 atmosphere. A co-solvent system of THF, benzene, or methylene chloride was added at this point depending on the solubility of the aryl halide. Then base, either triethylamine or *N,N*-diisopropylethylamine, was added and finally the terminal alkyne (1-1.5 mol % per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was then quenched with water, a saturated solution of NH_4Cl, or brine. The organic layer was diluted with methylene chloride or Et_2O and washed with water, a saturated solution of NH_4Cl, or brine (3×). The combined aqueous layers were extracted with methylene chloride or Et_2O (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each material.

General procedure for the deprotection of trimethylsilyl protected alkynes (Method A). The silylated alkyne was dissolved in methanol and potassium carbonate was added. The mixture was stirred overnight before poured into water. The solution was extracted with ether or ethyl acetate and washed with brine. After drying over magnesium sulfate the solvent was evaporated *in vacuo* to afford pure products. **(Method B).** The silylated alkyne was dissolved in pyridine in a plastic vessel. A mixed solution of 49% hydrofluoric acid and 1.0 M tetrabutylammonium fluoride in THF was added at room temperature. The solution was stirred for 15 min and quenched with silica gel. The mixture was poured into water and extracted with ether. The extract was washed with brine and dried over magnesium sulfate. After filtration the solvent was evaporated *in vacuo*. The crude products were purified by a flash chromatography on silica gel. Eluents and other slight modifications are described below for each material.

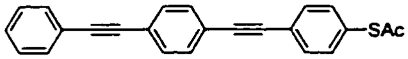


4-(Phenylethynyl)-1-(trimethylsilylethynyl)benzene (2, AMR-I-82). See the general procedure for the Pd/Cu coupling reaction. CuI (78 mg, 0.41 mmol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.20 mmol), and 1-Bromo-4-(2′-trimethysilylethynyl)benzene (1.0 g, 4.0 mmol) were added to a screw cap tube and purged with nitrogen for ~5 min. Phenylacetylene (0.60 mL, 5.5 mmol), triethylamine

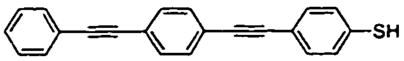
(2.0 mL, 14 mmol), and benzene (2 mL) were added with stirring at room temperature under an inert atmosphere. The tube was purged with nitrogen, sealed, and the reaction was stirred at 80 °C overnight. The mixture was diluted with methylene chloride and extracted with distilled water. The organic layer was dried with $MgSO_4$ and volatiles were removed via rotary evaporation. The resulting brown solid was eluted 2 × through a 4 × 20 cm column of silica gel using hexanes as the eluent. The product was obtained as a crystalline white solid (1.08 g, 99 %). TLC R_f=0.28 (hexanes). IR (KBr) 3053, 2957, 2897, 2153, 1602, 1509, 1441, 1406, 1249, 866, 844, 757, 692, 628, 550, 529 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.512 (m, 2 H), 7.441 (m, 4 H), 7.336 (m, 3 H), 0.253 (s, 9 H).



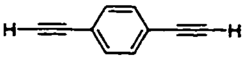
4-(Phenylethynyl)-1-(ethynyl)benzene (AMR-I-103, 123, 128, 138, 152, 167, II-145). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. A mixture of 4-(Phenylethynyl)-1-(trimethylsilylethynyl)benzene (0.94 g, 3.4 mmol), K_2CO_3 (1.9 g, 14 mmol), methanol (2.5 mL), and methylene chloride (4 mL) was stirred for 30 min. Methylene chloride was added and the resulting mixture was extracted with distilled water. The organic layer was dried with $MgSO_4$ and the volatiles were removed via rotary evaporation. The product was obtained as a pale yellow solid (0.63 g, 91 %). IR (KBr) 3278, 3079, 3062, 3053, 3033, 3017, 1602, 1500, 1440, 1406, 1265, 1249, 1181, 1111, 1101, 1070, 1025, 922, 842, 834, 759, 690, 666, 629, 548, 527, 460 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.515 (m, 2 H), 7.462 (m, 4 H), 7.341 (m, 3 H), 3.159 (s, 1 H).



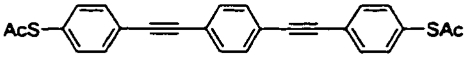
1-Thioacetyl-4-(4′-(phenylethynyl)-1′-(ethynyl)phenyl)benzene (4, AMR-I-168, II-147). See the general procedure for the Pd/Cu coupling reaction. Copper iodide (0.06 g, 0.30 mmol), bis(dibenzylideneacetone)dipalladium (0.09 g, 0.15 mmol), triphenylphosphine (0.16 g, 0.60 mmol), 1-iodo-4-thioacetylbenzene (0.84 g, 3.00 mmol) and 4-(phenylethynyl)-1-(ethynyl)benzene (0.5 g, 2.5 mmol) were added to a screw cap tube and air removed in vacuo then purged with nitrogen (3×). Diisopropylethylamine (1.7 mL, 10.0 mmol), and THF (15 mL) were added with stirring at room temperature under an inert atmosphere. The tube was purged with nitrogen, sealed, and the reaction was stirred at ambient for 16 h. TLC of the reaction mixture indicated complete consumption of starting material. The mixture was extracted with diethyl ether and filtered through celite and extracted with ammonium chloride (3×). The organic layer was dried with MgSO$_4$ and volatiles were removed via rotary evaporation. The residue purified by flash liquid chromatography using silica gel (1:1 hexanes: methylene chloride) yielding 0.102 g (12%) of the titled compound. IR (KBr) 3435.9, 3138.5, 2215.4, 1697.4, 1656.4, 1507.7, 1379.5, 1353.8, 1128.2, 1107.7, 1015.4, 943.6, 838.6, 828.1, 759.0, 756.7, 692.0, 620.5 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 7.54-7.50 (m, 2 H), 7.39 (d, *J*=8.5 Hz, 2 H), 7.34 (d, *J*=2 Hz, 3 H), 7.24 (d, *J*=8.5 Hz, 2 H), 7.16 (br s, 1 H), 7.03-6.98 (m, 3 H), 1.81 (s, 3 H). ^{13}C NMR (400 MHz, C$_6$D$_6$) δ 190.94, 134.24, 132.01, 131.62, 131.58, 128.91, 128.35, 127.21, 126.96, 124.12, 123.60, 123.28, 122.93, 91.87, 91.01, 90.90, 89.52, 29.55. HRMS calcd for $C_{23}H_{16}SO$: 352.0922. Found 352.0921.



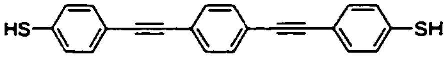
1-Thiol-4-(4′-(phenylethynyl)-1′-(ethynyl)phenyl)benzene (5, AMR-I-172).[13] To an oven dried 100 mL round bottom flask, 1-thioacetyl-4-(4′-(phenylethynyl)-1′-(ethynyl)phenyl)benzene (0.04g, 0.10 mmol), sodium hydroxide (0.01g, 0.20 mmol), and zinc dust (0.01g) along with a stir bar were added, and air removed in vacuo, then the flask was purged with nitrogen (3×). Degassed, deionized water (3 mL) was added and the reaction mixture was purged with Ar for 30 min to remove any residual oxygen. THF (10 mL) was then added to the reaction mixture that was allowed to stir overnight at ambient temperature under a positive pressure of Ar. The following morning the reaction mixture had become dry; therefore, THF (5 mL) was added and the solids redissolved. Degassed 3 M HCl (0.15 mL) was then added to the reaction mixture and allowed to stir for 30 m. The reaction mixture was dried by Ar sparge and degassed water (5 mL) was added then benzene (3× 5 mL) was added and the organic layer was extracted and placed in an oven dried 50 mL round bottom flask. Solvent was removed in vacuo leaving a golden yellow solid (0.03g) corresponding to a 97% yield. The solid was stored in the dry box until reacted with the $Os_3(CO)_{12}(NCMe)_2$ cluster. ^1H NMR (300 MHz, C_6D_6) δ 7.53-7.50 (m, 2 H), 7.34 (s, 4 H), 7.22 (d, *J*=8.4 Hz, 2 H), 7.02-6.99 (m, 3 H), 6.72 (d, *J*=8.4 Hz, 2 H), 2.96 (s, 1 H).



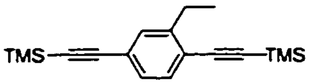
1,4-(Ethynyl)benzene (AMR-I-185). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. To a 100 round bottom flask, 1,4-(trimethylsilylethynyl)benzene (8.1g, 3.00 mmol), potassium carbonate (2,07g, 15 mmol), methylene chloride (20 mL) and methanol (20 mL) were added along with a stirbar. The reaction mixture was stirred for 2 h at ambient temperature. The reaction mixture was washed with water and extracted with methylene chloride. The organic layer was dried with magnesium chloride and solvent was removed in vacuo. The reaction gave 0.38 g of the desired material, 100% yield. No purification was needed and the compound was taken directly to the next compound. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.43 (s, 4 H), 3.16 (s, 2 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 132.03, 122.56, 83.04, 79.11.



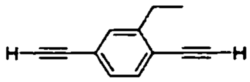
1-Thioacetyl-4(4′-((4″-thioacetyl)phenylethynyl)-1′-(ethynyl)phenyl)benzene (7, AMR-I-186). See the general procedure for the Pd/Cu-catalyzed coupling reaction. To an oven dried large screw cap tube was added 1,4-(ethynyl)benzene (0.32g, 2.50 mmol), 1-iodo-4-thioacetylbenzene (1.69g, 6.00 mmol), bis(dibenzylideneacetone)dipalladium (0.09 g, 0.15 mmol), triphenylphosphine (0.16 g, 0.60 mmol), and copper iodide (0.06g, 0.30 mmol) along with a stirbar. Air was removed in vacuo then the flask was nitrogen purged (3×). THF (20 mL) and diisopropylethylamine (1.74 mL, 10 mmol) were added to the reaction mixture and the tube was capped and allowed to stir at ambient temperature overnight. The reaction mixture was washed with NH_4Cl (aq) and extracted with methylene chloride. The organic layer was dried with magnesium chloride and solvents were removed in vacuo. The desired compound was purified using flash liquid chromatography in a 3 × 20 inch column with 8 inches of silica gel using a 1:1 mixture of methylene chloride/ hexanes as the eluent. The desired compound had a $R_f = 0$ which was retrieved with a methylene chloride flush giving 0.72g (68%) of the desired compound. IR (KBr) 3456.4, 3128.2, 2194.9, 1917.9, 1687.2, 1651.3, 1620.5, 1548.6, 1507.7, 1379.5, 1348.7, 1266.7, 1112.8, 1010.3, 959.0, 820.5, 759.0, 692.3, 620.5 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.73 (AB q, *J*=2.35 Hz, $\Delta\upsilon$= 6.58 Hz, 4 H), 7.59 (s, 2 H), 7.40 (s, 2 H), 7.10 (AB q, *J*=4.6 Hz, $\Delta\upsilon$=4.3 Hz, 4 H), 2.41 (s, 6 H). ^{13}C NMR (400 MHz, C_6D_6) δ193.07, 143.09, 134.02, 131.96, 131.42, 130.29, 128.18, 90.51, 90.45, 30.26. HRMS calcd for $C_{26}H_{18}O_2S_2$: 426.0748. Found 426.0747.



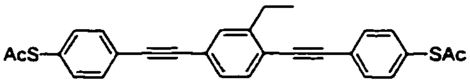
1-Thiol-4(4′-((4″-thiol)phenylethynyl)-1′-(ethynyl)phenyl)benzene (8, AMR-I-190, 192).[13] To an oven dried 100 mL round bottom flaskwas added 1-thioacetyl-4(4′-((4″-thioacetyl)phenylethynyl)-1′-(ethynyl)phenyl)benzene (0.05g, 0.12 mmol), sodium hydroxide (0.02 g, 0.48 mmol), and zinc dust (0.01g) along with a stir bar were added and air removed in vacuo and then the flask was purged with nitrogen (3×). Degassed, deionized water (6 mL) was added and the reaction mixture was purged with Ar for 30 min to remove any residual oxygen. THF (15 mL) was added to the reaction mixture that was then allowed to stir overnight at ambient under a positive pressure of Ar. The following morning the reaction mixture had dried; therefore, 5 mL of THF was added and the solids redissolved. Degassed 3 M HCl (0.30 mL) was then added to the reaction mixture and allowed to stir for 30 m. The reaction mixture was dried by Ar sparge and degassed water (5 mL) was added then benzene (3× 5 mL) was added and the organic layer was extracted and placed in an oven dried 50 mL round bottom flask. Solvent was removed in vacuo leaving a golden yellow solid (0.04g) corresponding to a 100% yield. The solid was stored in the dry box until reacted with the $Os_3(CO)_{12}(NCMe)_2$ cluster. The compound was found to insoluble in benzene, methylene chloride, THF, and diethyl ether, yet sparingly soluble in acetonitrile. The named compound was found to be insoluble in all common NMR solvents; therefore, no NMR spectra could be obtained.



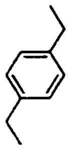
2-Ethyl-1,4-bis(trimethylsilylethynyl)benzene (10, AMR-I-76, 79). See the general procedure for the Pd/Cu-catalyzed coupling reaction. To a nitrogen purged screw capped tube, $Pd(PPh_3)Cl_2$ (0.021 g, 0.03 mmol), CuI (0.012g, 0.06mmol), and a stir bar were added. The reaction vessel was capped with a rubber septa and air was removed in vacuo for 15 min and then backfilled with nitrogen. 1-Iodo-3-ethyl-4-(trimethylsilylethynyl)benzene (0.201 g, 0.6 mmol) dissolved in 2 mL of triethylamine was added. Reaction was then capped with a screw cap and stirred overnight. Reaction was checked for completion by TLC and the reaction mixture was diluted with diethyl ether and extracted with distilled water. After drying the organic layer over magnesium sulfate, the solvent was removed in vacuo to afford a crude product that was purified by column chromatography (silica gel). The reaction afforded 0.175g (98%) of the title compound as a yellow-brown compound. R_f= 0.55 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 1 H), 7.28 (s, 1 H), 7.19 (dd, *J* = 6.3, 1.6 Hz, 1 H), 2.74 (q, *J* = 7.6 Hz, 2 H), 1.21 (t, *J* = 7.5 Hz, 3 H), 0.23 (s, 9 H), 0.22 (s, 9 H).



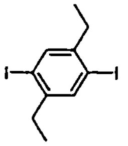
2-Ethyl-1,4-diethynylbenzene (AMR-I-77, 80). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. To a 50 mL round bottom flask, 2-ethyl-1,4-bis(trimethylsilylethynyl)benzene (0.128g, 0.43 mmol), potassium carbonate (0.28g, 2.15 mmol), 3 mL of methanol, and 3 mL of methylene chloride were added along with a stir bar. The reaction mixture was capped with a rubber septa and stirred under nitrogen for 2 h, then checked by TLC. The mixture was diluted with diethyl ether and extracted with distilled water. The organic layer was dried over magnesium sulfate and excess solvent was removed in vacuo. The reaction afforded 0.0615g (93%) of the desired compound that was pure by NMR standards, therefore no purification was required. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 1 H), 7.33 (s, 1 H), 7.25 (dd, *J* = 7.9, 1.6 Hz, 1 H), 3.31 (s, 1 H), 3.12 (s, 1 H), 2.78 (q, *J* = 7.6 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3 H).



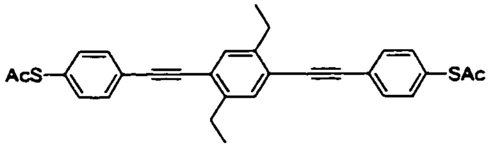
1,4-Bis(4′-thioacetylphenylethynyl)-2-ethylbenzene (11, AMR-I-81). See the general procedure for the Pd/Cu-catalyzed coupling reaction. To a screw cap tube, 1-iodo-4-thioacetylbenzene (0.250g, 0.9 mmol), bis(dibenzylideneacetone)palladium(0) (0.29g, 0.05 mmol), triphenylphosphine (0.060g, 0.23 mmol), and copper iodide (0.017g, 0.09 mmol) were added and then the vessel was capped with a rubber septa and introduced into the drybox. THF (1.5 mL), 2-ethyl-1,4-diethynylbenzene (0.0553g, 0.36 mmol), and then Hünig's base (0.186g, 1.44 mmol) were added. The reaction vessel was capped, removed from the drybox, and stirred overnight. The reaction was diluted with diethyl ether and extracted with distilled water. After drying the organic layer over magnesium sulfate, the solvent was removed in vacuo to afford a crude product that was purified by gravity liquid chromatography (silica gel). The reaction afforded 0.085g (91%) of the title compound as a yellow compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.1 Hz, 4 H), 7.46 (d, J = 8.1 Hz, 1 H), 7.40 (d, J = 1.7 Hz, 1 H), 7.38 (d, J = 8.2 Hz, 2 H), 7.38 (d, J = 8.3 Hz, 2 H), 7.33 (dd, J = 8.1, 1.7 Hz, 1 H), 2.86 (q, J = 7.6 Hz, 2 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.30 (t, J = 7.5 Hz, 3 H).



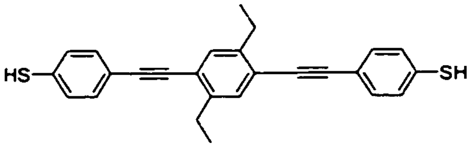
1,4-Diethylbenzene (AMR-I-276).[14] To an oven dried thick walled Parr bomb vessel were added 4-ethylacetophenone (14.82 g, 100 mmol), HCl (20 mL), 10% Pd/C (2.0 g), and ethanol (100 mL). The vessel was attached to the hydrogenator and allowed to react for 2 d at 70 °C and 60 psi of H_2 pressure. Upon completion, the reaction mixture was filtered through a pad of Celite to remove the Pd/C. The reaction was quenched with NaOH (3 M, 150 mL). The reaction mixture was further diluted with methylene chloride and extracted with water (3×). The combined organic layers were dried over $MgSO_4$. The solvents were removed carefully in vacuo to afford the desired product (13.27 g, 99 % yield) as a clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 4 H), 2.63 (q, *J*=7.5 Hz, 4H), 1.23 (t, *J*= 7.5 Hz, 6H).



1,4-Diethyl-2, 5-diiodobenzene (13, AMR-I-202, 278).[15] To an oven dried round bottom flask was added 1,4-diethylbenzene (1.34g, 10 mmol), periodoic acid (0.91g, 4 mmol), iodine (2.03g, 16 mmol), acetic acid (8.1 mL), water (1.62 mL), sulfuric acid (0.24 mL). A West condenser was attached and the reaction was heated to 100 C for 2.5 h. The reaction mixture was cooled and poured into an aqueous sodium bisulfite solution and the brown solids were collected. The solids were dissolved in diethyl ether and stirred with activated charcoal (Norit A) for 5 h. The mixture was filtered through a celite pad that was washed with additional diethyl ether. The ether was removed leaving a white crystalline material (3.92 g, 100%). IR (KBr) 3128.2, 2964.1, 2861.5, 1456.4, 1384.1, 1379.5, 1343.6, 1312.8, 1251.3, 1184.6, 1030.8, 979.5, 959.0, 882.0. 779.5, 712.8 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 2 H), 2.62 (q, *J*=7.5 Hz, 2 H), 1.16 (t, *J*=7.6 Hz, 3 H). ^{13}C NMR (400 MHz, C_6D_6) δ 145.67, 138.43, 100.13, 33.09, 14.43. HRMS calcd for $C_{10}H_{12}I_2$: 385.9029. Found 385.9027.



1-Thioacetyl-4(4′-((4″-thioacetyl)phenylethynyl)-1′-(ethynyl)-2′, 5′-(diethyl) phenyl)benzene (15, AMR-I-212). See the general procedure for the Pd/Cu-catalyzed coupling reaction. To an oven dried large screw cap tube was added 1,4-diethyl-2,5-diiodobenzene (0.77g, 2.00 mmol), 1-ethynyl-4-thioacetylbenzene (0.78g, 4.40 mmol), bis(dibenzylideneacetone)dipalladium (0.07g, 0.12 mmol), triphenylphosphine (0.13 g, 0.48 mmol), and copper iodide (0.05g, 0.24 mmol). Air was removed in vacuo and the flask was nitrogen purged (3×). THF (15 mL) and diisopropylethylamine (1.40 mL, 8 mmol) were added to the reaction mixture and the tube was capped and heated at 50-55 C overnight. The reaction mixture was allowed to cool and was then filtered through a pad a celite. Then washed with diethyl ether. The mixture was washed with NH_4Cl (aq) and extracted with diethyl ether. The organic layer was dried with magnesium chloride and solvents were removed in vacuo. The desired compound was separated using flash liquid chromatography in a 3 × 20 inch column with 8 inches of silica gel using a 1:1 mixture of methylene chloride/ hexanes as the eluent. The desired compound had a R_f=0 which was retrieved with a methylene chloride flush giving 0.33g (35%) of the desired compound. IR (KBr) 3435.9, 3138.5, 2964.1, 2861.5, 1692.3, 1656.4, 1589.7,1559.0, 1497.4, 1384.6, 1271.8, 1179.5, 1117.9, 1092.3, 1010.3, 9478.7, 882.1, 825.6, 743.6, 687.2, 620.5 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J*=9.2 Hz, 4 H), 7.38 (d, *J*=9.2 Hz, 4 H), 7.37 (s, 2H), 2.81 (q, *J*=8.5 Hz, 4 H), 2.43 (s, 6 H), 1.28 (t, *J*=8.5, 6H). ^{13}C NMR (400 MHz, C_6D_6) δ 193.16, 143.40, 134.06, 131.85, 131.45, 127.84, 124.45, 122.18, 93.26, 89.70, 30.26, 27.15, 14.72. HRMS calcd for $C_{30}H_{26}O_2S_2$: 482.1374. Found 482.1365.



1-Thiol-4(4′-((4″-thiol)phenylethynyl)-1′-(ethynyl)-2′,5′-(diethyl) phenyl)benzene (16, AMR-I-220).[13] To an oven dried 100 mL round bottom flask, 1-thioacetyl-4(4′-((4″-thioacetyl)phenylethynyl)-1′-(ethynyl)-2′,5′-(diethyl)phenyl)benzene (0.05g, 0.10 mmol), sodium hydroxide (0.02g, 0.40 mmol), and zinc dust (0.01g) along with a stir bar were added and air removed in vacuo then purged with nitrogen (3×). Degassed, deionized water (5 mL) was added and the reaction mixture was purged with Ar for 30 min to remove any residual oxygen. THF (10 mL) was then added to the reaction mixture that was then allowed to stir overnight at ambient under a positive pressure of Ar. The following morning the reaction mixture had dried; therefore, 5 mL of

THF was added and the solids went into solution. Degassed 3 M HCl (0.30 mL) was then added to the reaction mixture and allowed to stir for 30 min. The reaction mixture was dried by Ar sparge and degassed water (5 mL) was added then benzene (3× 5 mL) was added and the organic layer was extracted and placed in an oven dried 50 mL round bottom flask. Solvent was removed in vacuo leaving a golden yellow solid (0.04g) corresponding to a 100% yield. The solid was stored in the dry box until reacted with the $Os_3(CO)_{12}(NCMe)_2$ cluster. The compound was found to insoluble in benzene, methylene chloride, THF, and diethyl ether, yet sparingly soluble in acetonitrile. The named compound was found to be insoluble in all common NMR solvents; therefore, no NMR spectra could be obtained.

References and Notes

(1) *Handbook of Conducting Polymers*, Skotheim, T. A., Ed.; Dekker: New York, 1986.

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(7) 24.0 mg of $HSC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5$ (0.0773 mmol) dissolved in 4 mL of methylene chloride and was added to a solution of 75.0 mg of $Os_3(CO)_{10}(NCMe)_2$ (0.0804 mmol) dissolved in 50 mL of methylene chloride. After stirring for 2h at 25°C, the solvent was removed and the residue separated by TLC on silica gel by using a hexane/CH_2Cl_2 (3/1) solvent mixture. The reaction yielded a yellow band containing 44.1 mg $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_5)$, 49%. IR (νCO in hexane, cm^{-1}): 2100 (m), 2069 (vs), 2060 (m), 2026 (vs), 2020 (m), 2003

(m), 1992 (w), 1987 (w). ^{1}H NMR (δ in $CDCl_3$): 7.52-7.25 (m, 13 H, Ph), -17.04 (s, 1 H, Os-H). Anal. Calcd. (found): C, 33.10 (32.98; H, 1.22 (1.37).

(8) Crystal Data: space group = $P\bar{1}$, *a* = 15.019(3)Å, *b* = 13.831(2)Å, *c* = 9.299(1)Å, a = 90.21(10°, b = 72.67(2)°, γ = 114.77, Z = 2, 3221 reflections, R = 0.035. Diffraction measurements at 20°C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN MOTIF structure solving program library (v 1.8) of the Molecular Structure Corp., The Woodlands, TX on a Silicon Graphics Indigo^2 computer. An absorption correction (DIFABS) was applied.

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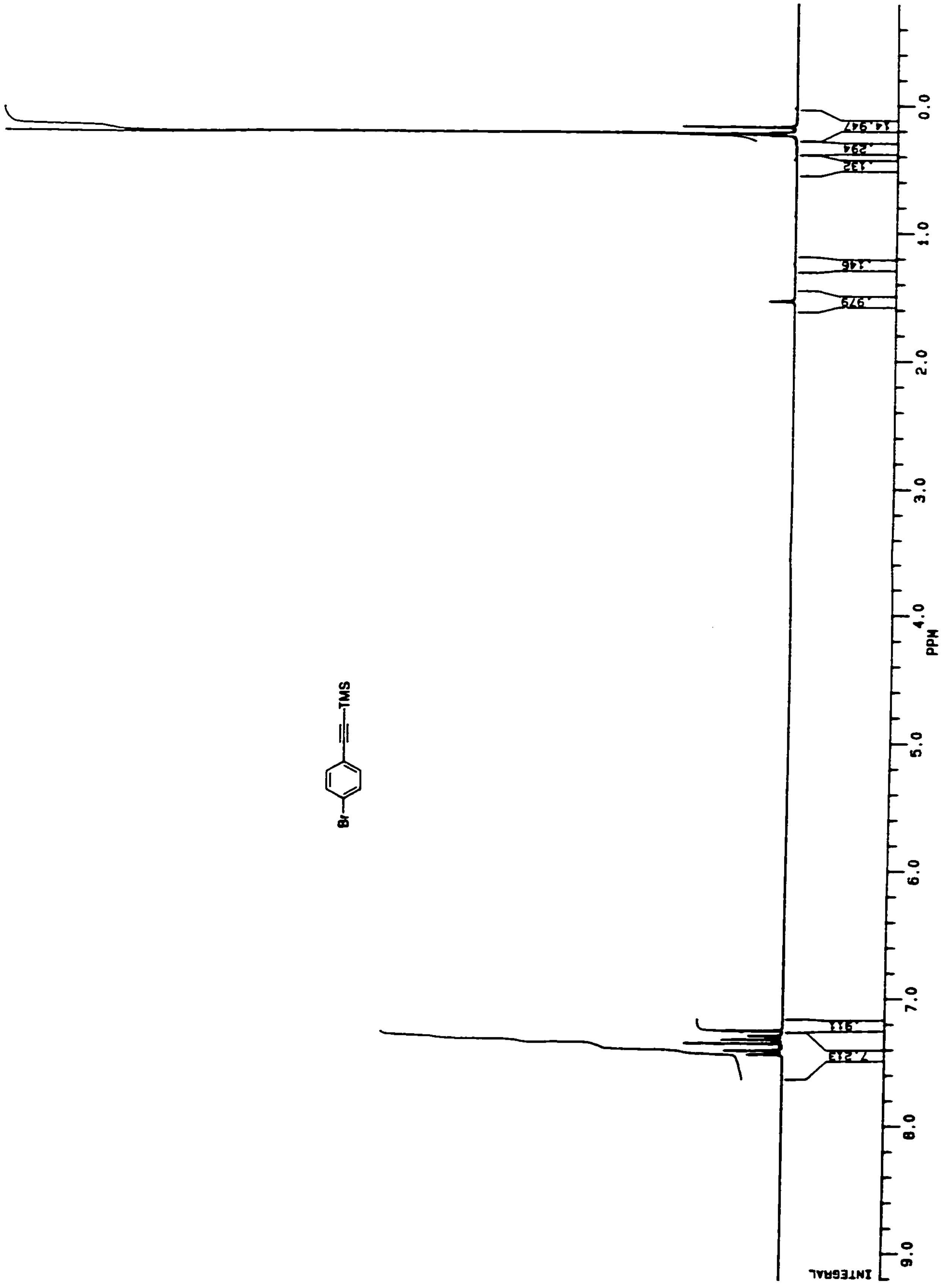
Spectral Section for
Chapter 4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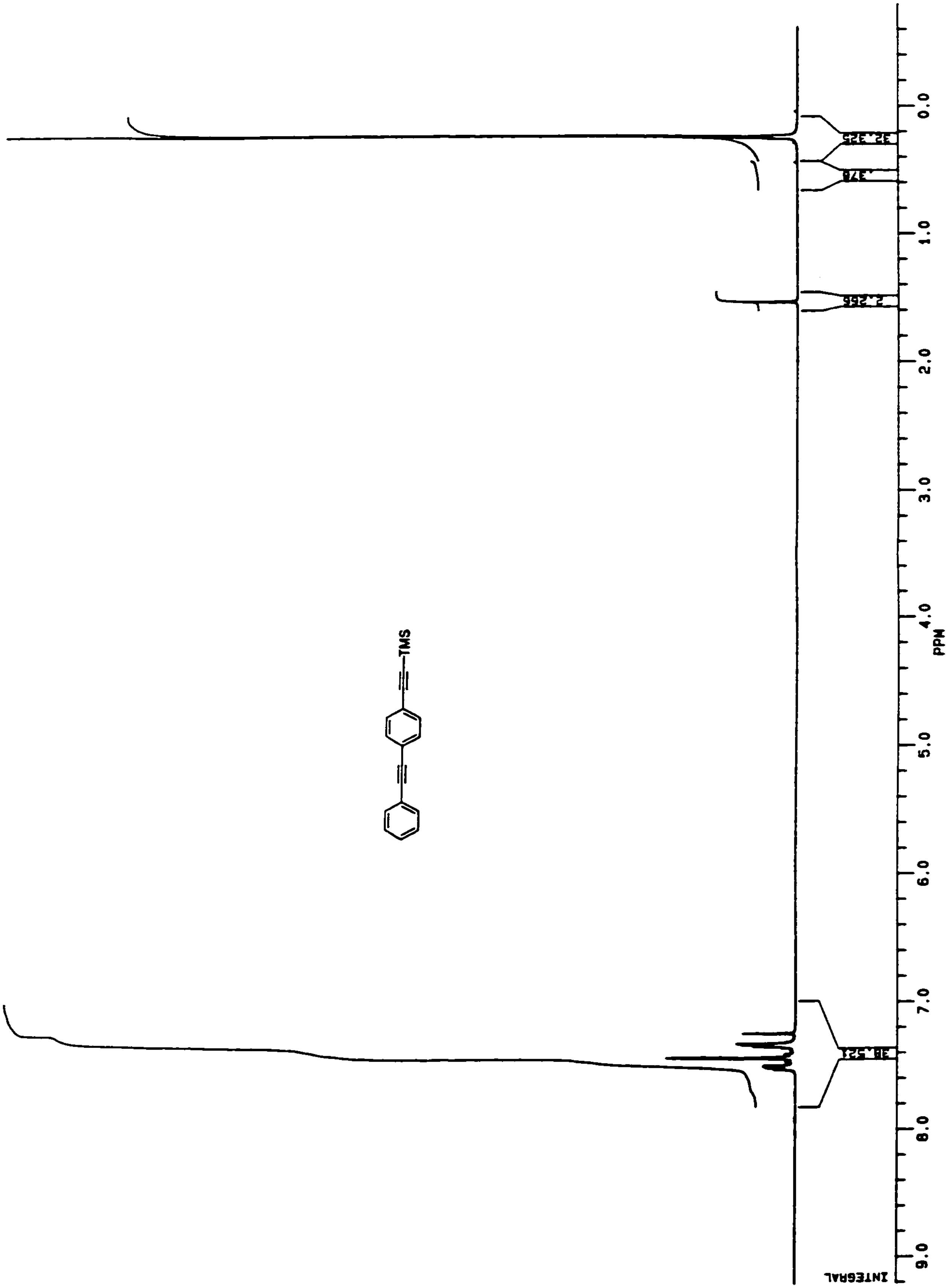
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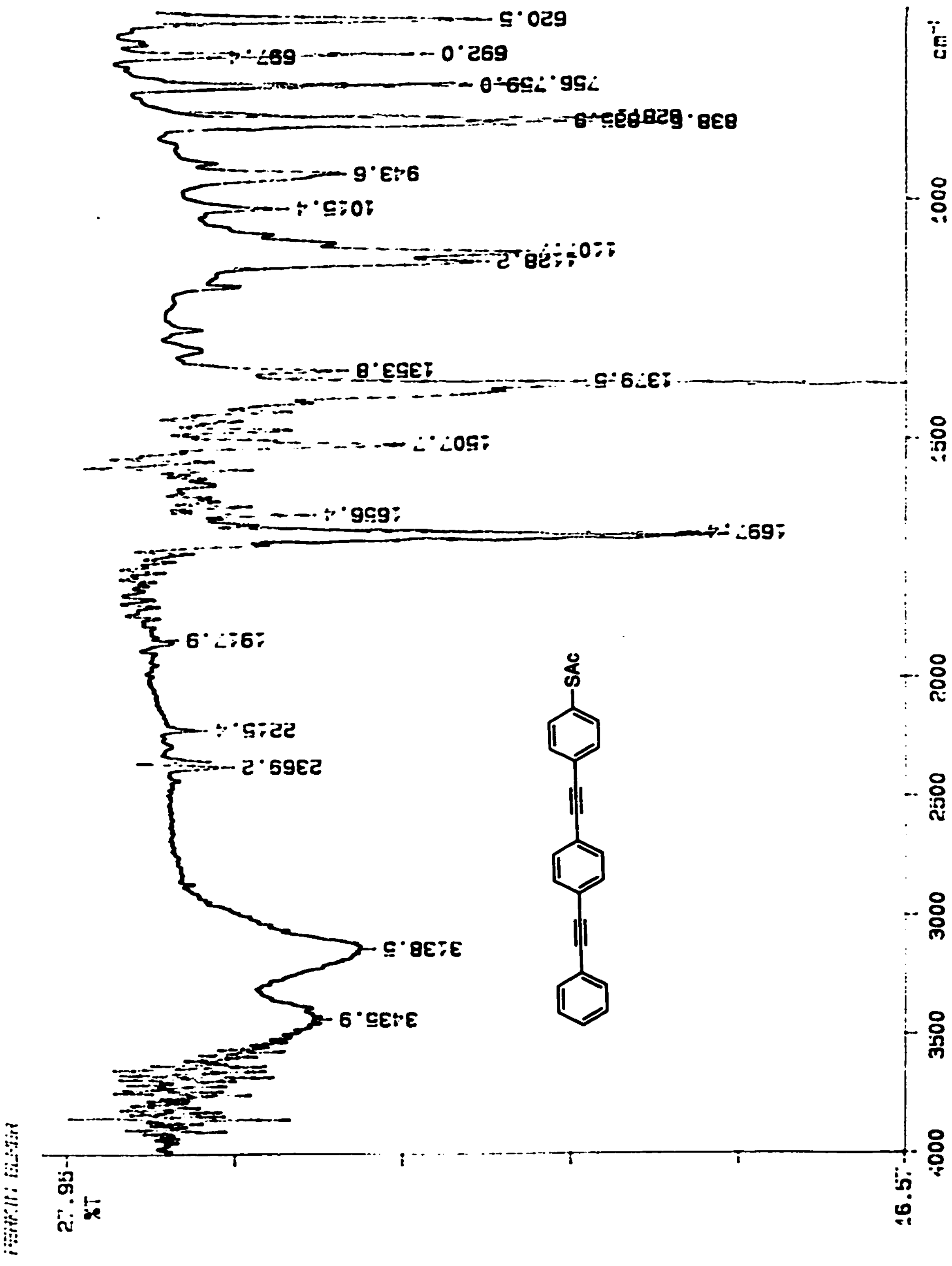
38.521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2365.2
2215.4
1917.9
1697.4
1656.4
1507.7
1379.5
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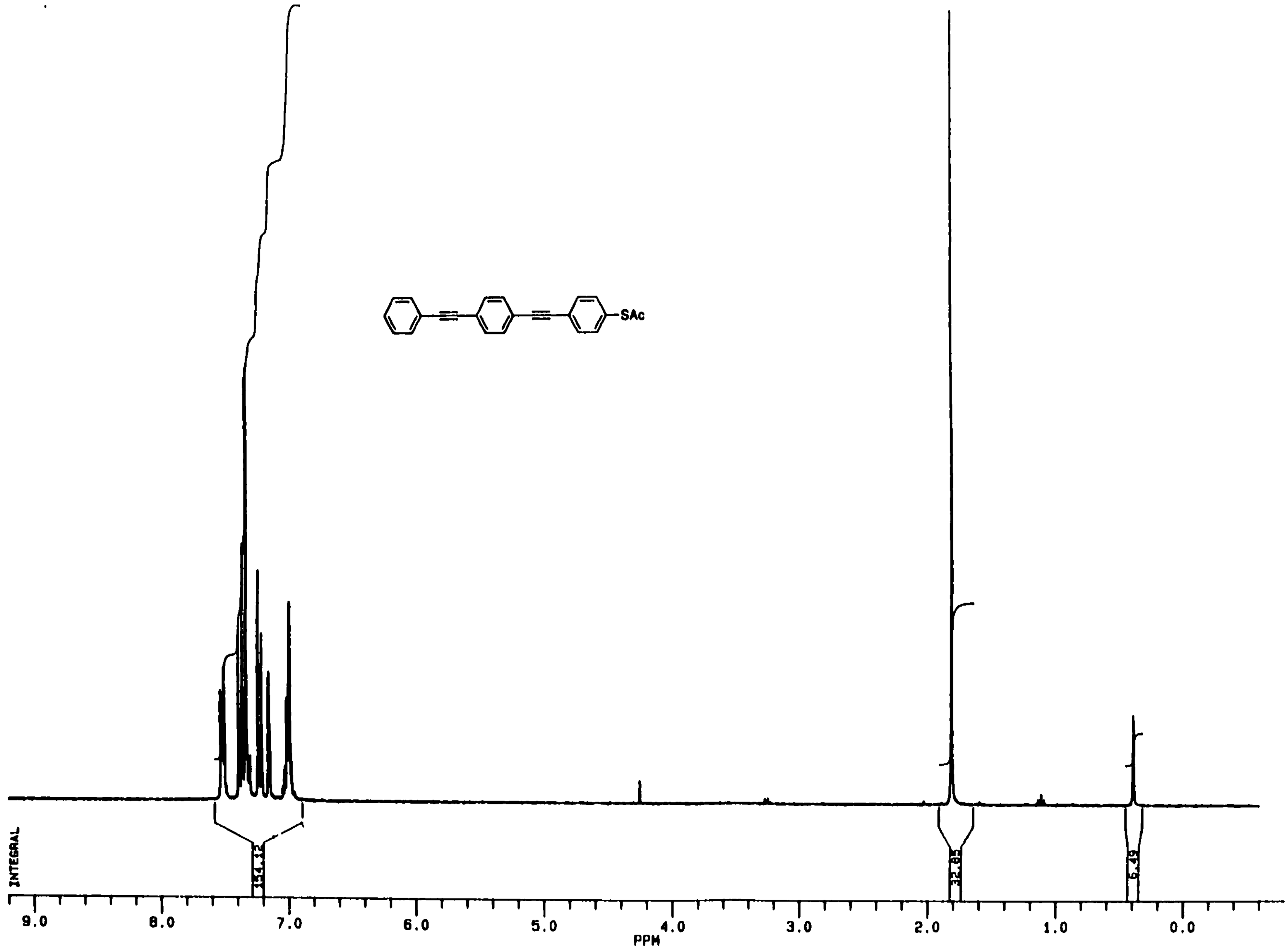
620.5
SAc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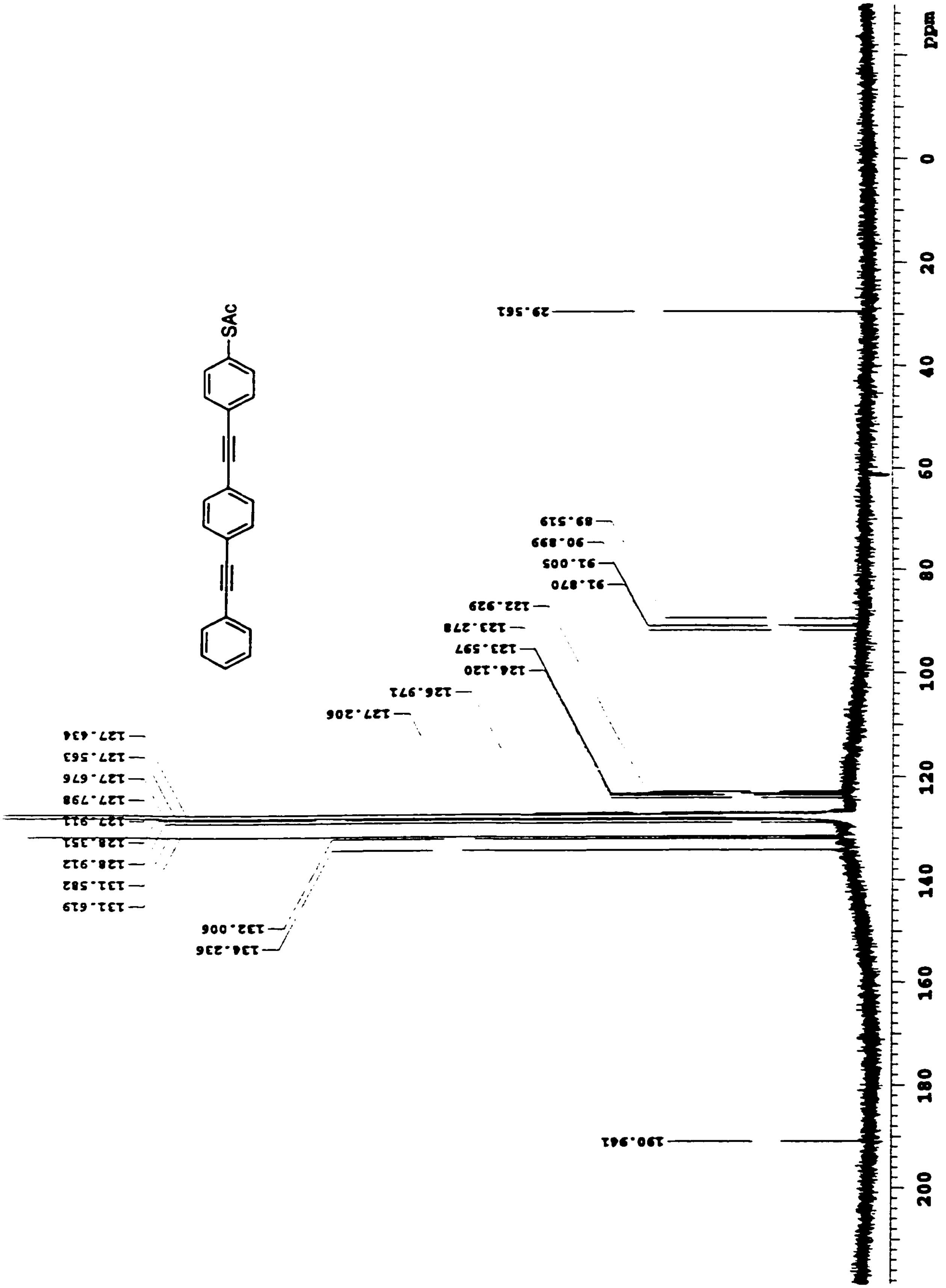
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127.563
127.676
127.798
127.911
128.351
128.912
131.582
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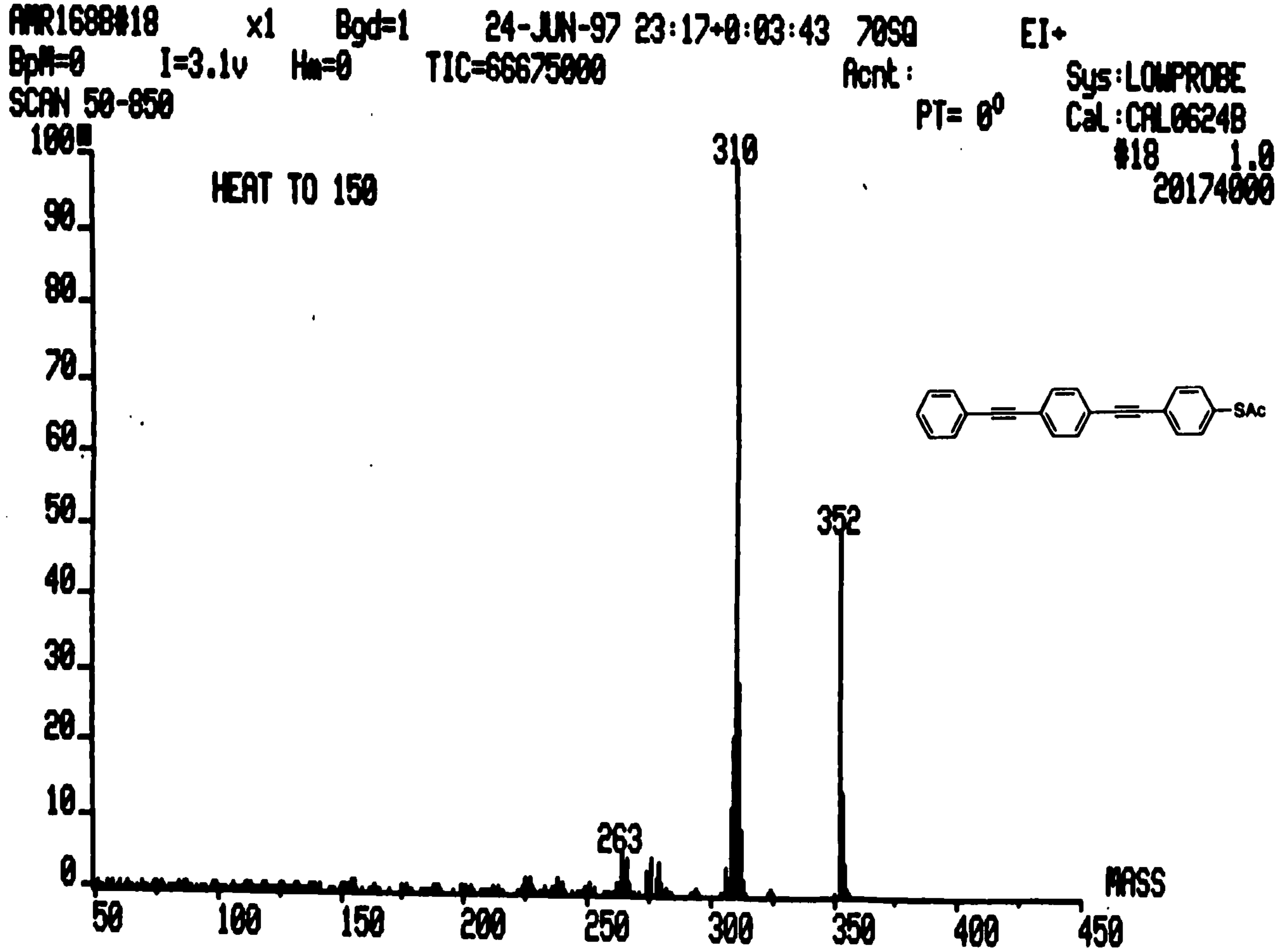
120
140
160
180
200



H: Nes 7/17

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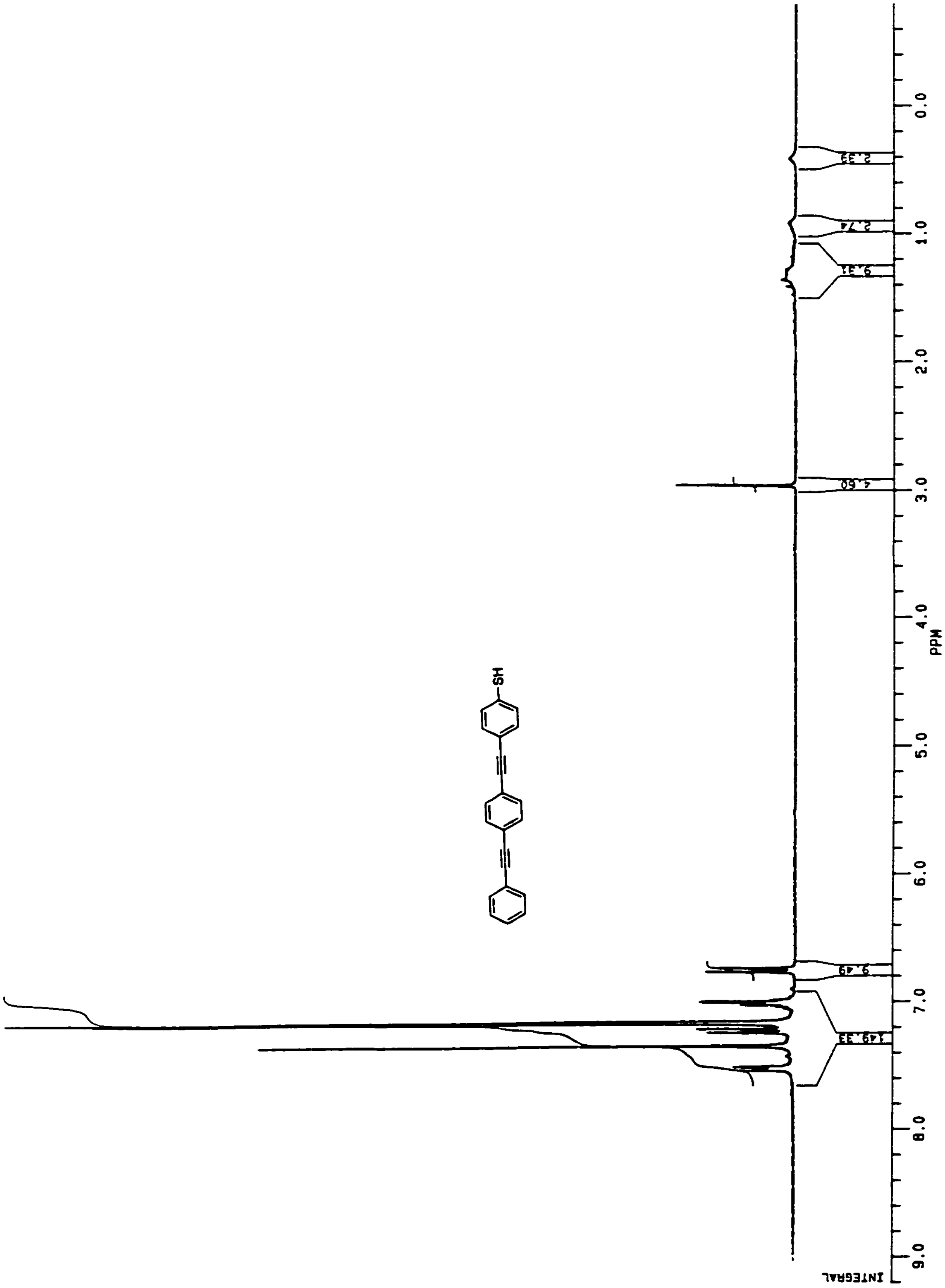
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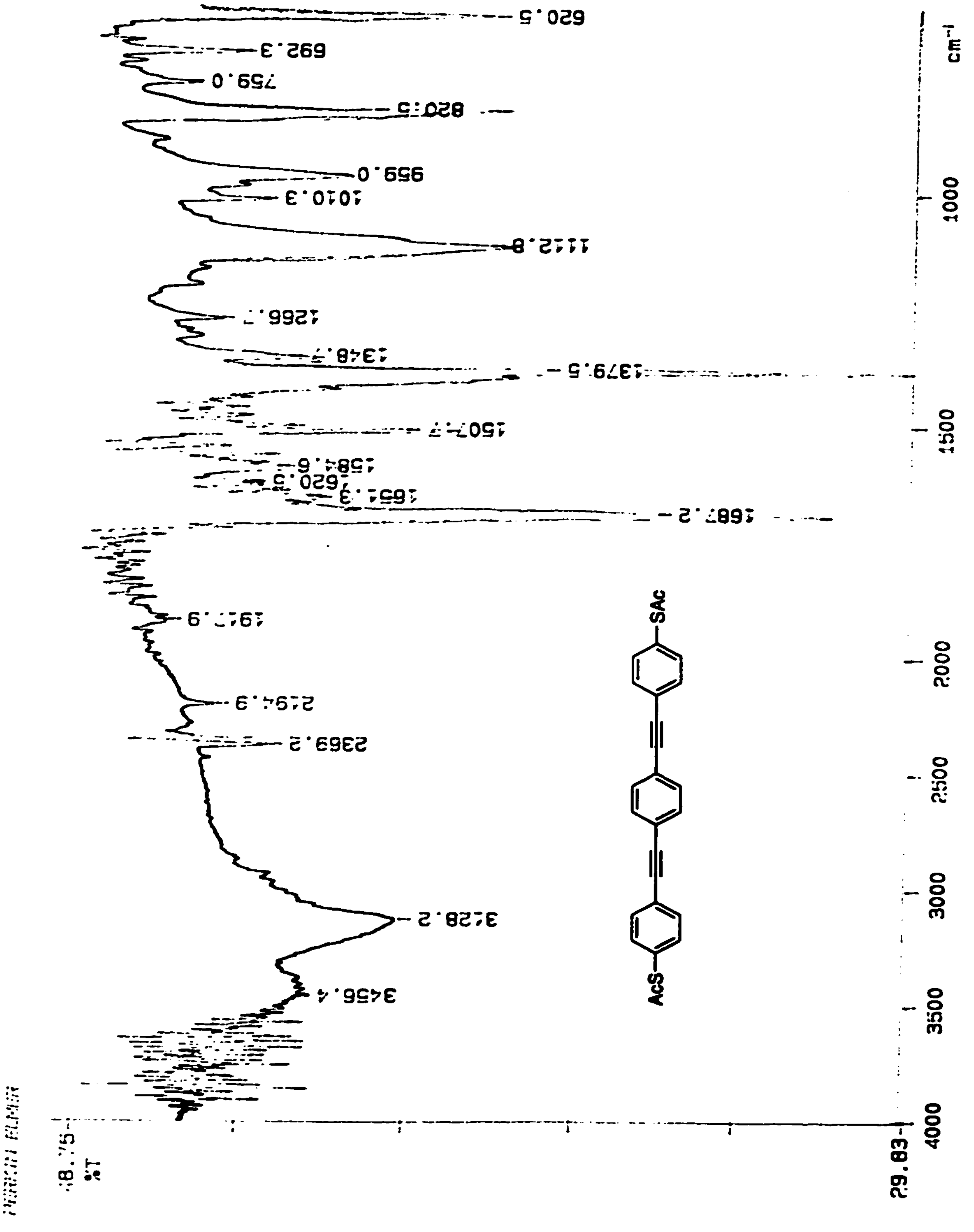
9.49
149.33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1620.5
1654.3
1687.2
1917.9
2194.9
2369.2
3128.2
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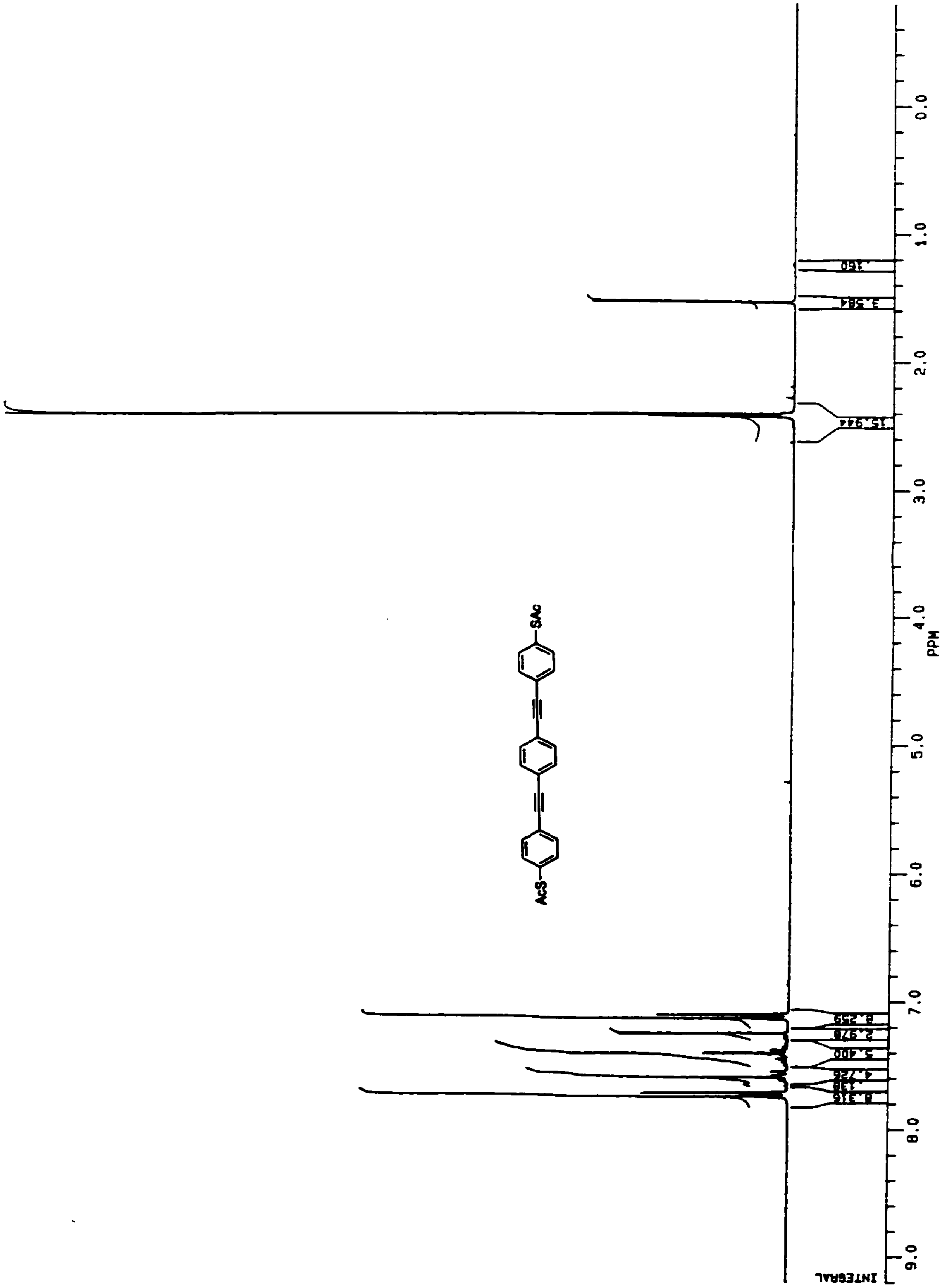
%T
PERKIN ELMER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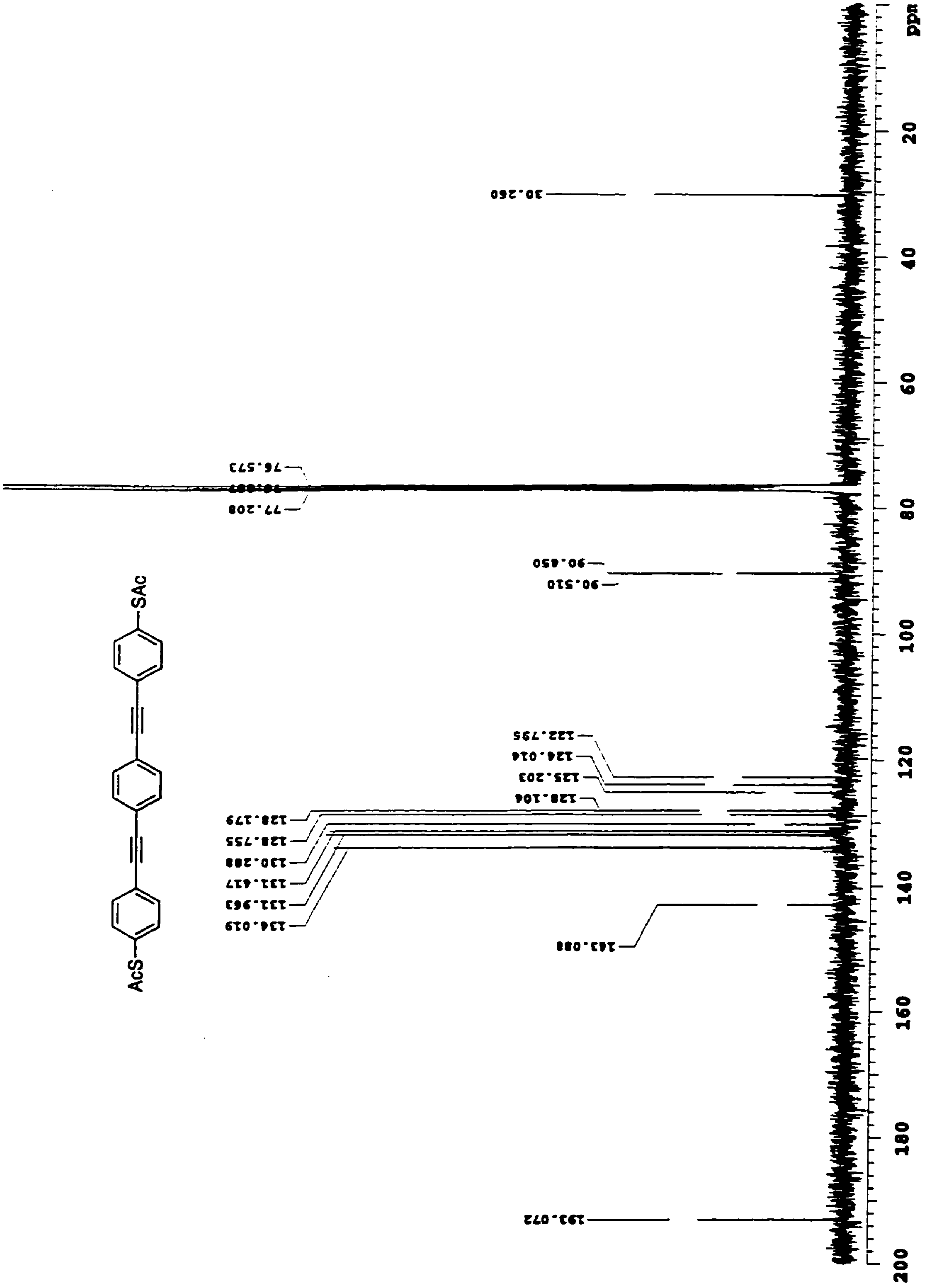
.138
8.316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122.795
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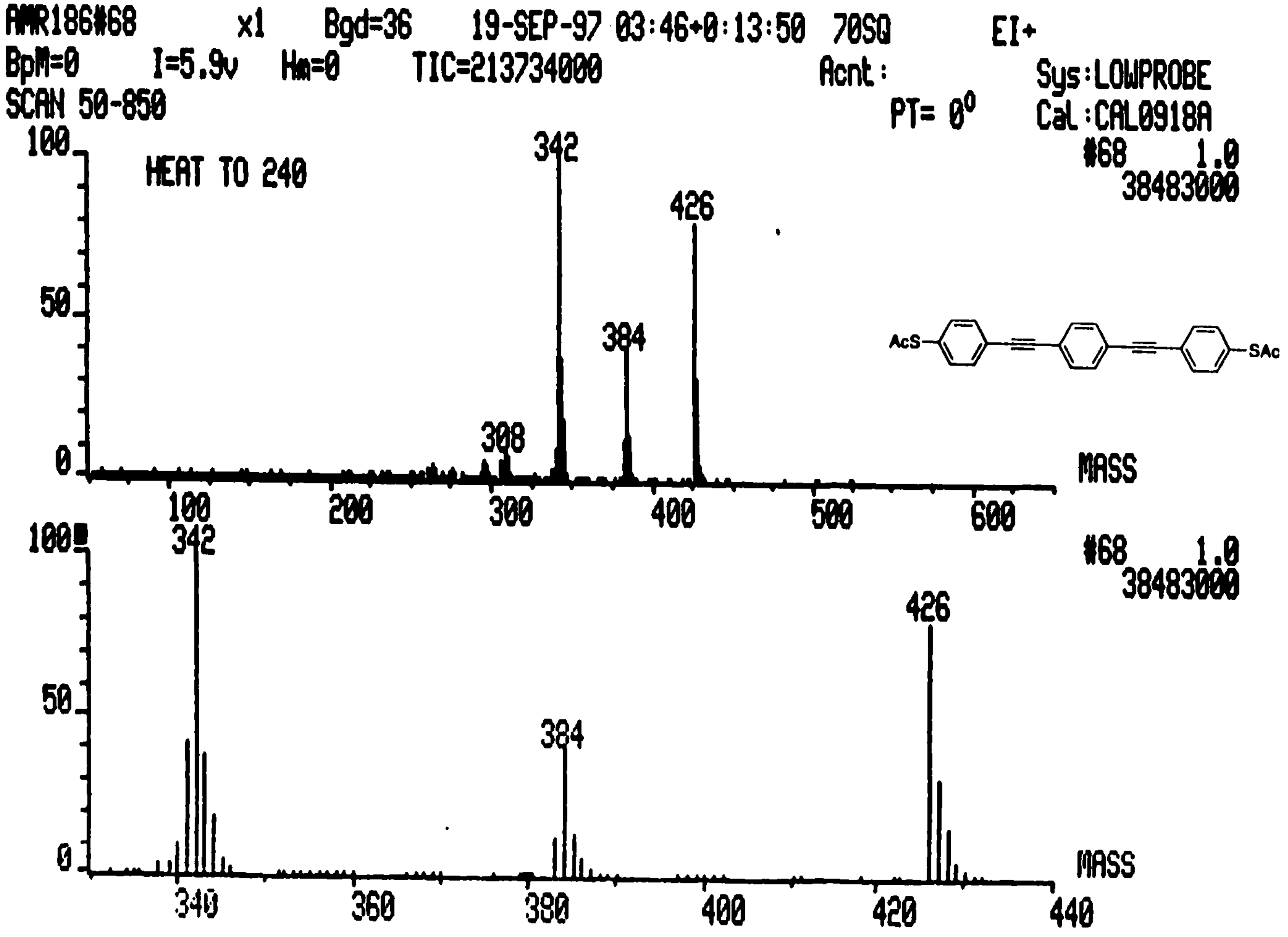
180
200



Accurate Mass
9/23

obser mass = 426 0747
calc mass = 426 0747

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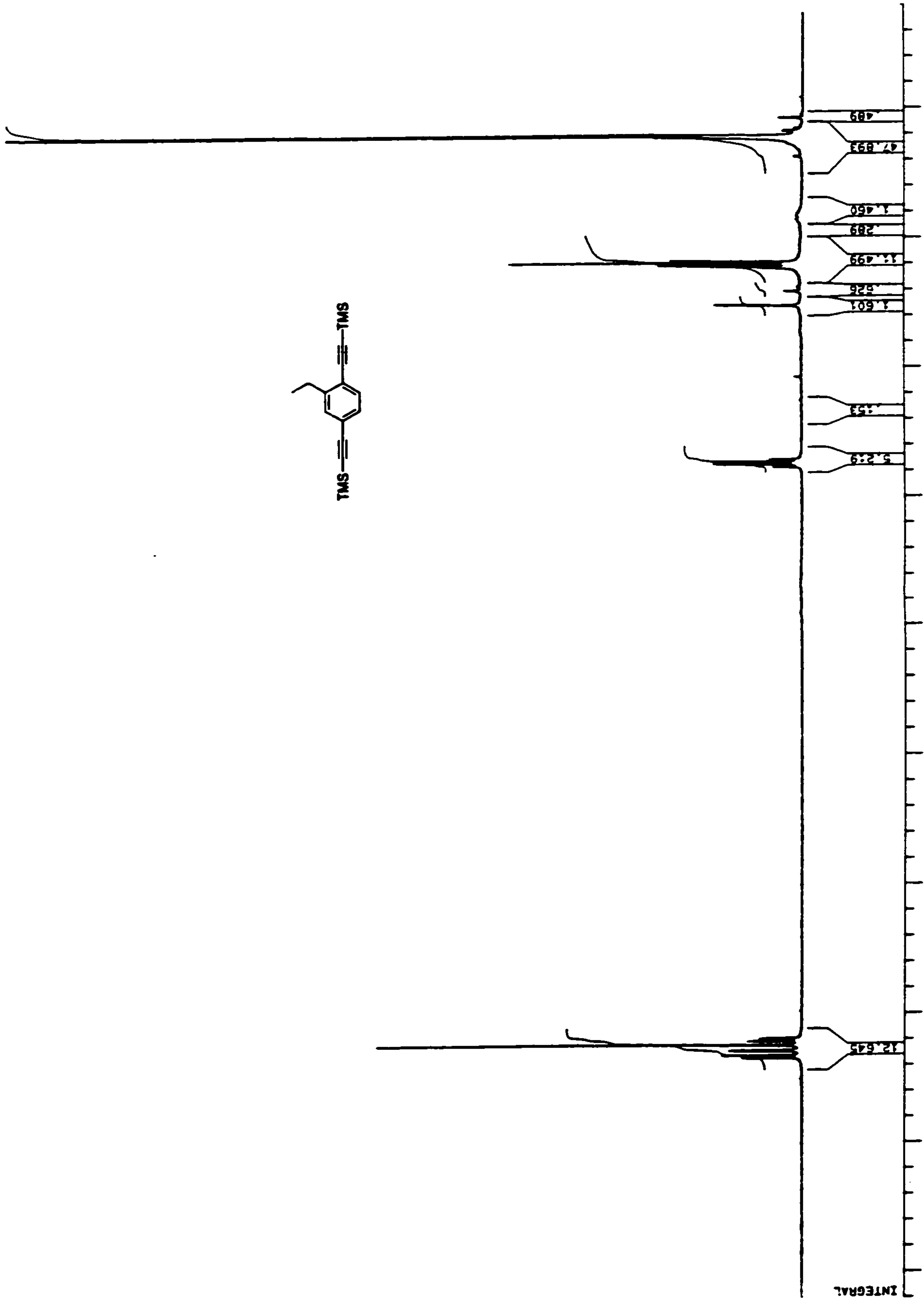
Error = 0.2 ppm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TMS
PPM
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.289
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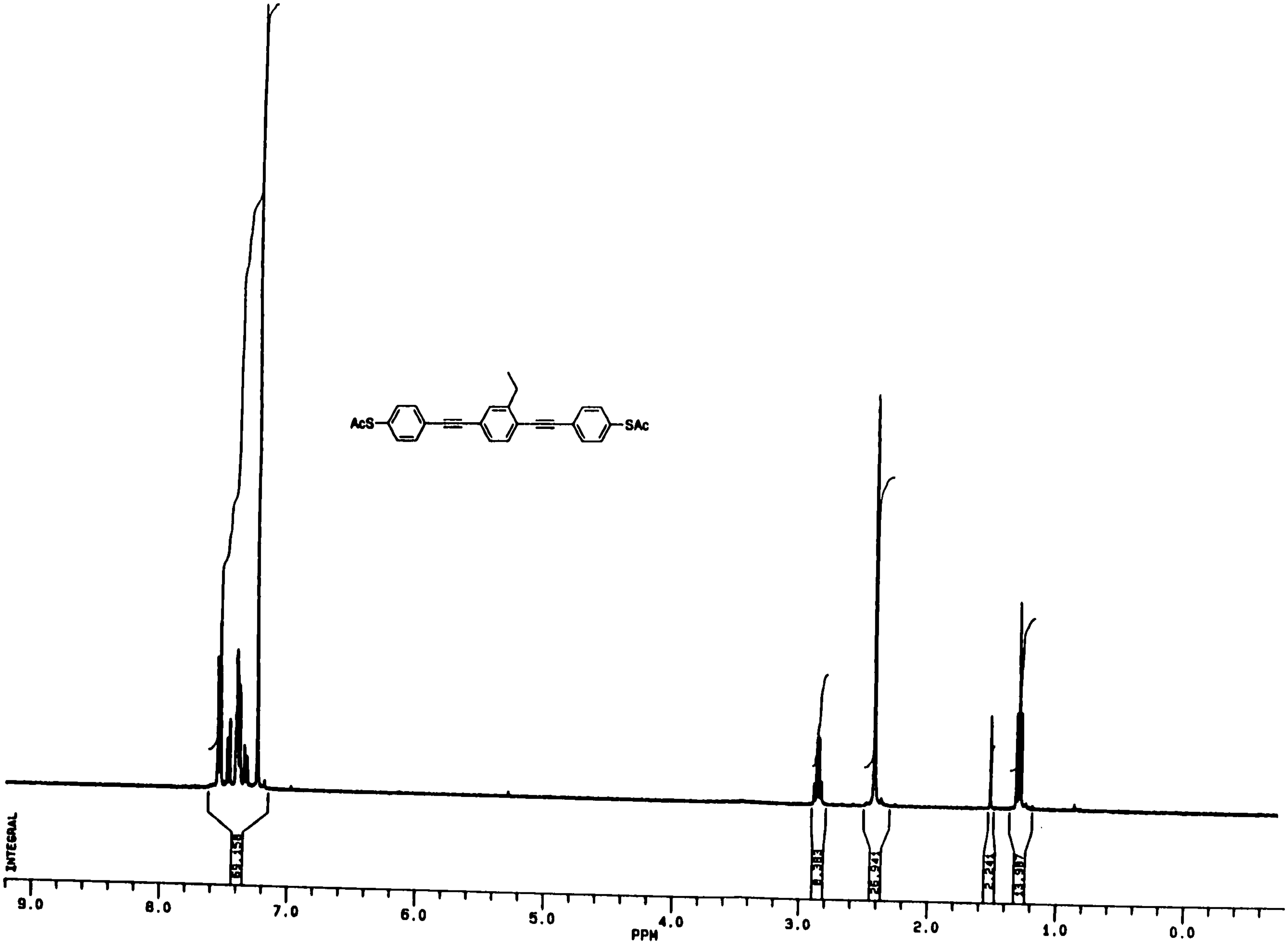
.626
1.601
.153
5.269
12.645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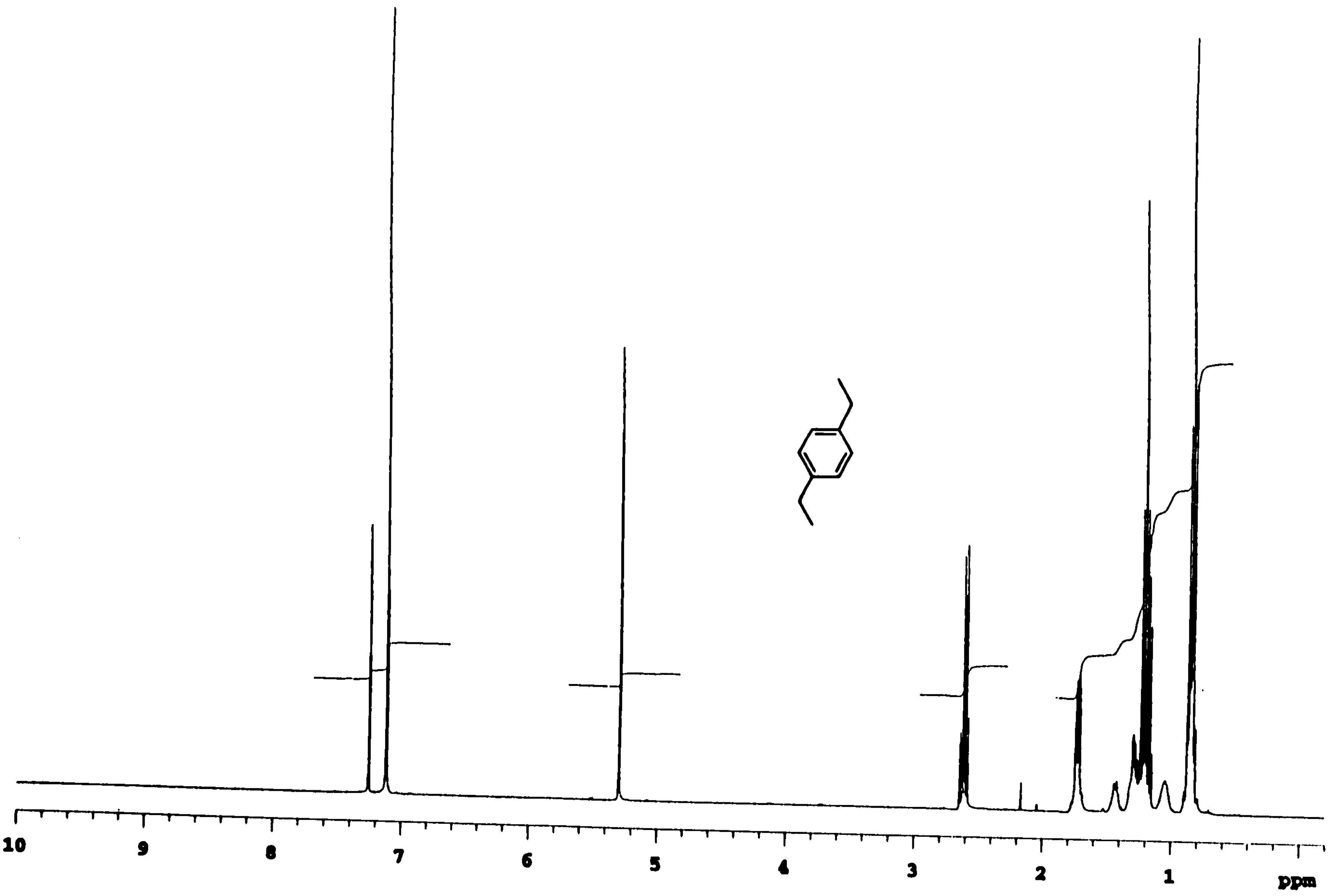
1.0
0.0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5
4
3
2
1
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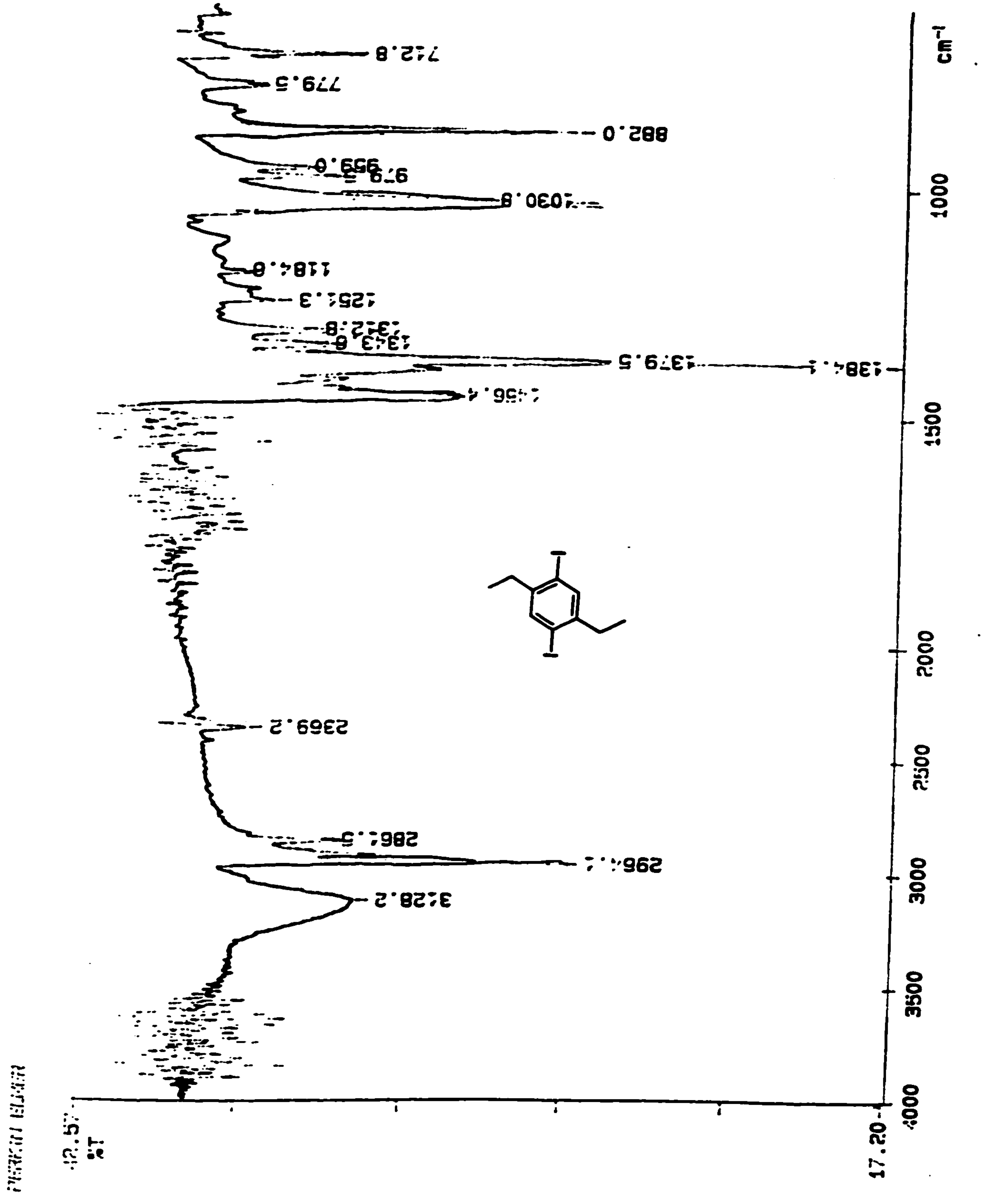
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3000
2500
2000
1500
1000
cm⁻¹
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2369.2
1456.4
1384.1
1379.5
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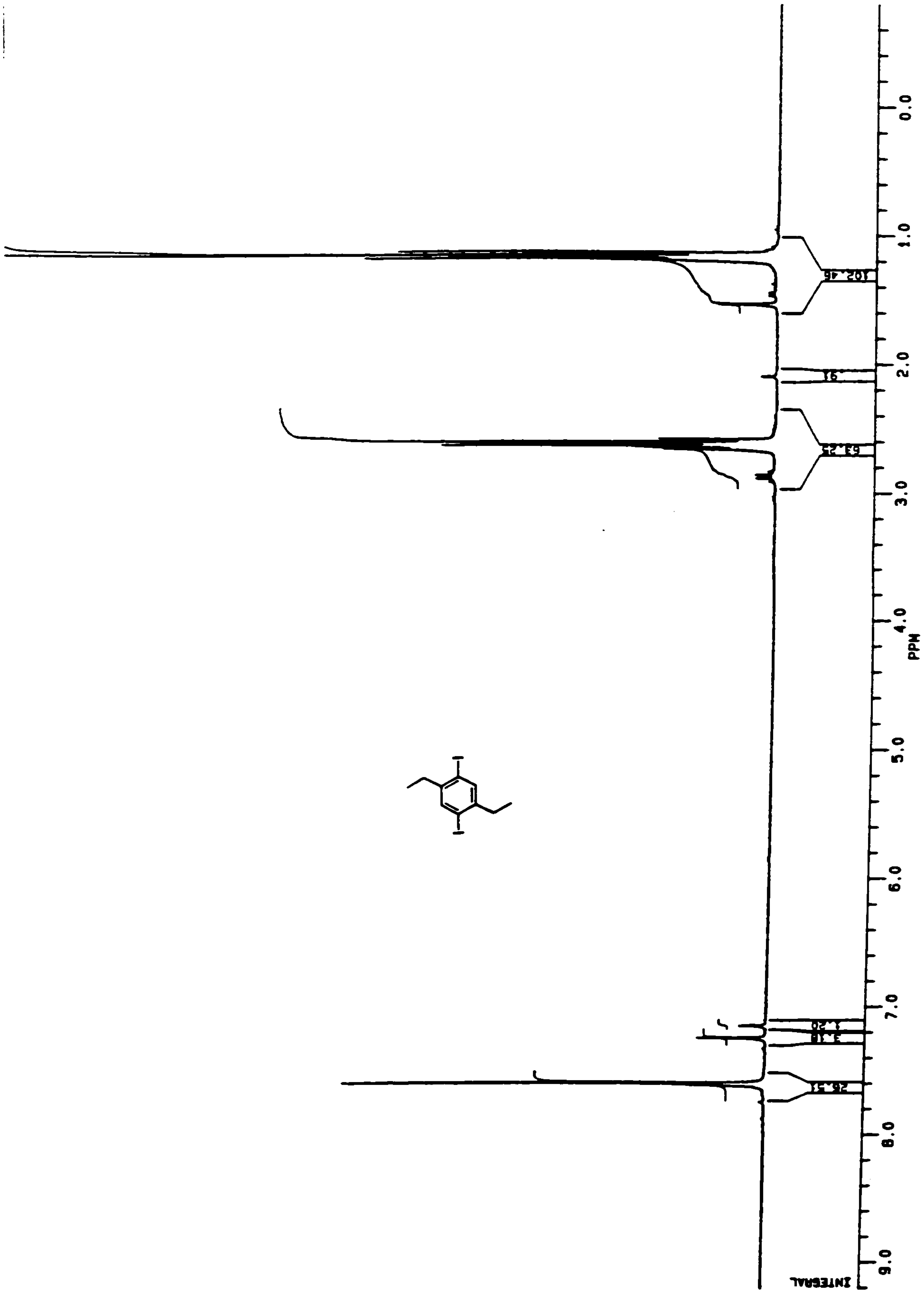
779.5
712.8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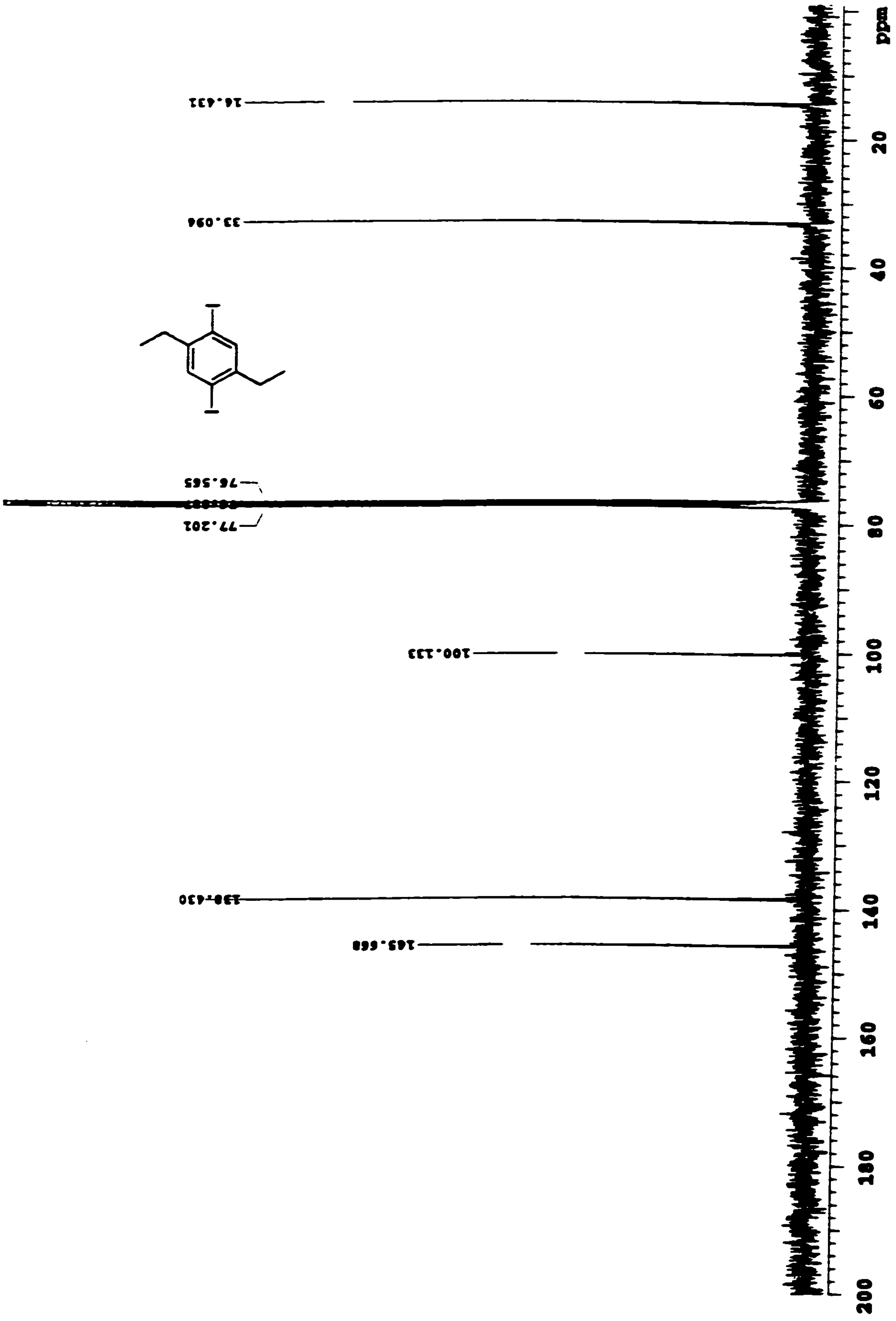
102.46
I
I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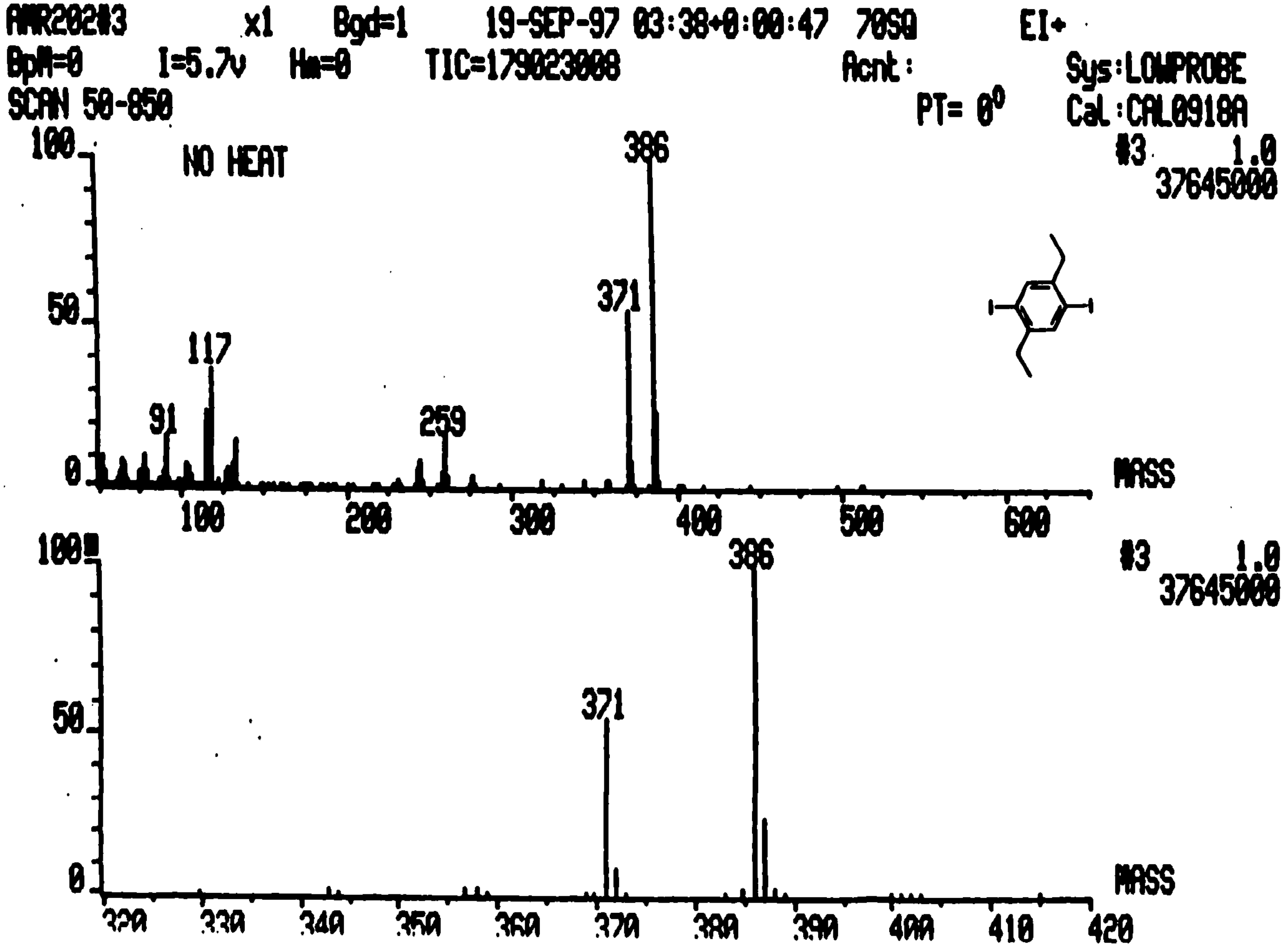

Accurate Mass
1/23

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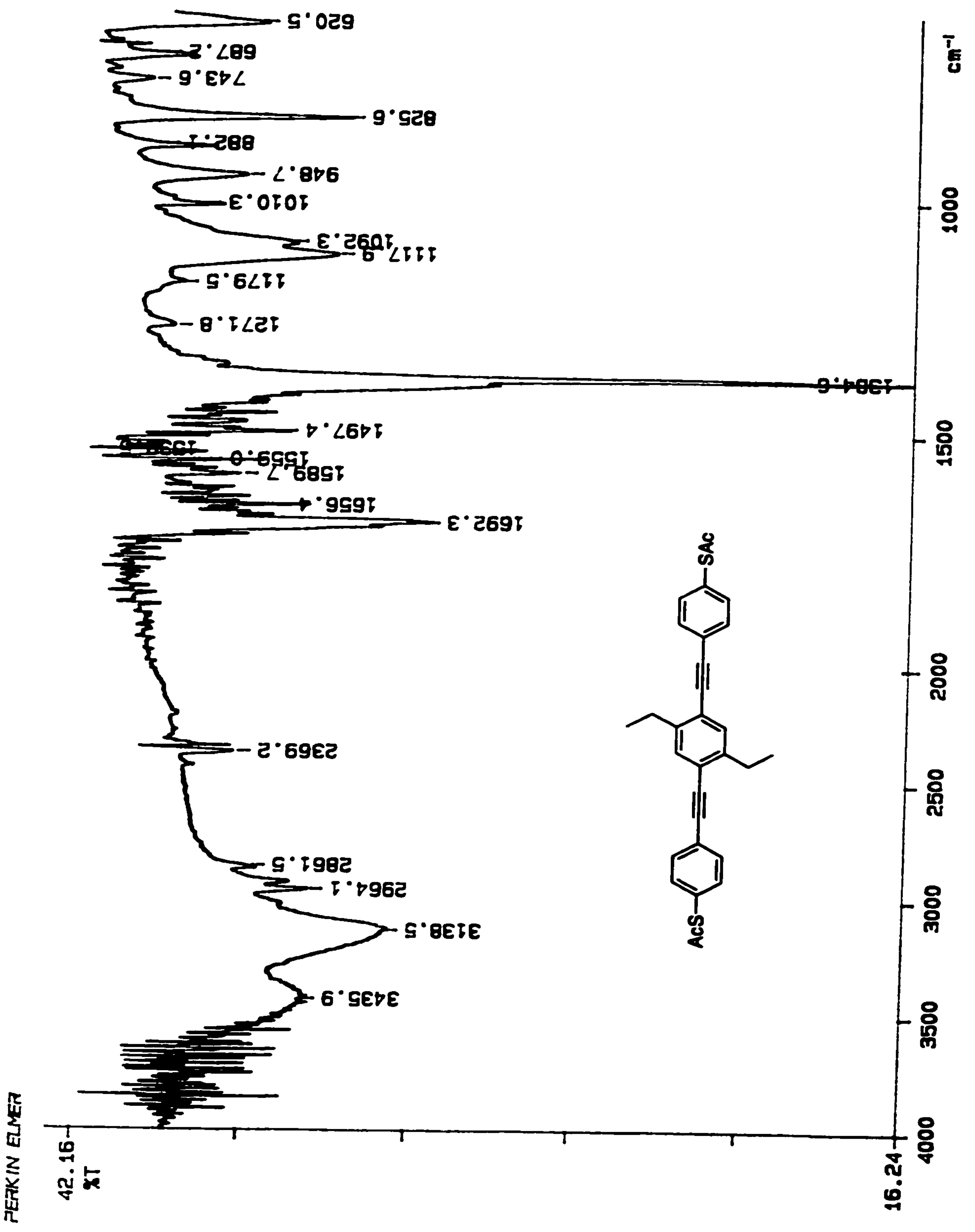
Error = 0.5 ppm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1656.4
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1497.4
1384.6
1271.8
1179.5
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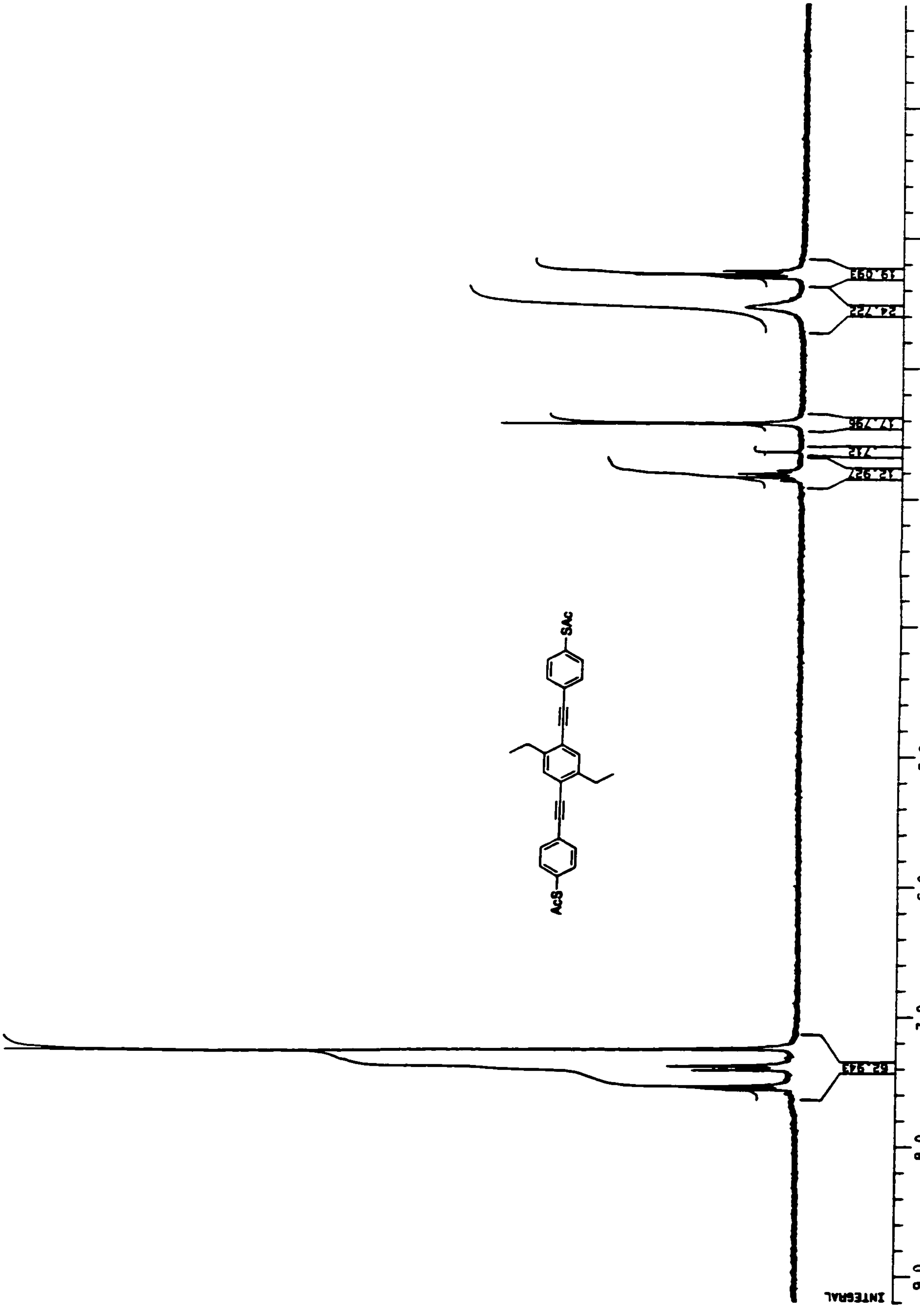
620.5
AcS
SAc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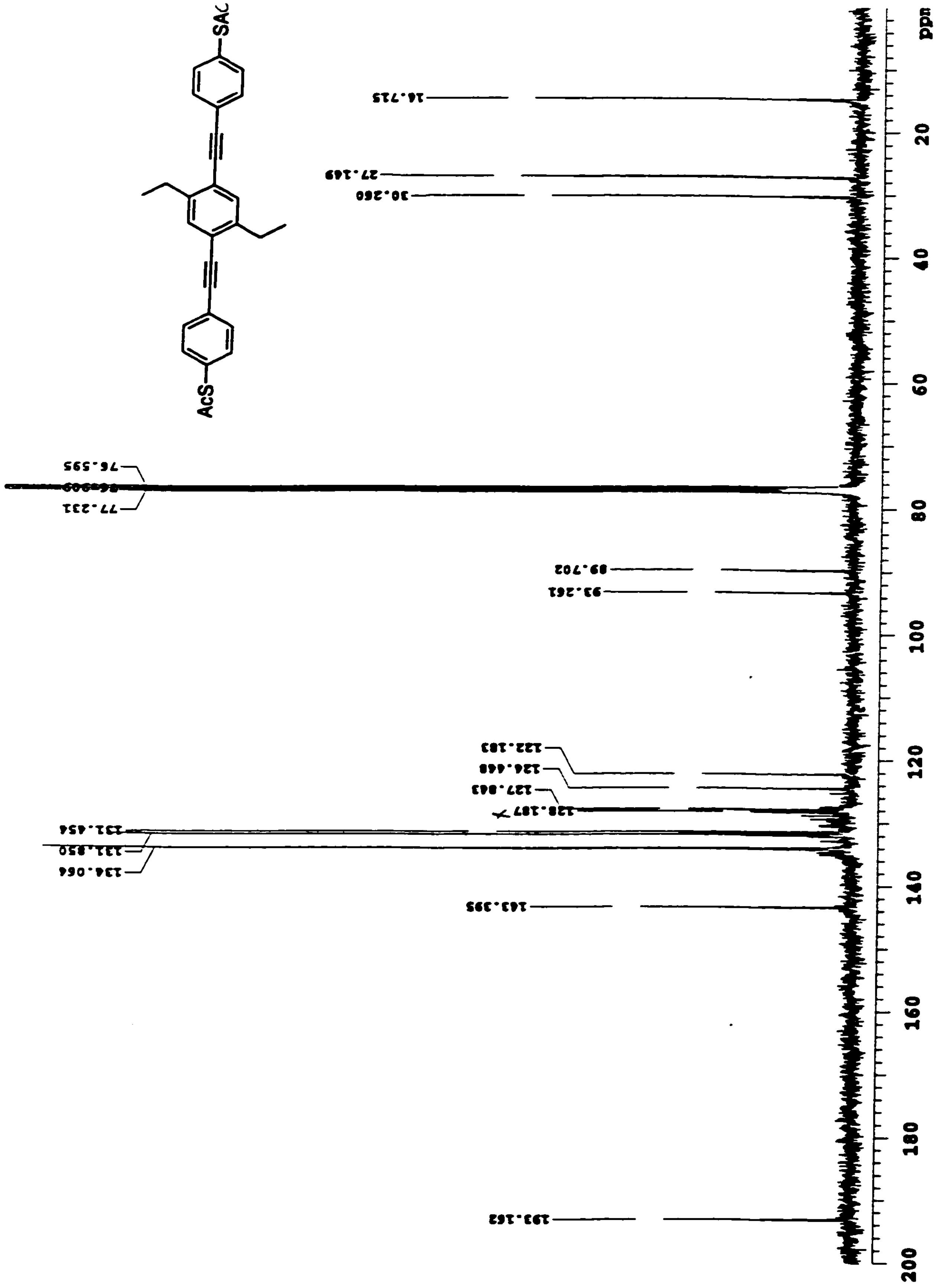
PPM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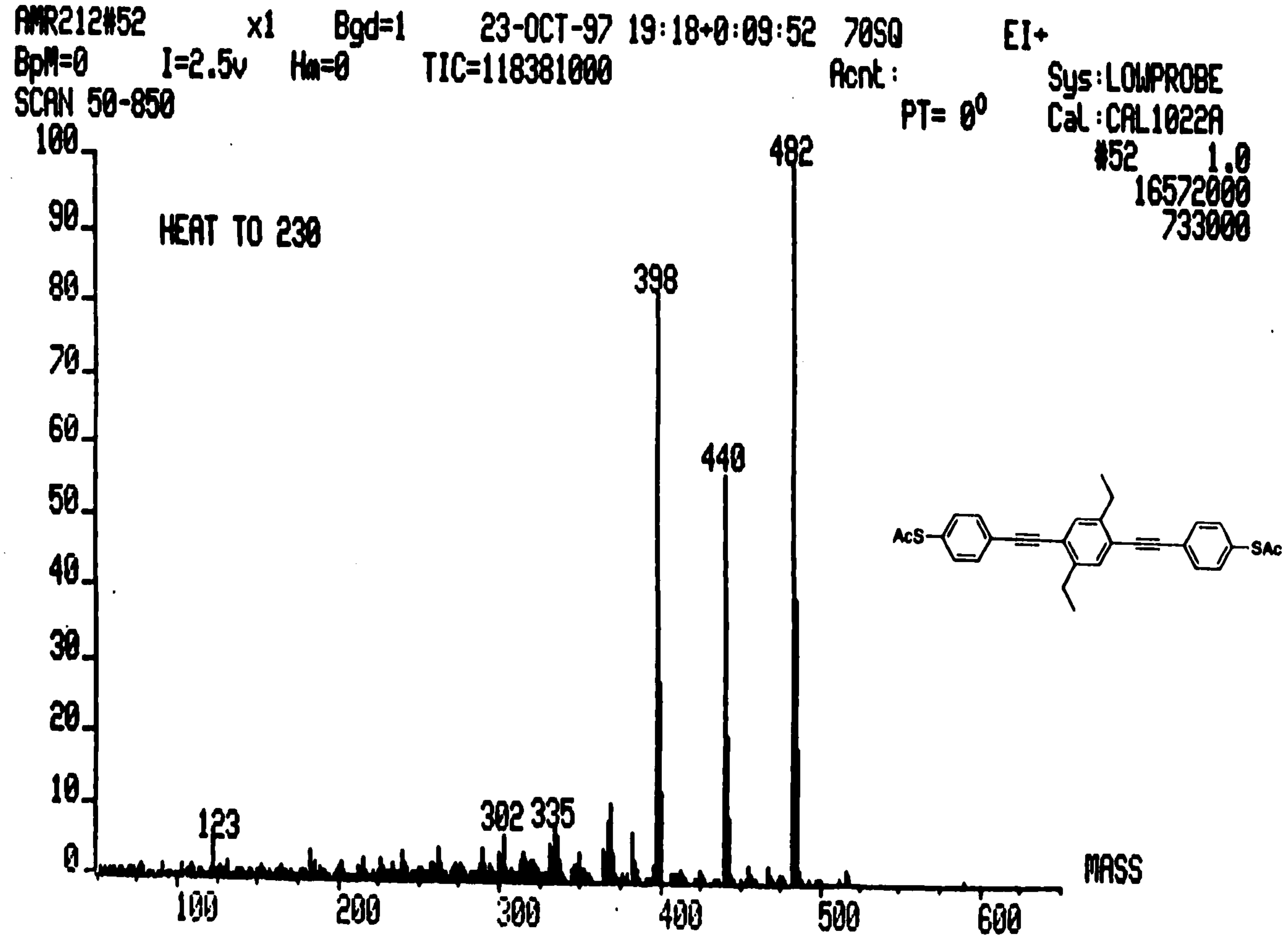

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                                                                          #52      1.0
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                                                                             733000
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Accurate Mass
10/29

obsvd mass : 482·1365
calc mass : 482·1374

Error = 1.9 ppm

Chapter 5

STM Ablation of an Insulating Monolayer and Subsequent Insertion of a Conductive Molecular Wire to the Revealed Au Layer

One of the major obstacles facing molecular scale electronics is how will these molecules be connected to the outside world. This fabrication challenging is truly a daunting task. Scanning probe microscopy offers a method for manipulating and modifying materials at the atomic level.[1-3] Preliminary work has been done utilizing self-assembled monolayers (SAMs) as a substrate.[4-9] We demonstrate reproducible *in situ* scanning tunneling microscope (STM) lithography SAM patterning and subsequent replacement of conjugated molecules in an insulating matrix at selectively patterned locations(Figure 1).[10]

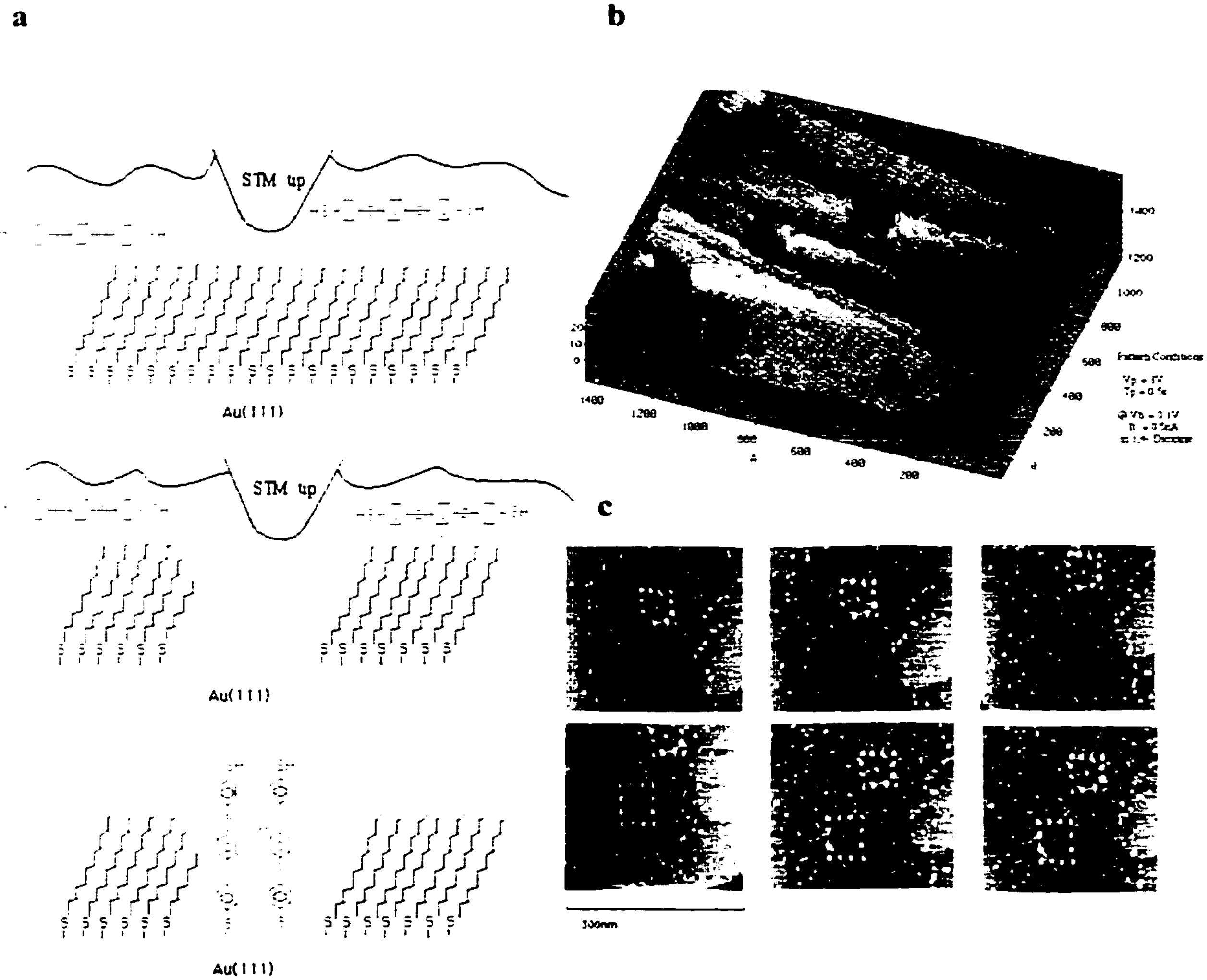

a
b
STM tip
Au(111)
STM tip
Au(111)
Au(111)
1400
1200
1000
800
600
400
200
0
c
300nm

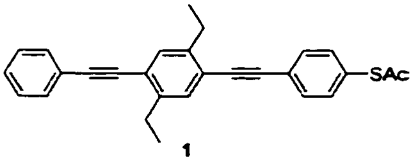
Figure 1: a) Schematic of STM ablation and subsequent insertion of the dithiol molecular wire. b) AFM image of the ablated hole and c) STM image of the inserted molecular wires, brighter regions, in the ablated sites in the insulated monolayer.

The initial substrate is a gold surface with an adsorbed SAM. An annealed Au/Cr (250 nnV50 nm) film on glass exhibited a Au(111) surface with terraces of up to several hundred nanometers with herringbone reconstruction.[11] A dodecanethiol SAM was deposited from solution at room temperature.[12] Subsequent mounting in a Teflon liquid cell of an ambient STM chamber allowed for immersion in 1,4-dioxane (Aldrich) solvent for the replacement experiments.

A tube-scanning ambient STM was used for both imaging and lithographic patterning. Tips were prepared from Pt/Ir (70%/30%) wires and then coated with epoxy leaving the end exposed.[13] Images were taken in constant current mode with 1.5 V tip bias (V_b) and approximately 15 pA set-point tunneling current (I_t). To perform lithography, we applied square voltage pulses to the SAM substrate with pulse amplitude (V_b) varying from 1.8 to 3.6 V and pulse duration (T_p) from 0.5 μs to 0.5 s. A constant dc bias voltage (V_b) of 0.1 V was kept on the STM tip during the voltage pulses. A larger time constant (relative to the pulse width) in the feedback electronics is used to both maintain the tip at a constant height and avoid tip crashing.

We have studied the patterning yield of this STM lithography as a function of pulse voltage and pulse width. The yield was defined as the percent of successful patterned structures (out of 50 pulses). Under appropriate pulse conditions patterns were produced with over 90% yield when positive pulses (sample positive with respect to the tip) were applied. There is an apparent threshold voltage for pattern formation.[7] Greater tip sample distance required higher threshold voltage. At pulse voltages above 3.4 V pits deeper than 1.4 nm were produced, suggesting that some of the underlying gold was removed. Pulse duration was varied at various pulse voltages for fixed tip-sample separation. Reproducible patterns were created at pulse widths greater than about 0.1 s. We used positive pulses to remove the SAM in this work since we observed that negative pulses created moundS,[6-8] which may be the result of material deposition from the tip.[14]

Subsequent to dodecanethiol removal, we introduced conjugated molecules into the liquid cell for "decoration" of the patterned sites. The conjugated molecule used is 2′-ethyl-4:1′-ethynylphenyl-4′:1′′-ethynylphenyl-1,4′′-thioacetylbenzene **1**, previously made in Chapter 4.



1

Upon addition of NH_4OH, the protective acetyl endgroups in **1** are removed and cause conversion into the thiolate form, a convenient method for utilizing oxidatively unstable dithiols and which have been shown to self-assemble onto Au.[15] The mechanism for replacement adsorption is that the thiol group of the rigid rod aromatic, α,ω-dithiol binds to the exposed surface; at the concentration used (10 μM), one can estimate that there are approximately 40 collisions per second of molecules the thiolate with the exposed Au surface.

To demonstrate replacement, we added 10 μM of A in 1,4-dioxane along with several microliters of NH_4OH to the liquid cell under slightly positive Argon pressure. Lithography was performed on the dodecanethiol surface while in solution. The molecule B is similar to one previously investigated[15] in which conductivity higher than alkanethiol was observed, resulting in bright spots in the STM image, Figure 1. The widths of the peaks are approximately 10 nm indicating the insertion of a bundle of approximately 400 B molecules. The height is about 0.7 nm above the background, which is consistent with the known length of B and dodecanthiol molecules of 2.2 and 1.4 nm, respectively.[15]

Several scans over one hour showed no pattern degradation. Please note that all STM studies were preformed by the other co-authors on reference 10; my contribution was the synthesis of molecular scale wire **1**.

We have demonstrated the controlled insertion of conjugated molecules in an insulating background, providing a general method for generating intermixed SAMs of arbitrary shapes and compositions. The sharpness and regularity of the STM tip should play an important role; we suggest that future work utilizing a carbon nanotube STM tip might implement single molecule replacement.

Reference

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(3) Lyo, I. W.; Avouris, P. *Science* **1991**, *253*, 173.

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Chapter 6

The Use of Dipole Possessing Molecular Scale Wire SAMs to Control Schottky Barriers in Organic Electronic Devices

Recently, the use of organic molecules in electronic devices has found great utility. Highly conductive, organic compounds have many advantages over traditional inorganic light emitting diodes (LEDs) including ease of fabrication, possible mechanical properties, and cost effectiveness.[1] A few of the areas of promise include light emitting diodes (LEDs),[2-5] transistors,[6] and photodetectors.[7] Large electronic barriers have been evident at the contact point of the metal and organic LED and have been a source of limitation and instability of these molecules.[7] The metal/organic interface in LEDs have been shown to follow ideal Schottky behavior, that is, the electron Schottky barrier is determined by the energy difference between the metal work function and the electron affinity (ionization potential) of the organic material.[8,9] The tuning of this barrier, with functionalized molecular scale wires, may lower the Schlottky barrier. Thus allowing for better conduction of an electron or hole from the metal contact to the organic LED.

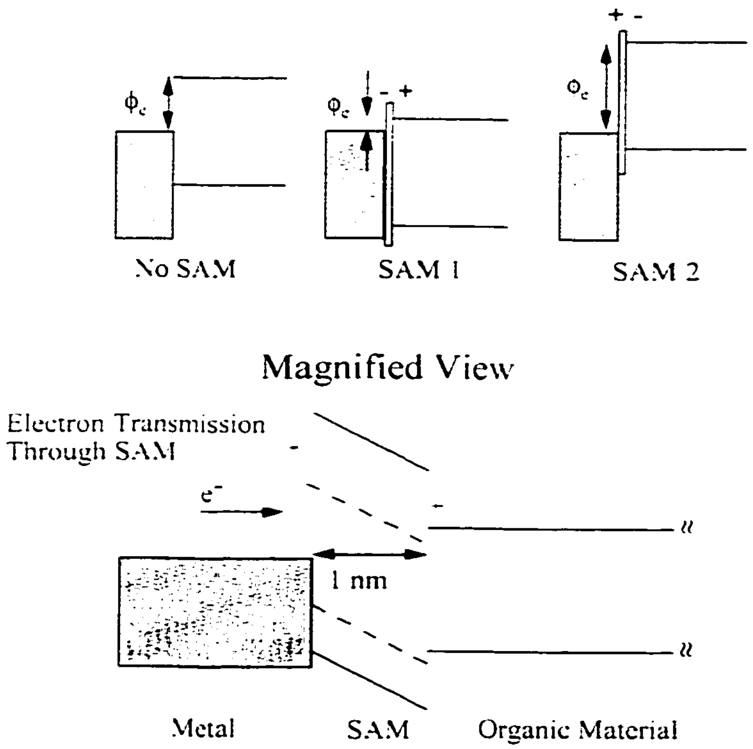
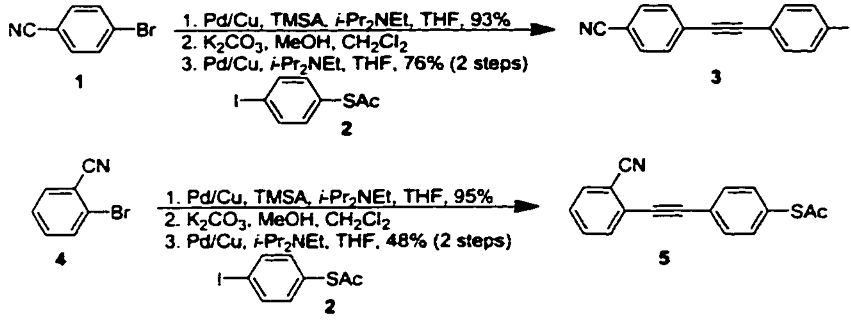


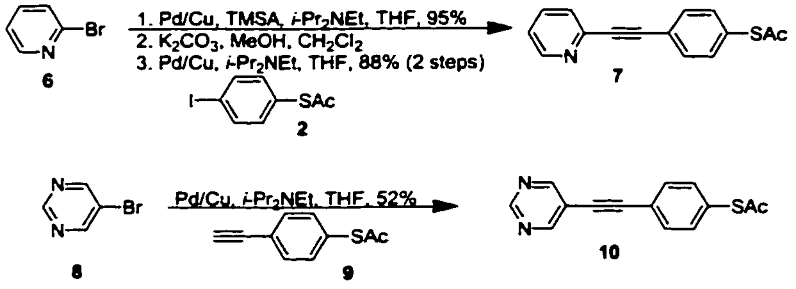
Figure 1: Schematic illustration of the effect of incorporating a monolayer (with significant dipole moment) between a metal electrode and an organic material used in an organic electronic device (i.e. diode or transistor).

It has been demonstrated that electronically conductive SAMs, i.e. oligo(phenylene ethynylene)s, lower the barrier for injection of an electron from a metal contact to the organic substrate and therefore tune the Schottky energy barrier between the metal and organic surfaces.[10] We are currently synthesizing molecules to act as interfaces between the metal contacts and the organic substrates in LEDs. By tailoring the Schottky barrier of the metal/organic interface, we are hoping to improve the efficiency of the LEDs by matching the Fermi of the metal and the lowest unoccupied molecular orbital (LUMO) of the organic substrate. The Cu/SAM injection of holes at low voltage could also improve ohmic contact. We envisioned highly conjugated phenylene ethynylene molecules that possess a dipole moment as good candidates for these compounds and thiol endgroups for attachment to numerous metal probes.


NC
Br
1
1. Pd/Cu, TMSA, i-Pr2NEt, THF, 93%
2. K2CO3, MeOH, CH2Cl2
3. Pd/Cu, i-Pr2NEt, THF, 76% (2 steps)
I
SAc
2
NC
SAc
3
CN
Br
4
1. Pd/Cu, TMSA, i-Pr2NEt, THF, 95%
2. K2CO3, MeOH, CH2Cl2
3. Pd/Cu, i-Pr2NEt, THF, 48% (2 steps)
I
SAc
2
CN
SAc
5

(1)

Molecules **3** and **5** were synthesized by Pd/Cu-catalyzed cross couplings in high yields, eq 1. Surprisingly, these molecules where extremely difficult to separate by column chromatography and recrystallizations. They were finally purified by multiple cold hexanes washes.


Br
N
6
1. Pd/Cu, TMSA, i-Pr2NEt, THF, 95%
2. K2CO3, MeOH, CH2Cl2
3. Pd/Cu, i-Pr2NEt, THF, 88% (2 steps)
I
SAc
2
N
SAc
7
N
N
Br
8
Pd/Cu, i-Pr2NEt, THF, 52%
SAc
9
N
N
SAc
10

(2)

Two additional molecules were synthesized for testing as LEDs interfaces, eq 2. Again, these molecules were produced in a straightforward fashion by Pd/Cu-catalyzed cross couplings in high yields. The use for these organic SAMs has demonstrated improvement for charge injection from the Cu probe using SAMs with electron withdrawing moieties.[11] Additionally, compounds **7** and **8** demonstrated a shift in the zero current to positive bias which indicates an increase in the effective work function of the metal electrode by the voltage. This increase in the work function has led to improved hole injection, with a molecule that is similar to **1** yet possesses a nitro moiety instead of the cyano group, according to Figure 2.[11]

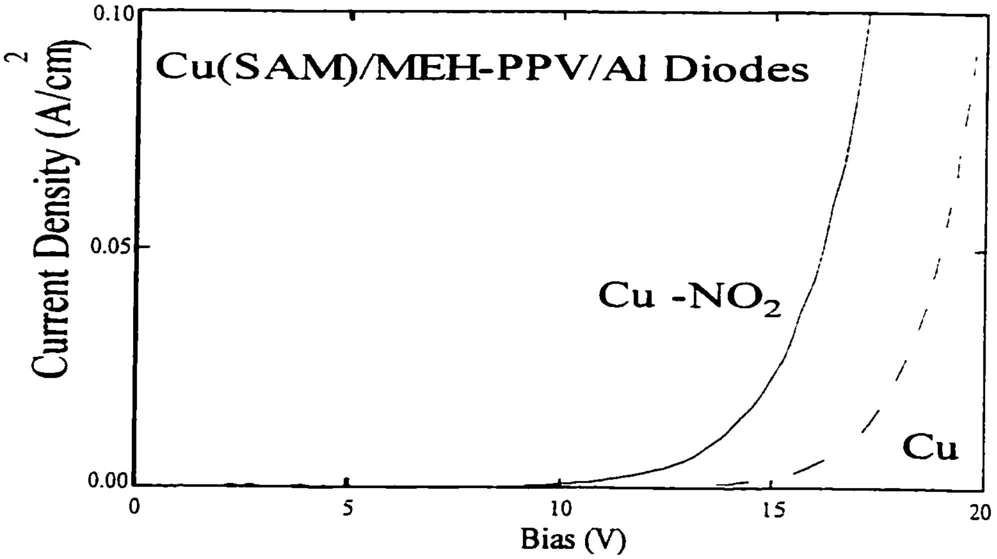


Figure 2: Copper (SAM)/MEH-PPV/Al diodes demonstrating improvement of charge injection from Cu using the nitro terminated SAM.

The current in the devices is dominated by hole injection from the Cu contact (the Al electrode is a poor electron injector) so the increased current from the Cu nitro SAM electrode (compared to the no SAM Cu electrode) indicates improved injection from the contact. The MEH-PPV film thickness is 100 nm in both cases.

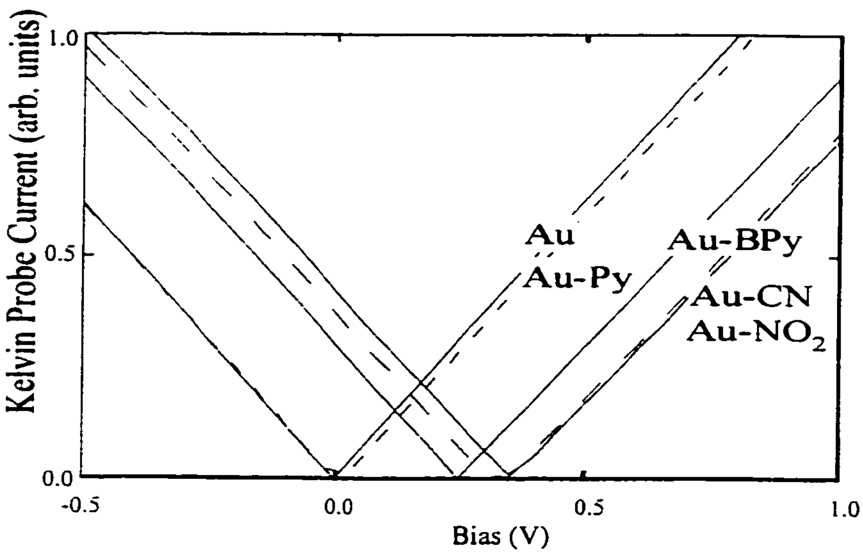
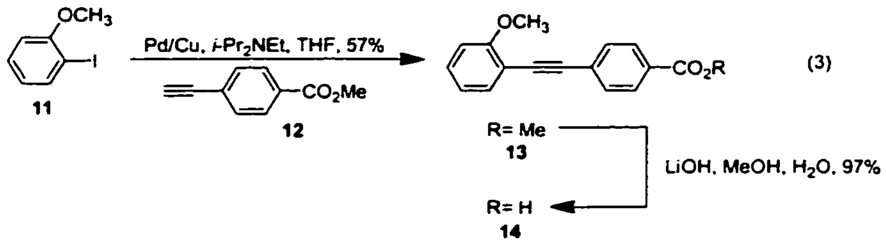


Figure 3: Kelvin probe current versus substance bias for a series of Au (SAM) electrodes.

The zero point of the current of Figure 3 is significant. The shift of zero current to positive bias indicates an increase in the effective work function of the metal electrode by the voltage. The effective work function of the Au-CN (**1**) electrode is about 0.35 eV higher than Au. This increase in the work function leads to improved hole injection. It should be noted that the LED testing was in the laboratory of Dr. Ian Campbell at Los Alamos National Laboratories and Tour group contributions was the synthesis of all SAM precursors.

To decrease to Schlottky barrier for electron injection in a LED, molecular scale wires with electron donating moieties and carboxylic groups for the formation of SAMs to aluminum oxide contact were synthesized.[12]


OCH3
I
11
Pd/Cu, i-Pr2NEt, THF, 57%
CO2Me
12
OCH3
CO2R
R= Me
13
R= H
14
LiOH, MeOH, H2O, 97%

(3)

Compound **11** was coupled using Pd/Cu-catalysis to **12** to afford methyl ester intermediate **13**. The methylester moiety was saponified in the presence of lithium hydroxide to afford compound **14**.[13] These compounds are currently being tested for their ability to lower the electron injection barrier between the aluminum oxide contact and organic LED.

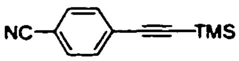
Experimental

General. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. All reagents and starting materials were purchased from Aldrich, Acros, Fischer, Fluka, and Alfa Aesar if not otherwise stated. Alkyllithium reagents were obtained from FMC. Pyridine, methyl iodide, triethylamine, and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride, and stored over 4 Å molecular sieves. Toluene and benzene were distilled over CaH_2. Methylene chloride and hexanes were distilled. Ethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Triethylamine and *N, N*-diisopropylethylamine was distilled over CaH_2. MeOH was dried over oven dried 3 Å molecular sieves. ^1H NMR spectra were recorded at 300, 400, or 500 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively or at 400 and 500 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively or at 400 MHz on Oxford Instruments 400 MHz NMR using Brüker XWIN NMR processing program. The ^{13}C NMR spectra were recorded at 75, 100, or 125 MHz on Brüker AM-300, WH-400, and AM-500 spectrometers, respectively at 100 and 125 MHz on Varian Mercury 400 and INOVA 500 spectrometers, respectively or at 125 MHz on Oxford Instruments 400 MHz NMR using Brüker XWIN NMR processing program. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0-ppm $CDCl_3$ resonance as an internal reference and are reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. Gas chromatography experiments were performed on a

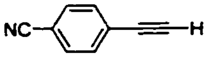
Hewlett-Packar GC model 5890A equipped with an Alltech column (cat # 932525, serial # 9059) 25 m × 0.25 mm D × 0.2 mm. Gravity column chromatography, silica gel plugs, and flash chromatography were preformed using 230-400 mesh silica gel from EM Science. Thin layer chromatography was preformed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Combustion analyses were obtained from Atlantic Microlab, Inc., P. O. Box 2288, Norcross, GA 30091.

General Procedure for the coupling of a Terminal Alkyne with an Aryl Halide Utilizing a Palladium-Copper Cross-Coupling (Castro-Stephens/Sonogashira Protocol).[14] To an oven dried round bottom flask equipped with a water cooled West condenser or screw capped pressure tube with a magnetic stirbar were added the aryl halide, bis(triphenylphosphine)palladium(II) chloride (3-5 mol % per halide), and copper(I) iodide (6-10 mol % per halide). Triphenylphosphine was used in some reactions to keep the palladium in solution. The vessel was then sealed with a rubber septum under a N_2 atmosphere. A co-solvent system of THF, benzene, or methylene chloride was added at this point depending on the solubility of the aryl halide. Then base, either triethylamine or *N,N*-diisopropylethylamine, was added and finally the terminal alkyne (1-1.5 mol % per halide) was added and the reaction was heated until complete. Upon completion of the reaction, the reaction mixture was then quenched with water, a saturated solution of NH_4Cl, or brine. The organic layer was diluted with methylene chloride or Et_2O and washed with water, a saturated solution of NH_4Cl, or brine (3×). The combined aqueous layers were extracted with methylene chloride or Et_2O (2×). The combined organic layers were dried over $MgSO_4$ and solvent removed in vacuo to afford the crude product that was purified by column chromatography (silica gel). Eluents and other slight modifications are described below for each material.

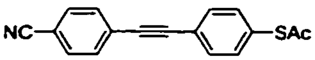
General procedure for the deprotection of trimethylsilyl protected alkynes (Method A). The silylated alkyne was dissolved in methanol and potassium carbonate was added. The mixture was stirred overnight before poured into water. The solution was extracted with ether or ethyl acetate and washed with brine. After drying over magnesium sulfate the solvent was evaporated *in vacuo* to afford pure products. **(Method B).** The silylated alkyne was dissolved in pyridine in a plastic vessel. A mixed solution of 49% hydrofluoric acid and 1.0 M tetrabutylammonium fluoride in THF was added at room temperature. The solution was stirred for 15 min and quenched with silica gel. The mixture was poured into water and extracted with ether. The extract was washed with brine and dried over magnesium sulfate. After filtration the solvent was evaporated *in vacuo*. The crude products were purified by a flash chromatography on silica gel. Eluents and other slight modifications are described below for each material.



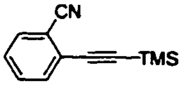
4-Trimethylsilylethynylbenzonitrile (AMR-II-101). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 4-Bromobenzonitrile (0.50g, 2.75 mmol) was coupled to trimethylsilylacetylene (0.59 mL, 4.13 mmol) copper(I) iodide (0.05 g, 0.28 mmol), bis(triphenylphosphine)palladium(II) chloride (0.10 g, 0.14 mmol), triphenylphosphine (0.14 g, 0.55 mmol), triethylamine (1.19 mL, 11.00 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 65 °C for 60 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.60. The reaction afforded 0.52 g (93 % yield) of the desired compound as off white crystals. IR (KBr) 3128.2, 2953.8, 2225.6, 2143.6, 1600.0, 1492.3, 1384.6, 1246.2, 1174.4, 841.0, 753.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J*=8.4 Hz, 2 H), 7.52 (d, *J*=8.3 Hz, 2 H), 0.26 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ132.15, 131.63, 127.73, 118.17, 111.53, 102.74, 99.35, -0.30. HRMS calcd $C_{12}H_{13}NSi$: 199.0817. Found: 199.0816.



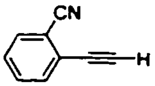
4-Ethynylbenzonitrile (AMR-II-107). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 4-Trimethylsilylethynylbenzonitrile (0.35 g, 1.72 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (1.19 g, 8.60 mmol), methanol (10 mL), and methylene chloride (10 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.



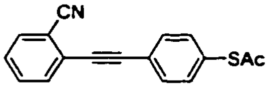
1-Thioacetyl-4(4′-cyano(phenylethynyl))benzene (3, AMR-II-109). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 4-ethynylbenzonitrile (0.22 g, 1.65 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.60 g, 2.15 mmol) as described above using copper(I) iodide (0.03 g, 0.17 mmol), bis(triphenylphosphine)palladium(II) chloride (0.06 g, 0.09 mmol), triphenylphosphine (0.09 g, 0.34 mmol), triethylamine (0.96 mL, 6.88 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 65 °C for 3 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.49. The compound was further purified by a hexanes washes to give 0.28 g (76 % yield, 2 steps) of the desired compound as yellow crystals over two steps. IR (KBr) 3117.9, 2225.6, 1692.3, 1379.5, 1266.7, 1164.1, 1112.8, 1010.3, 959.0, 825.6, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J*=8.6 Hz, 2 H), 7.59 (d, *J*=8.6 Hz, 2 H), 7.56 (d, *J*=8.62 Hz, 2 H), 7.42 (d, *J*=8.6 Hz, 2 H), 2.42 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 192.94, 134.22, 132.25, 132.10, 132.02, 129.16, 127.78, 132.32, 118.41, 111.77, 92.88, 89.22, 30.48. HRMS calcd $C_{17}H_{11}NOS$: 277.0561. Found: 277.0573.



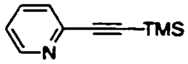
2-Trimethylsilylethynylbenzonitrile (AMR-II-101). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromobenzonitrile (0.50 g, 2.75 mmol) was coupled to trimethylsilylacetylene (0.59 mL, 4.13 mmol) using copper(I) iodide (0.05 g, 0.28 mmol), bis(triphenylphosphine)palladium(II) chloride (0.10 g, 0.14 mmol), triphenylphosphine (0.14 g, 0.55 mmol), triethylamine (1.19 mL, 11.00 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 65 °C for 60 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 methylene chloride/hexanes as the eluent. R_f (product): 0.60. The reaction afforded 0.52 g (93 % yield) of the desired compound as off white crystals. IR (KBr) 3066.7, 2953.8, 2902.6, 225.6, 2153.8, 1589.7, 1559.0, 1476.9, 1446.2, 1405.1, 1251.3, 1220.5, 1164.1, 1092.3, 1035.9, 953.8, 861.5, 764.1, 733.3, 697.4, 641.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J=7.7 Hz, 1 H), 7.53 (t, J=13.7 Hz, 1 H), 7.52 (d, J=11.7 Hz, 1 H), 7.38 (t, J=8.8 Hz, 1 H), 0.30 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 132.45, 132.35, 132.08, 128.35, 126.87, 117.20, 115.73, 102.16, 100.49, -0.19. HRMS calcd $C_{12}H_{13}NSi$: 199.0817. Found: 199.0814.



2-Ethynylbenzonitrile (AMR-II-113). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 2-Trimethylsilylethynylbenzonitrile (0.35 g, 1.72 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (1.19 g, 8.60 mmol), methanol (10 mL), and methylene chloride (10 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.

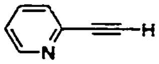


1-Thioacetyl-4(2′-cyano(phenylethynyl))benzene (5, AMR-II-115). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-ethynylbenzonitrile (0.22 g, 1.72 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.61 g, 2.15 mmol) as described above using copper(I) iodide (0.03 g, 0.17 mmol), bis(triphenylphosphine)palladium(II) chloride (0.06 g, 0.09 mmol), triphenylphosphine (0.09 g, 0.34 mmol), triethylamine (0.96 mL, 6.88 mmol), and THF (20 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 65 °C for 48 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:3 ethyl acetate/hexanes as the eluent. R_f (product): 0.38. The compound was further purified by a hexanes wash to give 0.23 g (48 % yield, 2 steps) of the desired compound as a yellow solid over two steps. IR (KBr) 3425.6, 3138.5, 2369.2, 2225.6, 1702.6, 1656.4, 1384.6, 1112.8, 1015.4, 943.6, 825.6, 769.2, 620.5 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J*=7.7 Hz, 1 H), 7.65 (d, *J*=8.4 Hz, 2 H), 7.64 (buried d, 1 H), 7.57 (t, *J*=7.6, 1 H), 7.44 (buried d, 1 H), 7.41 (d, *J*=8.7 Hz, 2 H), 2.44 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 192.96, 134.20, 132.64, 132.46, 132.35, 132.14, 129.27, 128.46, 126.81, 123.14, 117.41, 115.45, 95.08, 87.06, 30.48. HRMS calcd $C_{17}H_{11}NOS$: 277.0561. Found: 277.0574.

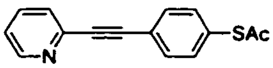


2-Trimethylsilylethynylpyridine (AMR-II-129). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Bromopyridine (0.45 mL, 3.16 mmol) was coupled to trimethylsilylacetylene (0.68 mL, 4.74 mmol) using copper(I) iodide (0.06 g, 0.32 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.16 mmol), triphenylphosphine (0.17 g, 0.63 mmol), triethylamine (1.38 mL, 12.64 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 70 °C for 48 h. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture 3:1 methylene chloride/hexanes as the eluent. R_f (product): 0.15. The reaction afforded 0.50 g (88 % yield) of the desired compound. IR (KBr) 3056.4, 2953.8, 2902.6, 2153.8, 1579.5,

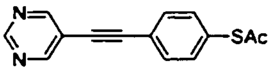
1559.0, 1456.4, 1425.6, 1246.2, 1220.5, 1148.7, 1046.2, 984.6, 866.7, 841.0, 774.4, 759.0, 733.3, 697.4, 651.3 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J*=3.1 Hz, 1 H), 7.63 (t, *J*=6.1 Hz, 1 H), 7.43 (d, *J*=7.7 Hz, 1 H), 7.20 (t, *J*=3.6 Hz, 1 H), 0.27 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 149.87, 143.03, 135.97, 127.20, 122.95, 103.65, 94.76, -0.07. HRMS calcd $C_{10}H_{13}NSi$: 175.0817. Found: 175.0812.



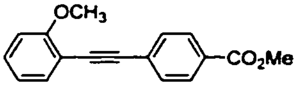
2-Ethynylpyridine (AMR-II-131). See the general procedure for the deprotection of trimethylsilyl-protected alkynes. 2-Trimethylsilylethynylpyridine (0.35 g, 1.95 mmol) was deprotected to the terminal alkyne using the procedure described above using potassium carbonate (1.35 g, 9.75 mmol), methanol (15 mL), and methylene chloride (15 mL). The reaction mixture was allowed to stir at room temperature for 2 h. The resultant mixture was subjected to an aqueous workup as described above. Due to the instability of conjugated terminal alkynes, the material was immediately reacted in the next step without additional purification or identification.



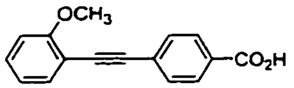
1-Thioacetyl-4(ethynylpyridine)benzene (7, AMR-II-133). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Ethynylpyridine (0.20 g, 1.95 mmol) was coupled to 1-iodo-4-thioacetylbenzene (0.66 g, 2.34 mmol) as described above using copper(I) iodide (0.02 g, 0.12 mmol), bis(triphenylphosphine)palladium(II) chloride (0.04 g, 0.06 mmol), triphenylphosphine (0.06 g, 0.23 mmol), *N,N*-diisopropylethylamine (1.36 mL, 7.80 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 50 °C for 16 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f (product): 0.38. The reaction afforded 0.26 g (53 % yield, 2 steps) of the desired compound as a yellow solid over two steps. IR (KBr) 3128.2, 2215.4, 1697.4, 1574.4, 1461.5, 1384.6, 1276.9, 1117.9, 1005.1, 948.7, 830.8, 779.5, 733.3, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J*=4.0 Hz, 1 H), 7.65 (t, *J*=5.8 Hz, 1 H), 7.59 (d, *J*=8.0 Hz, 2 H), 7.51 (d, *J*=4.0 Hz, 1 H), 7.38 (d, *J*=8.6 Hz, 2 H), 7.22 (t, *J*=3.7 Hz, 1 H), 2.41 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 193.01, 150.05, 143.04, 136.14, 134.12, 132.50, 128.94, 127.26, 123.39, 122.96, 90.12, 88.28, 30.46. HRMS calcd $C_{15}H_{11}NOS$: 253.0561. Found: 253.0562.



1-Thioacetyl-4(ethynylpyrimidine)benzene (10, AMR-II-121). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 3-Bromopyrimidine (0.18 g, 1.15 mmol) was coupled to 1-ethynyl-4-thioacetylbenzene (0.24 g, 1.38 mmol) as described above using copper(I) iodide (0.02 g, 0.12 mmol), bis(triphenylphosphine)palladium(II) chloride (0.04 g, 0.06 mmol), triphenylphosphine (0.06 g, 0.23 mmol), triethylamine (0.51 mL, 4.60 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 4 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 ethyl acetate/hexanes as the eluent. R_f (product): 0.53. The reaction afforded 0.15 g (52 % yield) of the desired compound as bright yellow solid over two steps. IR (KBr) 3425.6, 3128.2, 2215.4, 1702.6, 1656.4, 1543.6, 1384.6, 1117.9, 1097.4, 943.6, 820.6, 717.9, 615.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1 H), 8.85 (s, 2 H), 7.76 (d, *J*=8.1 Hz, 2 H), 7.42 (d, *J*=8.0 Hz, 2 H), 2.44 (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 192.84, 158.57, 156.79, 134.26, 132.22, 129.49, 122.82, 119.59, 95.46, 83.84, 30.50. HRMS calcd $C_{14}H_{10}N_2OS$: 254.0514. Found: 254.0513.



Methyl 2′-methoxy-4-(phenylethynyl)benzoate (13, AMR-II-223). See the general procedure for the Pd/Cu-catalyzed coupling reaction. 2-Iodoanisole (0.49 mL, 3.74 mmol) was coupled to methyl (1-ethynyl)benzoate (0.50 g, 3.12 mmol) as described above using copper(I) iodide (0.06 g, 0.31 mmol), bis(triphenylphosphine)palladium(II) chloride (0.11 g, 0.16 mmol), *N,N*-diisopropylethylamine (2.17 mL, 12.48 mmol), and THF (15 mL) in a screw capped pressure tube equipped with a magnetic stirbar. The reaction mixture was allowed to stir at 75 °C for 2.5 d. The resultant mixture was subjected to an aqueous workup as described above. The desired material was purified by gravity liquid chromatography using silica gel as the stationary phase and methylene chloride as the eluent. R_f (product): 0.59. An additional purification was performed using gravity liquid chromatography using silica gel as the stationary phase and a mixture of 1:1 diethyl ether/hexanes as the eluent. R_f (product): 0.54. The reaction afforded 0.47 g (57 % yield) of the desired compound as a white solid. IR (KBr) 3426.87, 2941.49, 2828.66, 2200.00, 1720.89, 1597.73, 1487.07, 1463.09, 1433.24, 1275.68, 1245.54, 1167.90, 1102.30, 1018.13, 853.62, 753.68, 691.05, 474.58 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (ABq, *J*=8.7 Hz, Δν=159.9 Hz, 4 H), 7.52 (dd, *J*= 7.6, 1.8, 1 H), 7.36 (td *J*=7.4, 1.7 Hz, 1 H), 6.98 (td, *J*=7.5, 1.0 Hz, 1 H), 6.94 (dd, *J*=8.4, 0.7 Hz, 1 H), 3.95 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.05, 160.50, 134.09, 132.88, 131.95, 130.73, 129.99, 129.84, 129.69, 128.76, 120.95, 112.31, 111.14, 93.06, 89.29, 56.26, 52.61. HRMS Calcd $C_{17}H_{14}O_3$: 266.0943. Found: 266.0945.



2′-Methoxy-4-(phenylethynyl)benzoic acid (14, AMR-II-279).[13] To a 100 mL round bottom flask equipped with a magnetic stirbar methyl 2′-methoxy-4-(phenylethynyl)benzoate (0.30 g, 1.16 mmol), lithium hydroxide (0.14, 5.82 mmol), methanol (18 mL), methylene chloride (10 mL), and water (6 mL) were added. The reaction mixture was allowed to stir at room temperature for 2 d. The reaction was quenched with water and extracted with methylene chloride (3×). The yellow aqueous phases were combined and acidified to pH=3 where upon a white solid precipitated. The solid material was collected on fritted funnel. No further purification was needed. The reaction afforded 0.28 g (97 % yield) of the desired material. IR (KBr) 3445.36, 2962.62, 2829.10, 2659.63, 2536.38, 2212.84, 1681.14, 1604.93, 1488.82, 1457.92, 1425.90,

1317.19, 1297.57, 1278.77, 1244.42, 1178.84, 1098.43, 1016.26, 954.64, 858.43, 757.58, 697.86, 554.07 cm^{-1}. ^{1}H NMR (400 MHz, DMSO) δ 13.00 (br s, 1 H), 7.80 (ABq, *J*=8.2 Hz, Δν=135.8 Hz, 4 H), 7.52 (dd, *J*=7.5, 1.7 Hz, 1 H), 7.42 (td, *J*=7.7, 1.7 Hz, 1 H), 7.12 (d, *J*=8.4 Hz, 1 H), 7.00 (td, *J*=7.4, 0.6 Hz, 1 H), 3.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.59, 160.67, 134.09, 132.20, 131.78, 131.27, 130.43, 127.88, 121.43, 112.32, 111.60, 93.08, 89.81, 56.61. HRMS Calcd $C_{16}H_{12}O_3$: 252.0786. Found: 252.0782.

References and Notes

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(11) Correspondence with Dr. Ian Campbell at Los Alamos National Laboratory, Los Alamos, NM.

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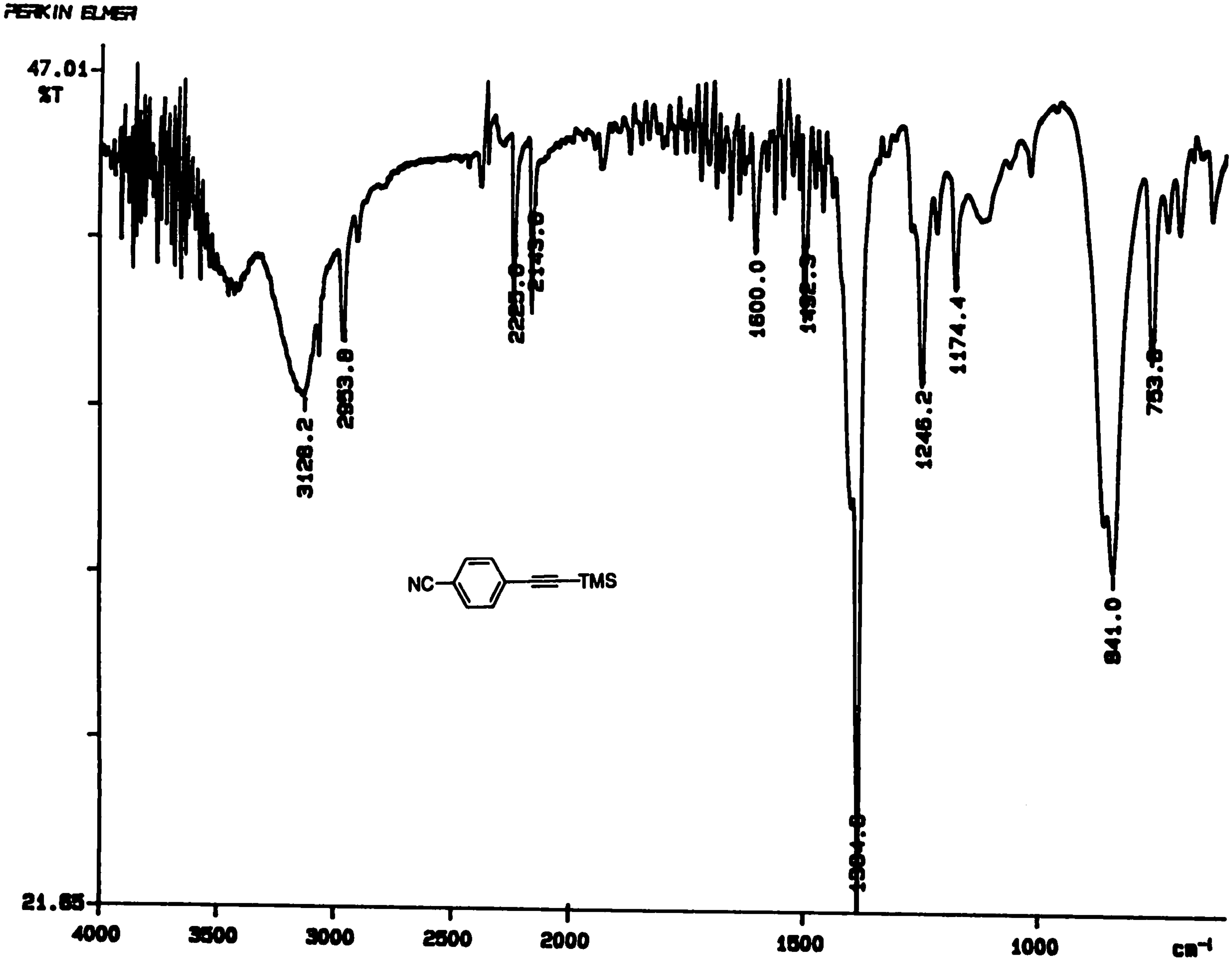
Spectral Section for

Chapter 6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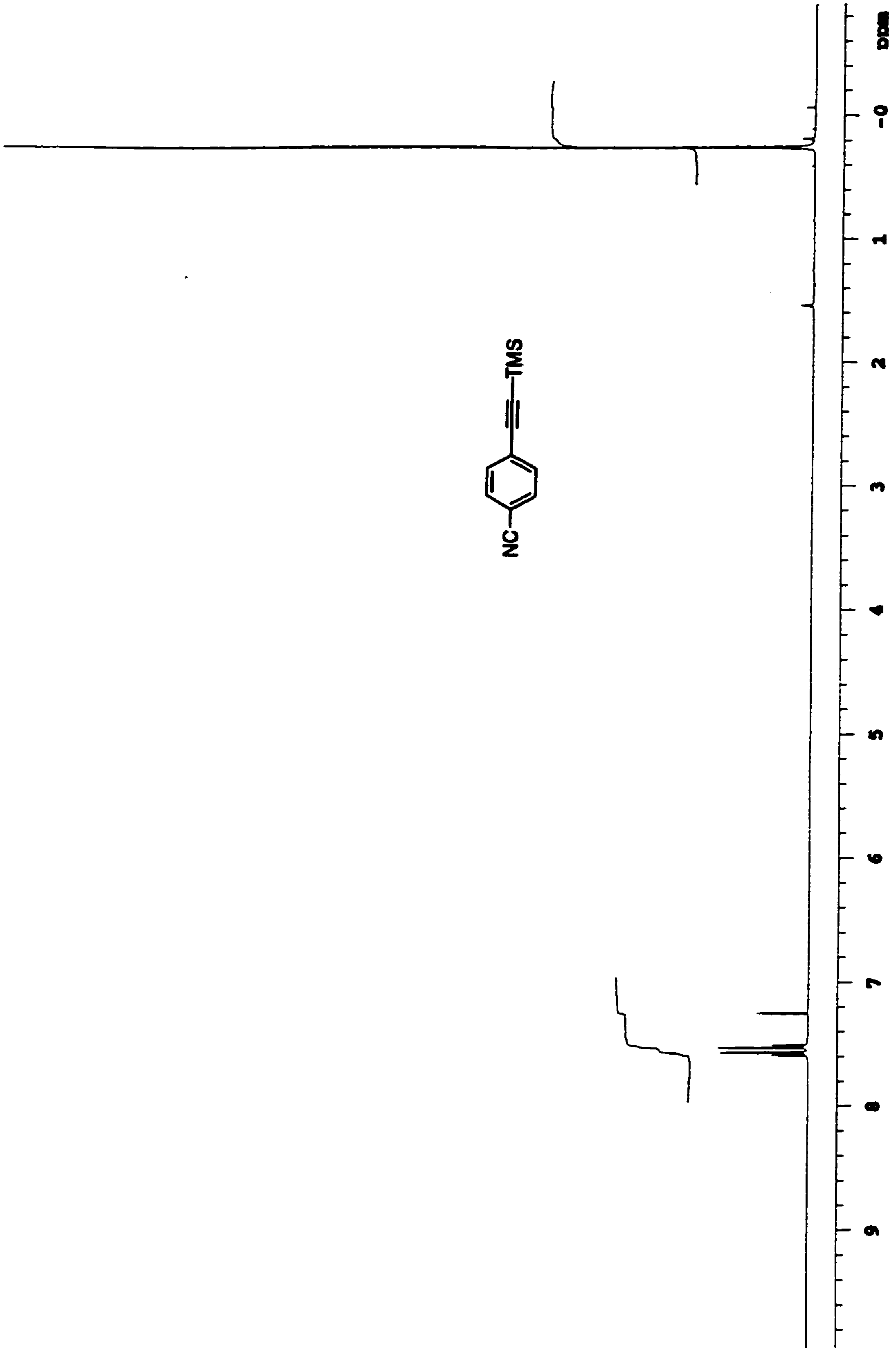
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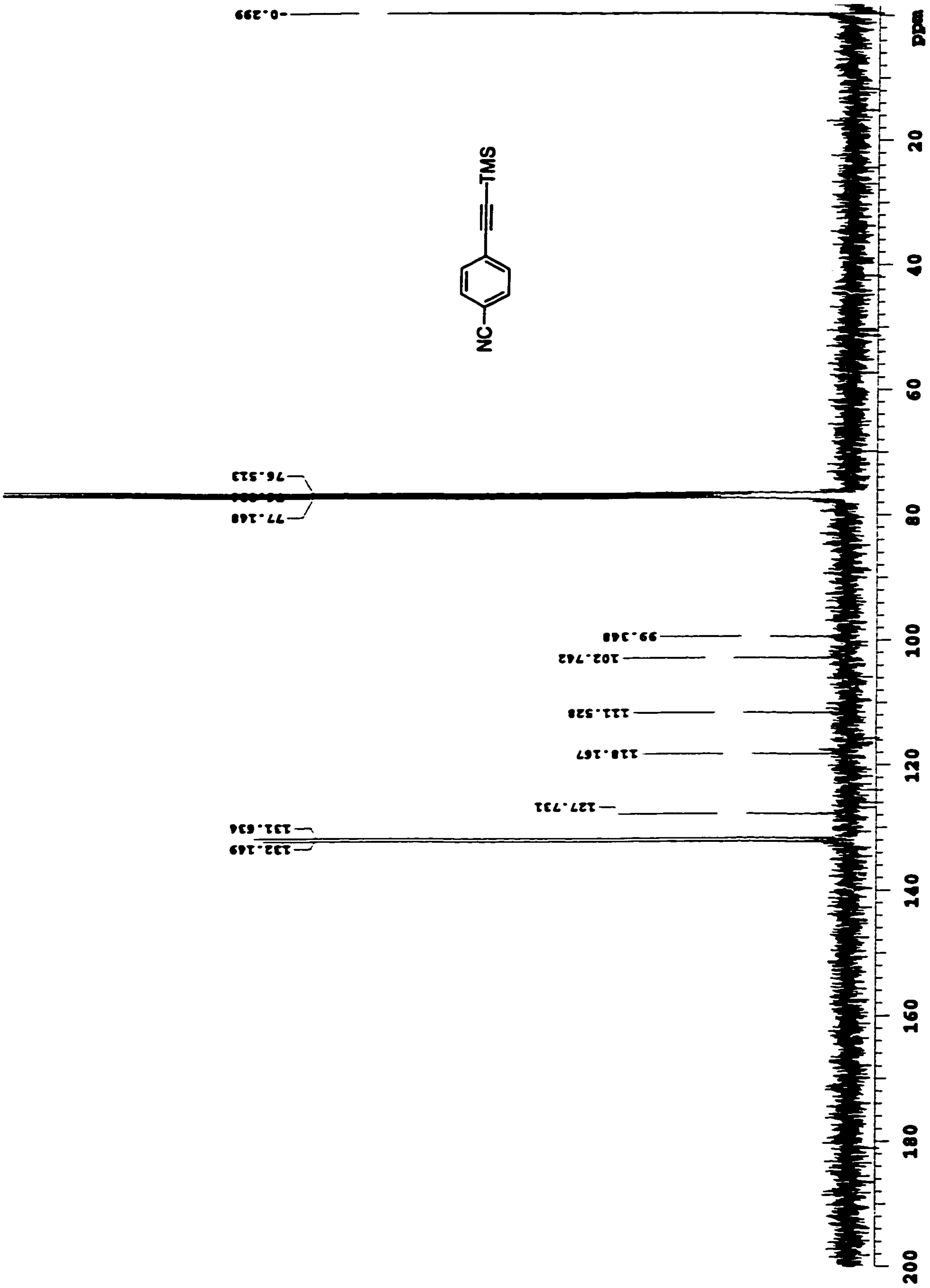
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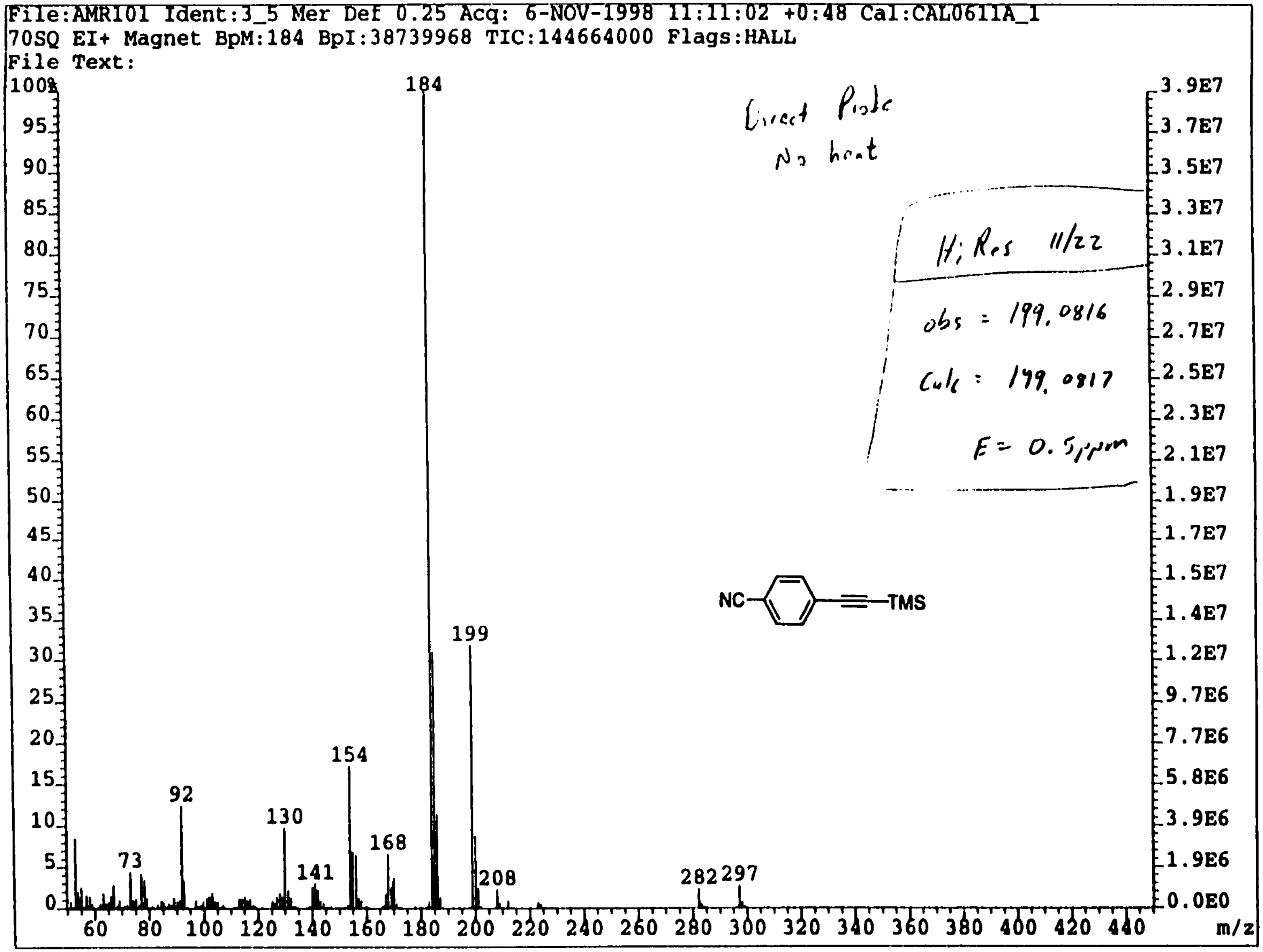

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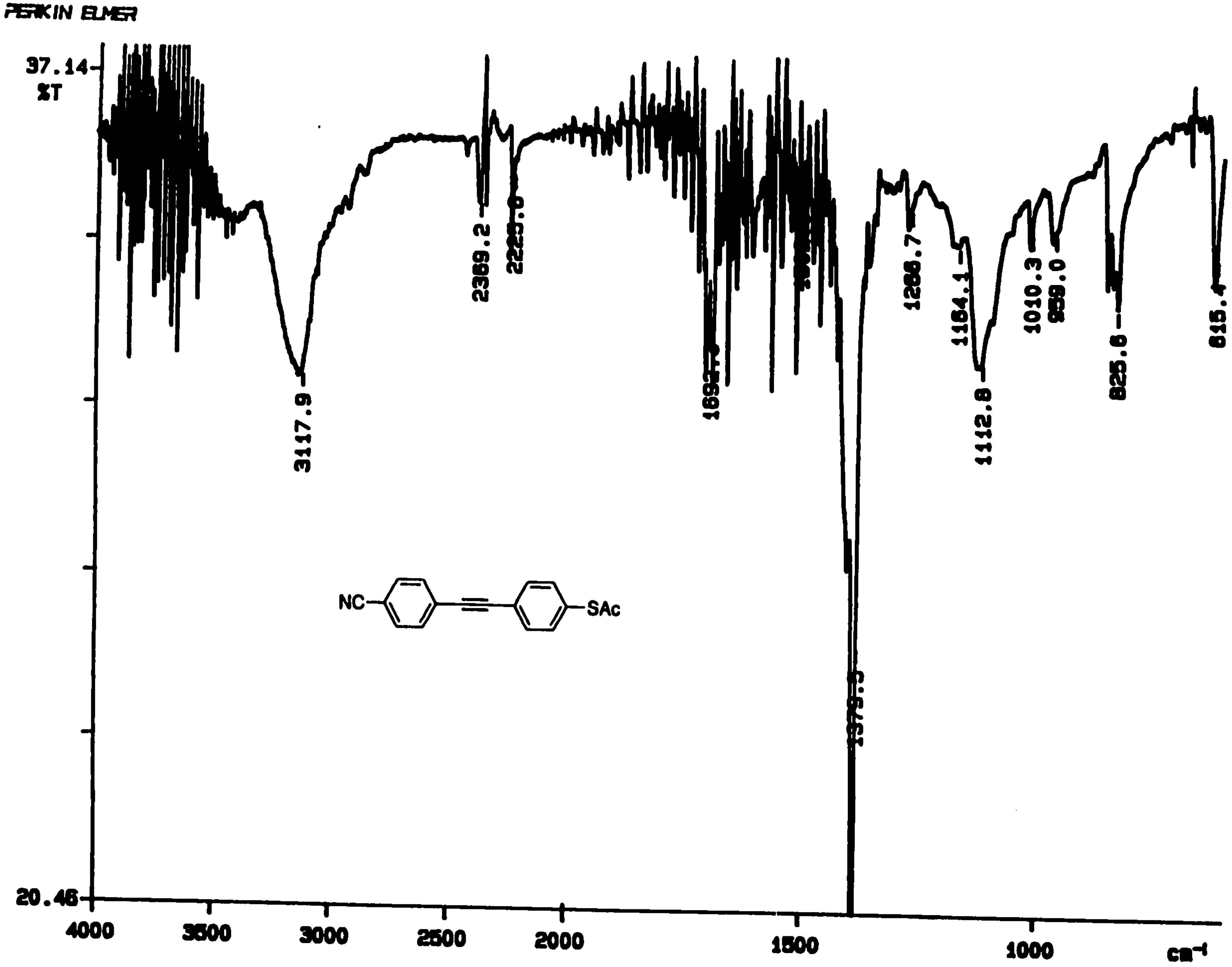
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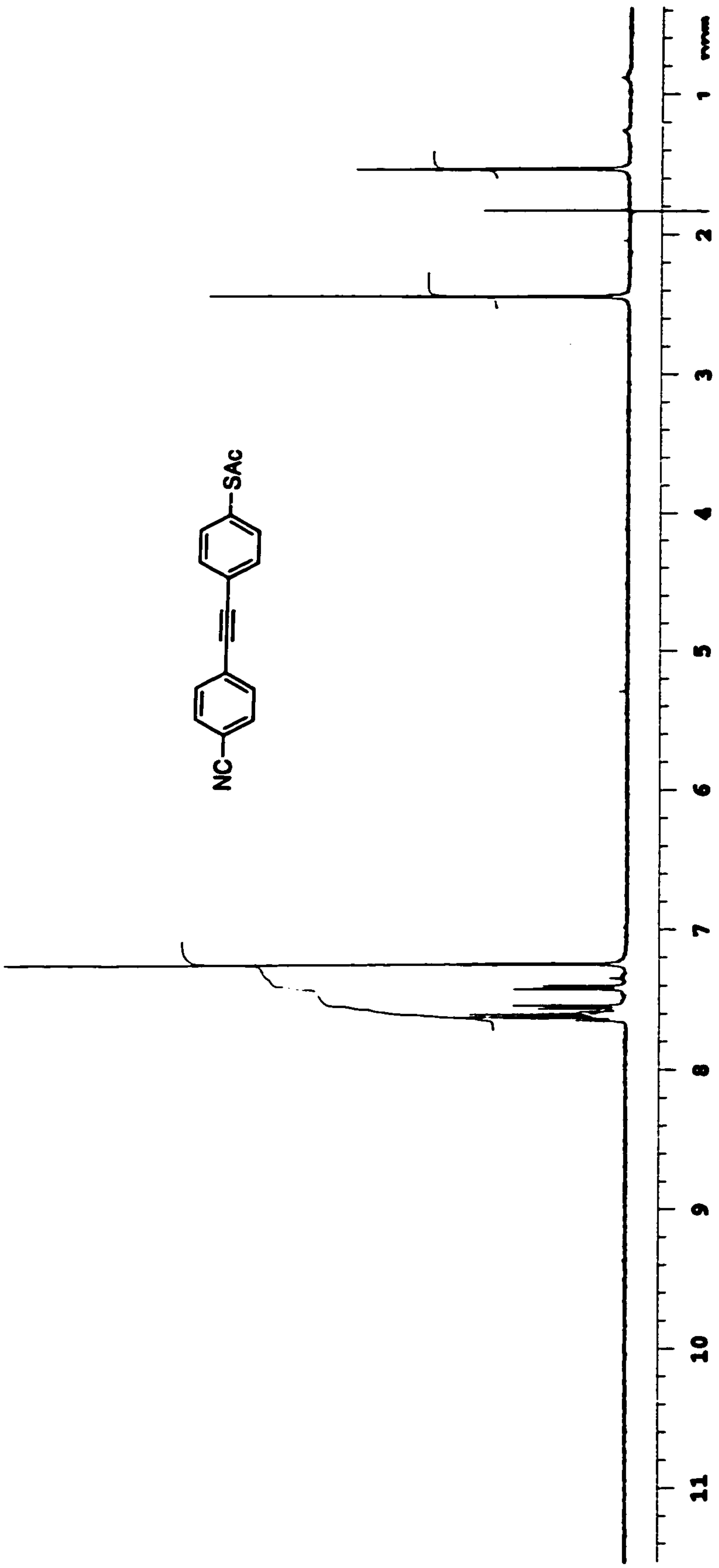
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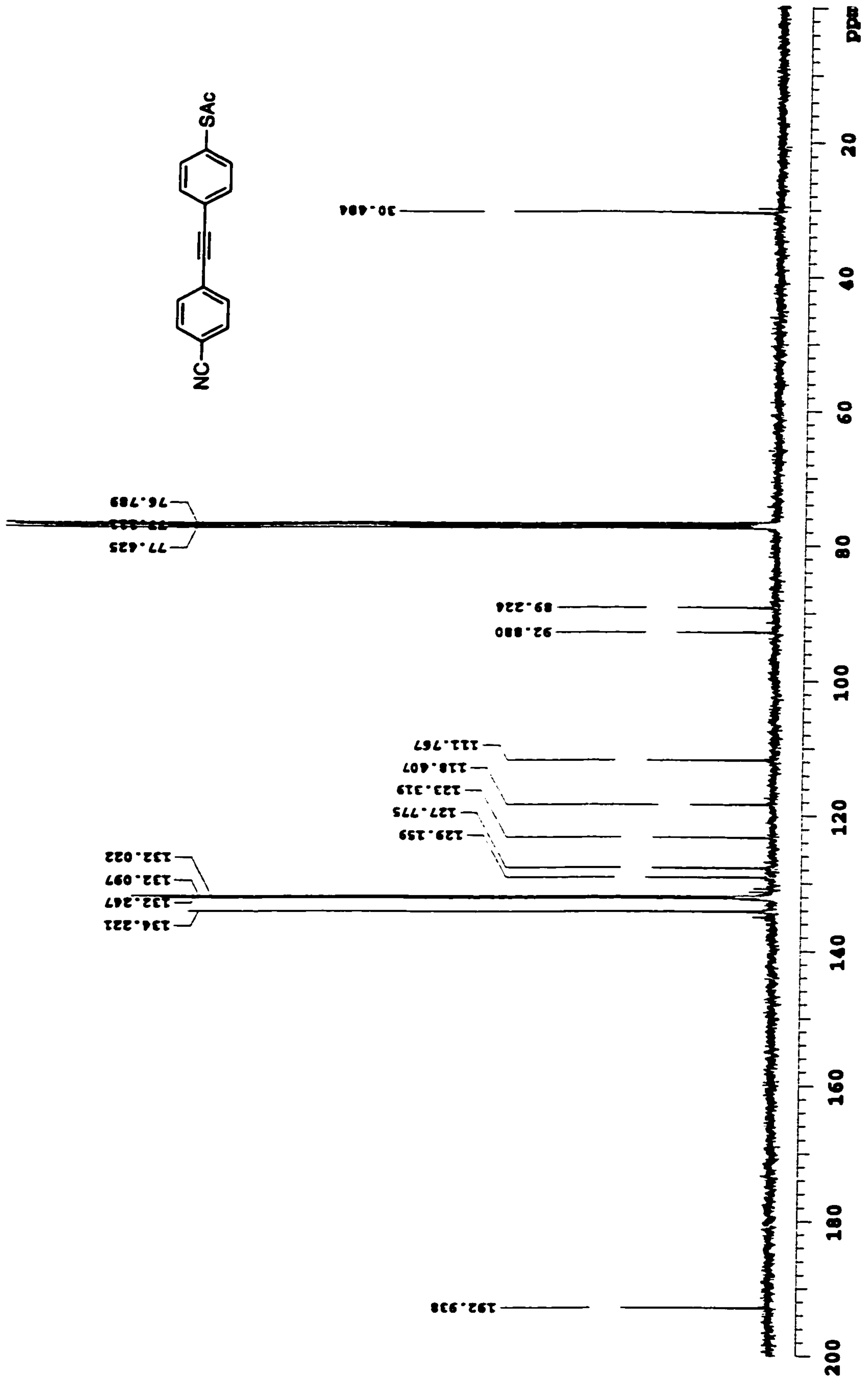
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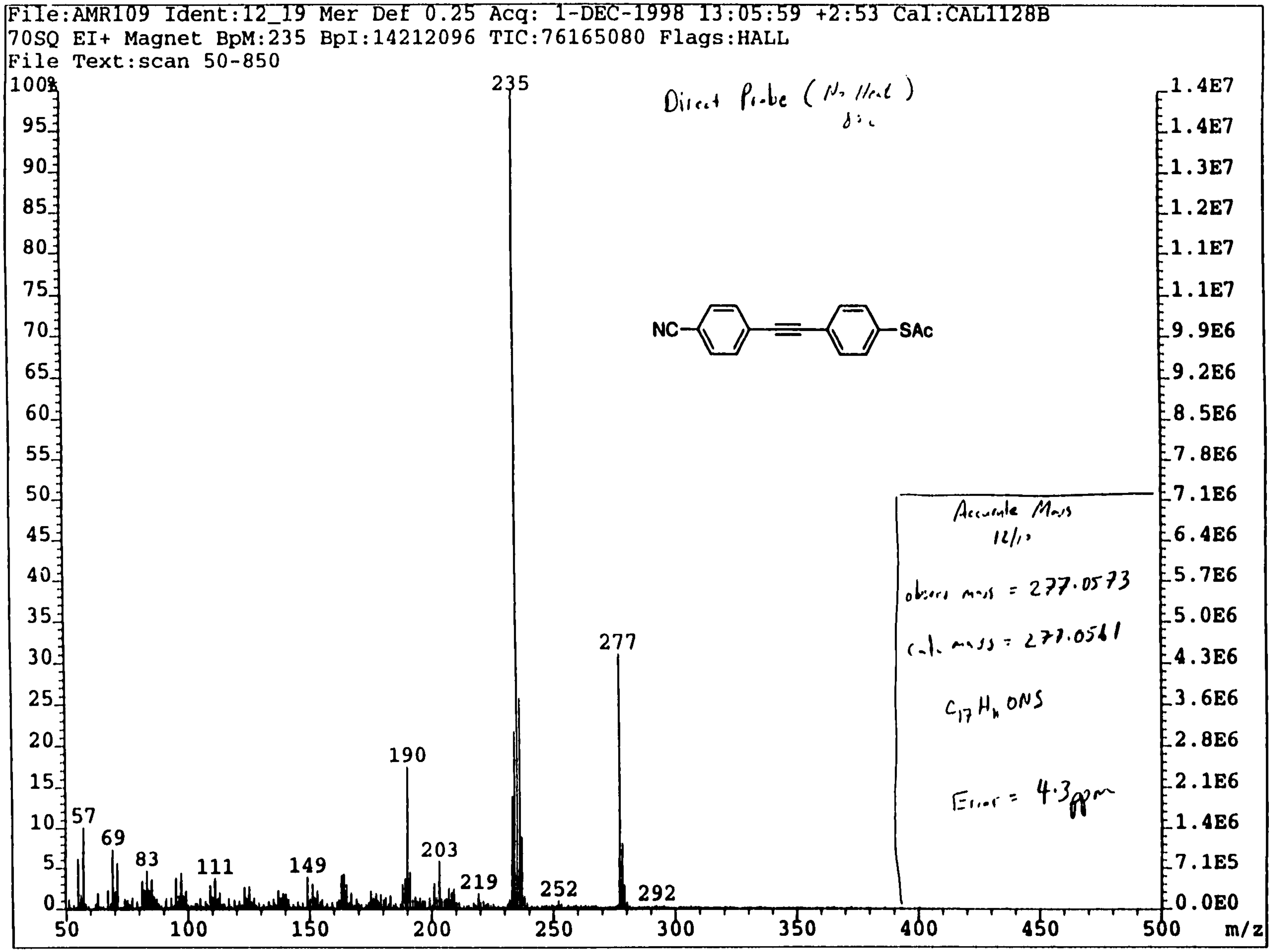

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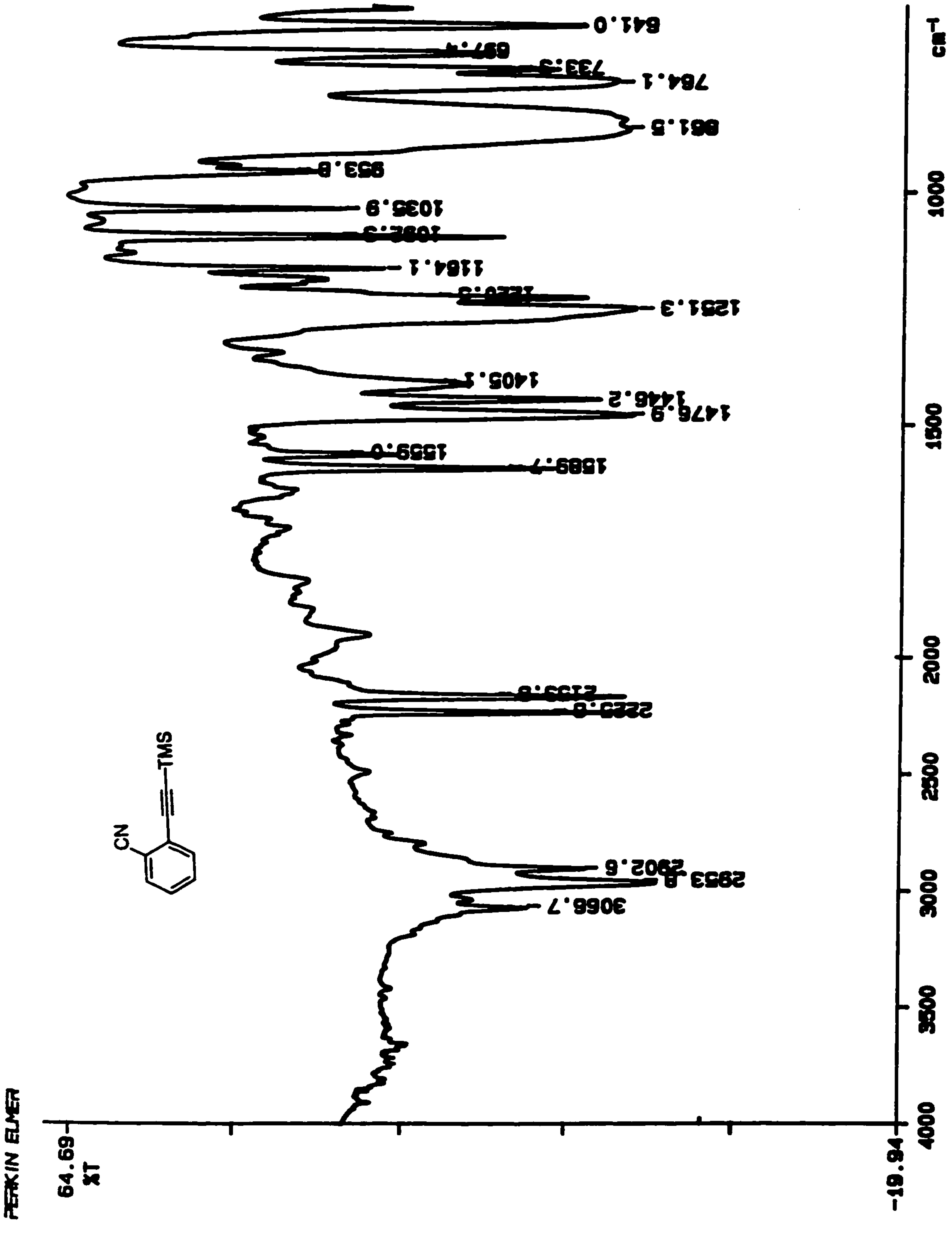
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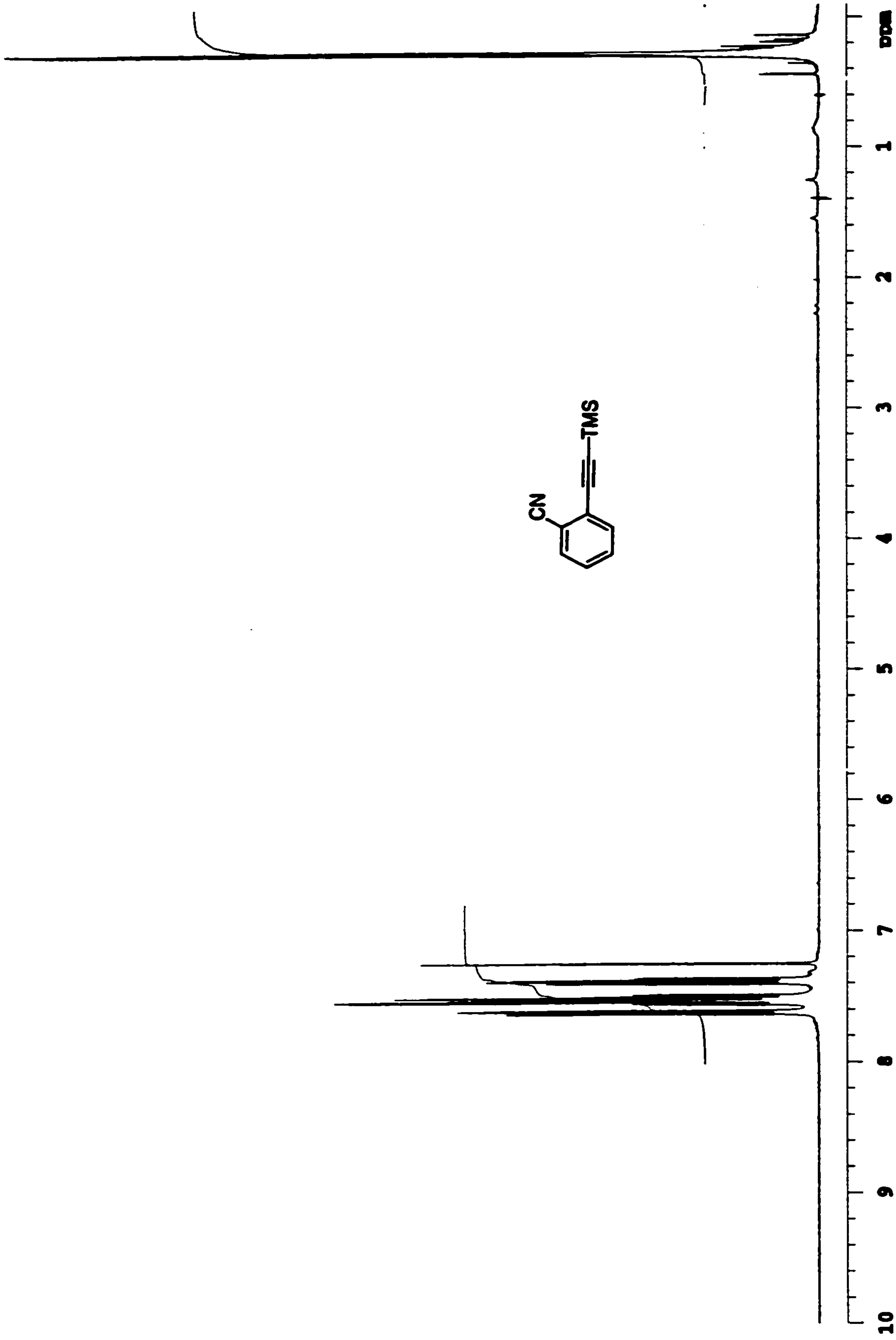
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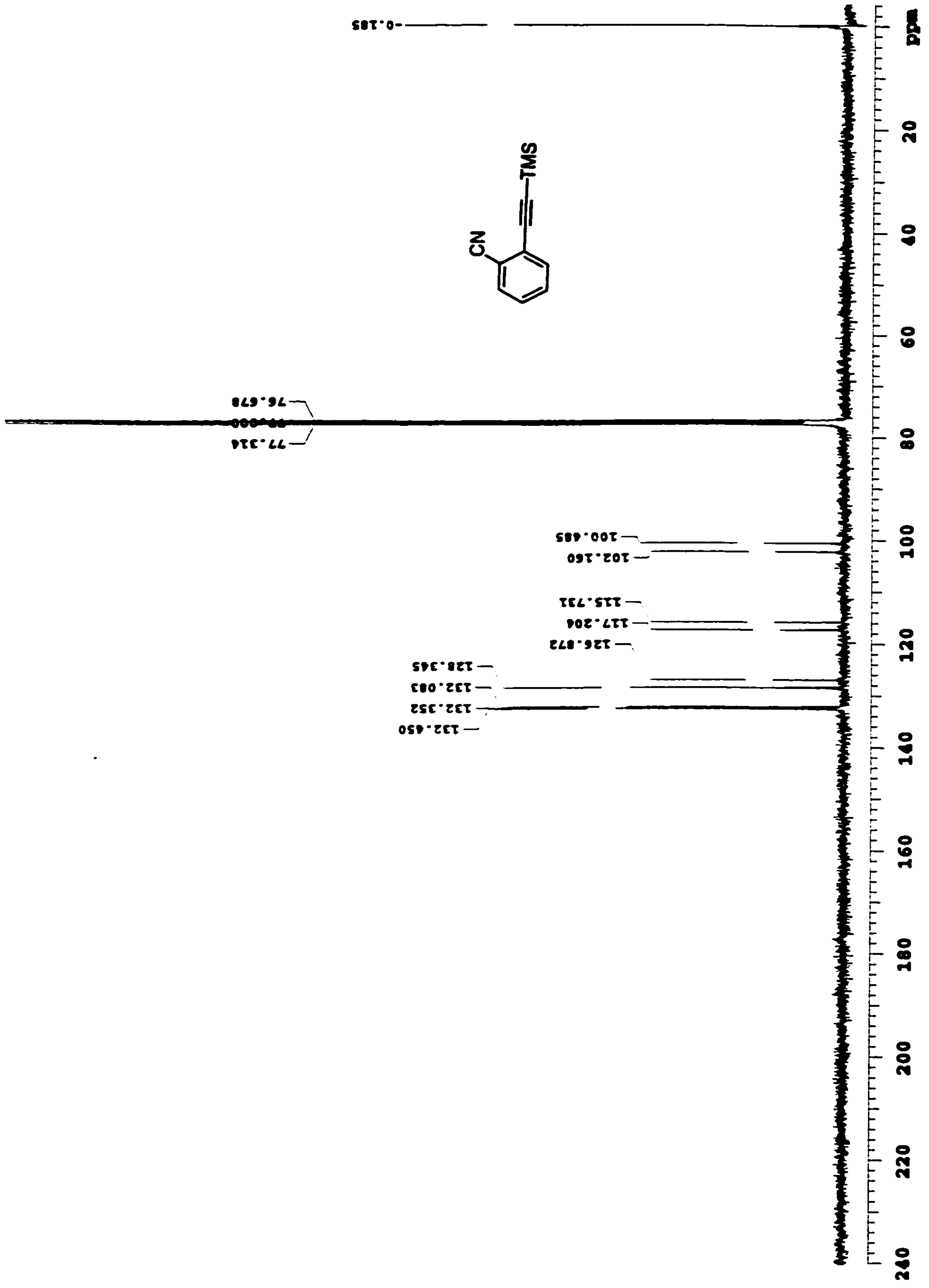
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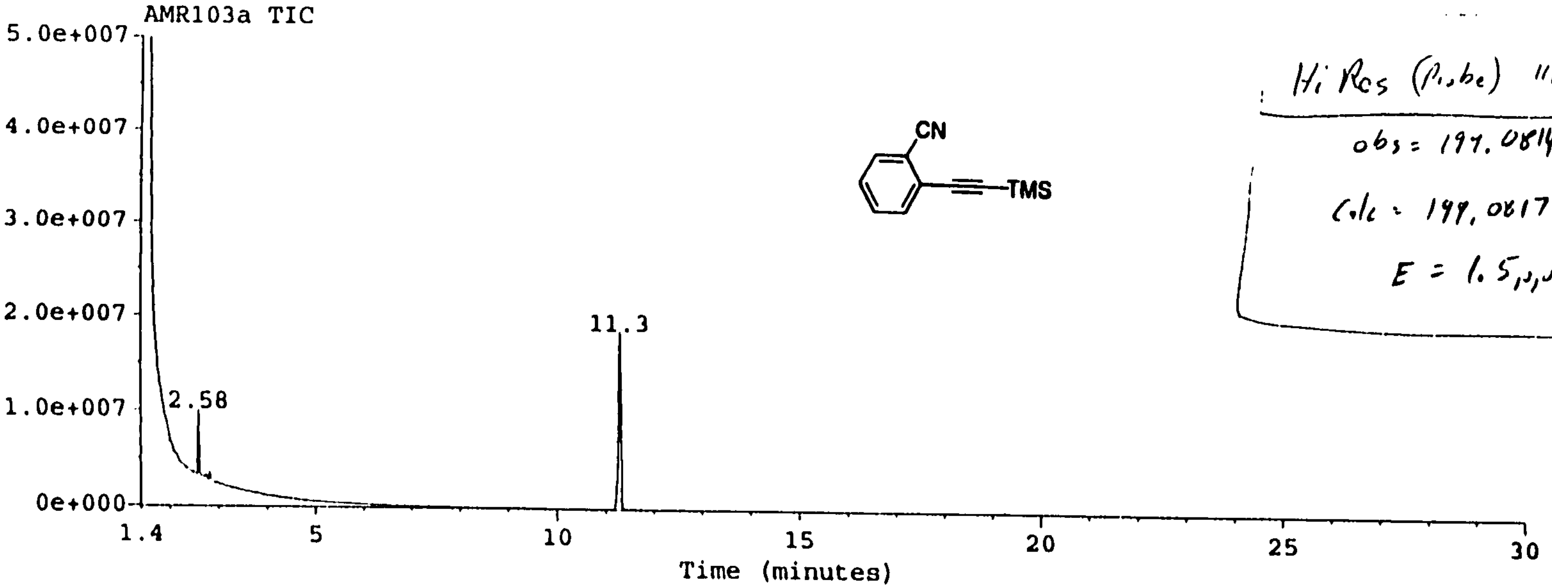
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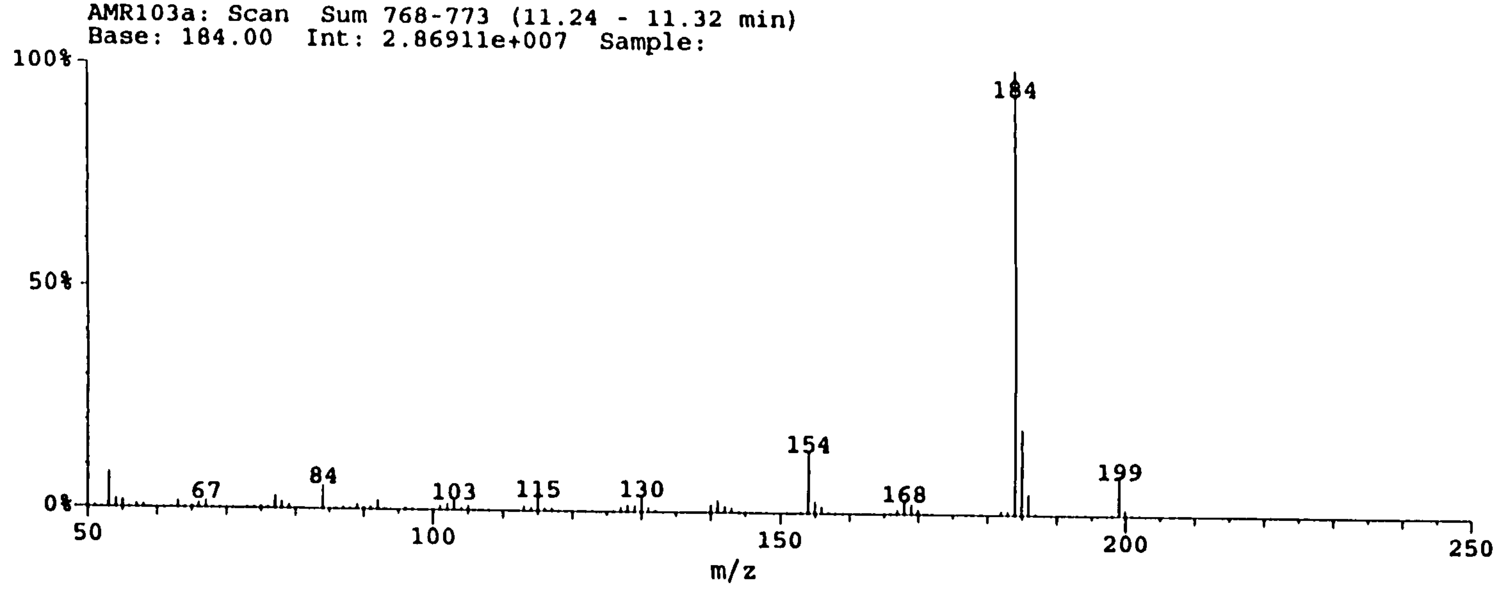
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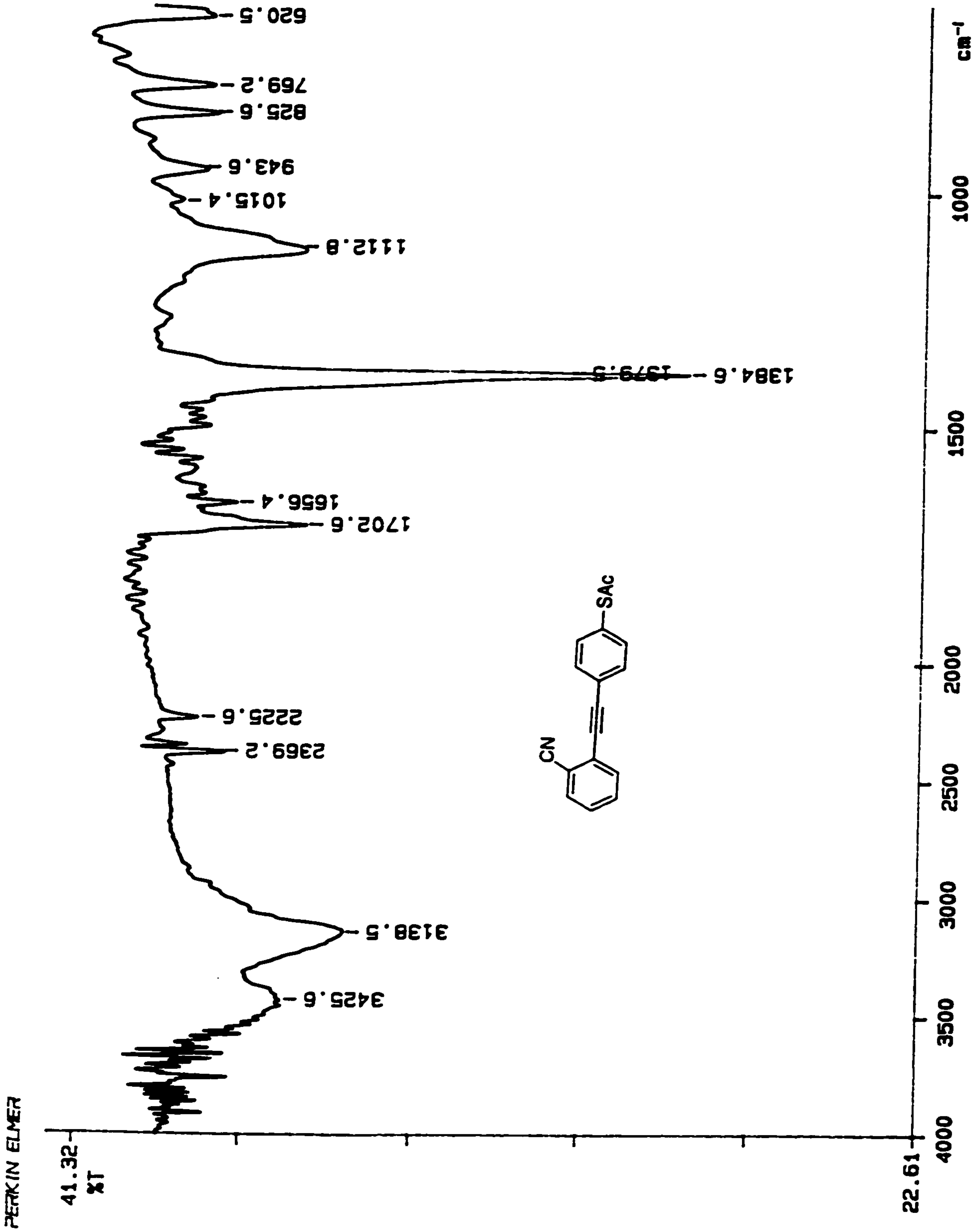
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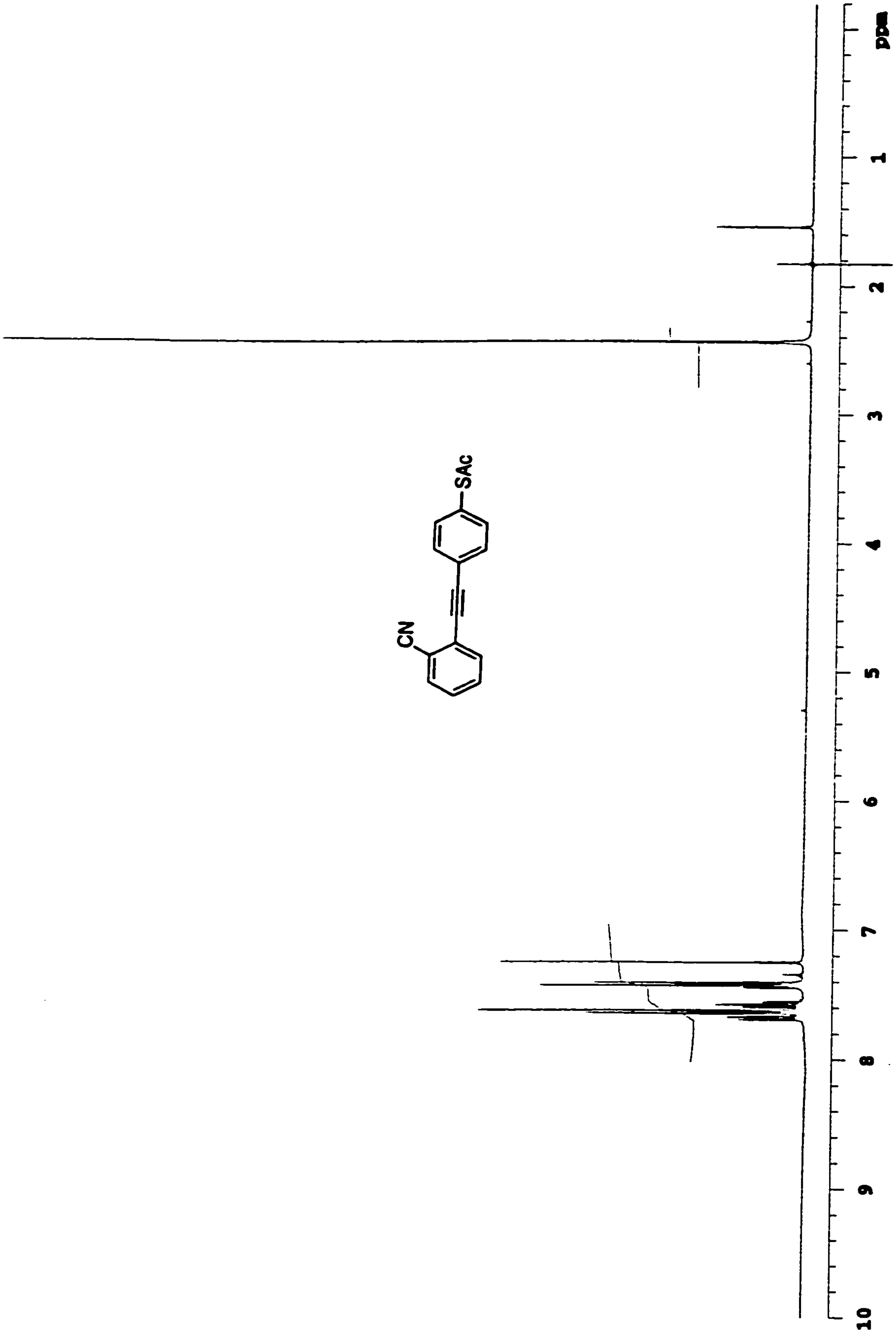
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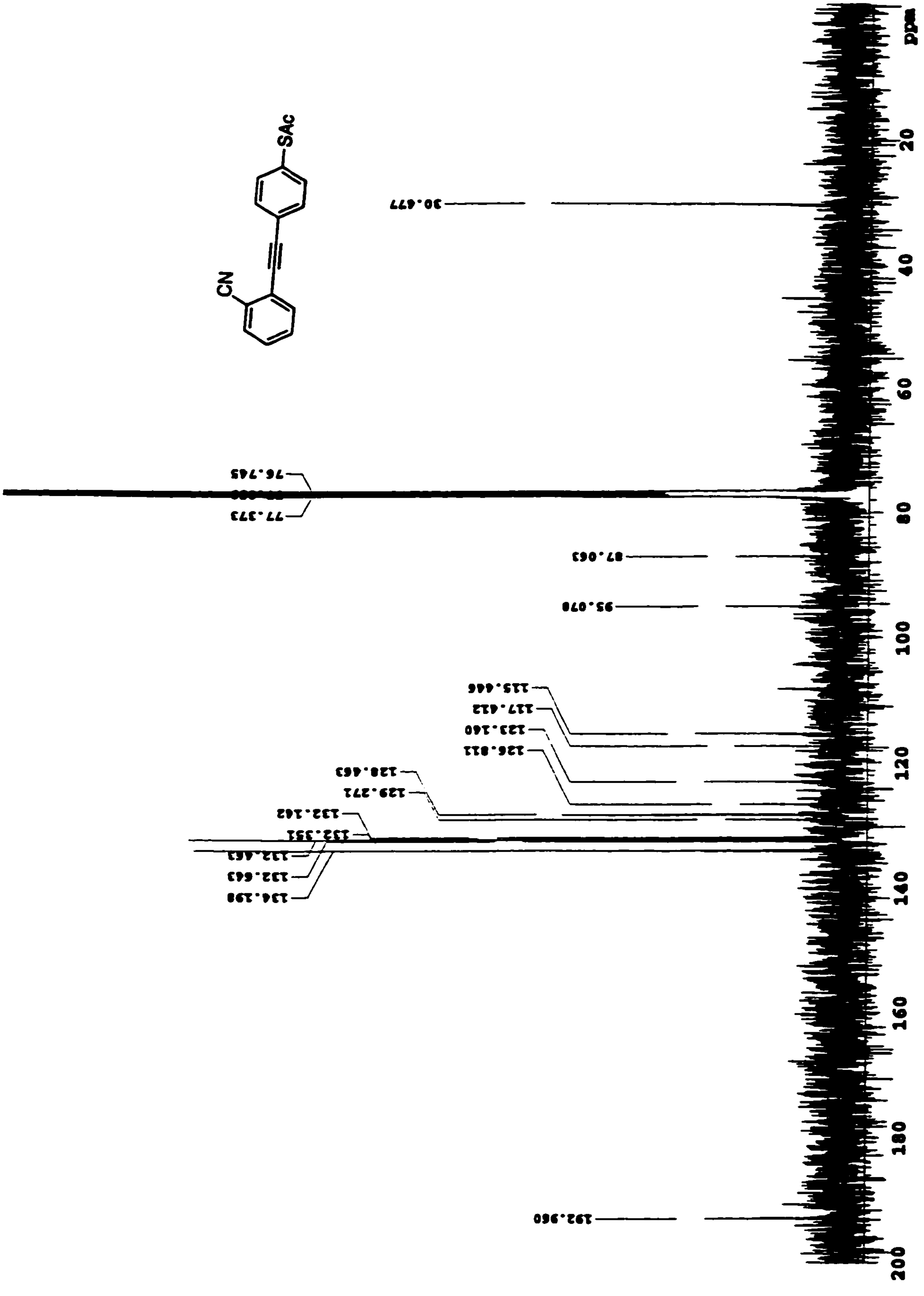
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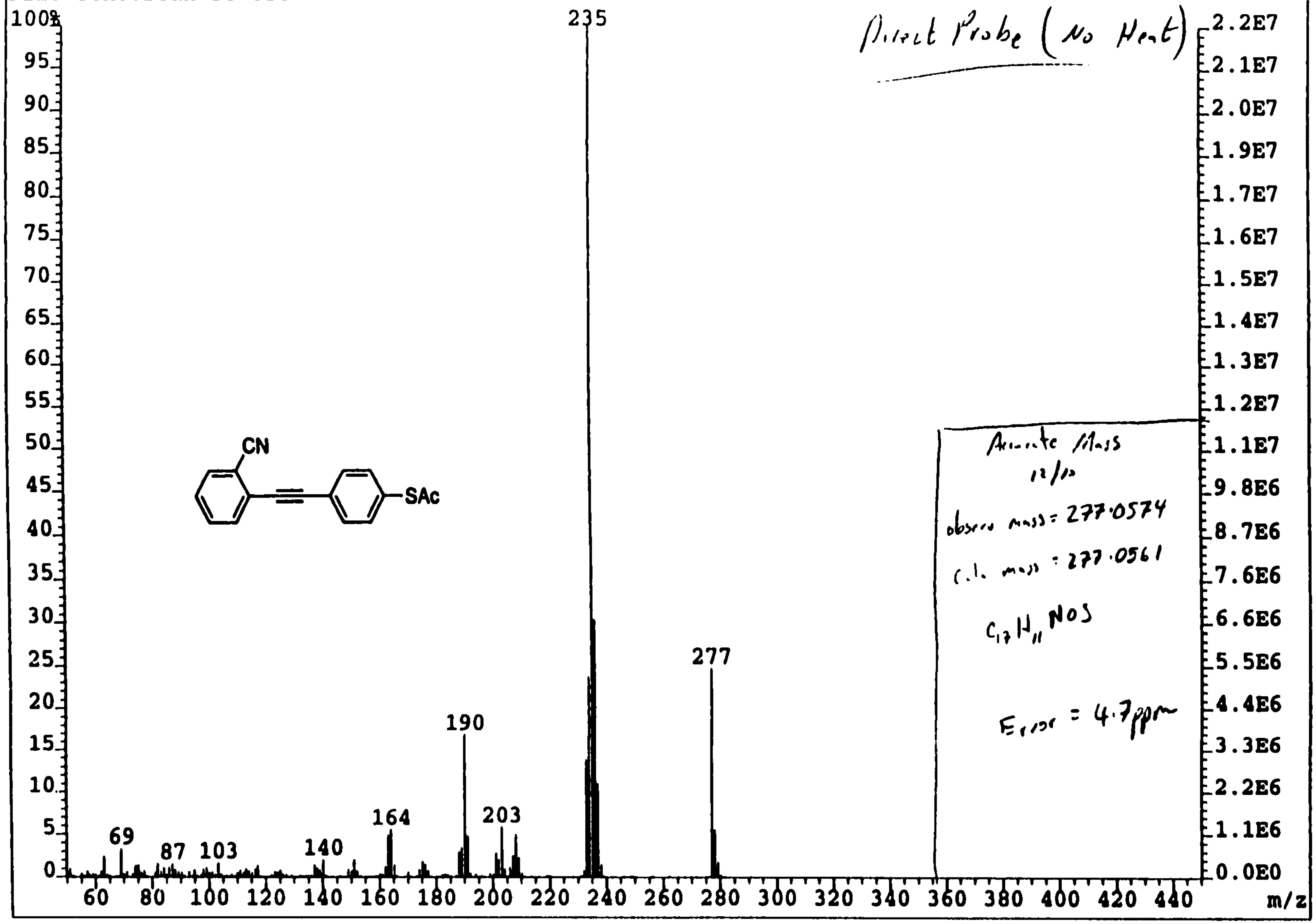

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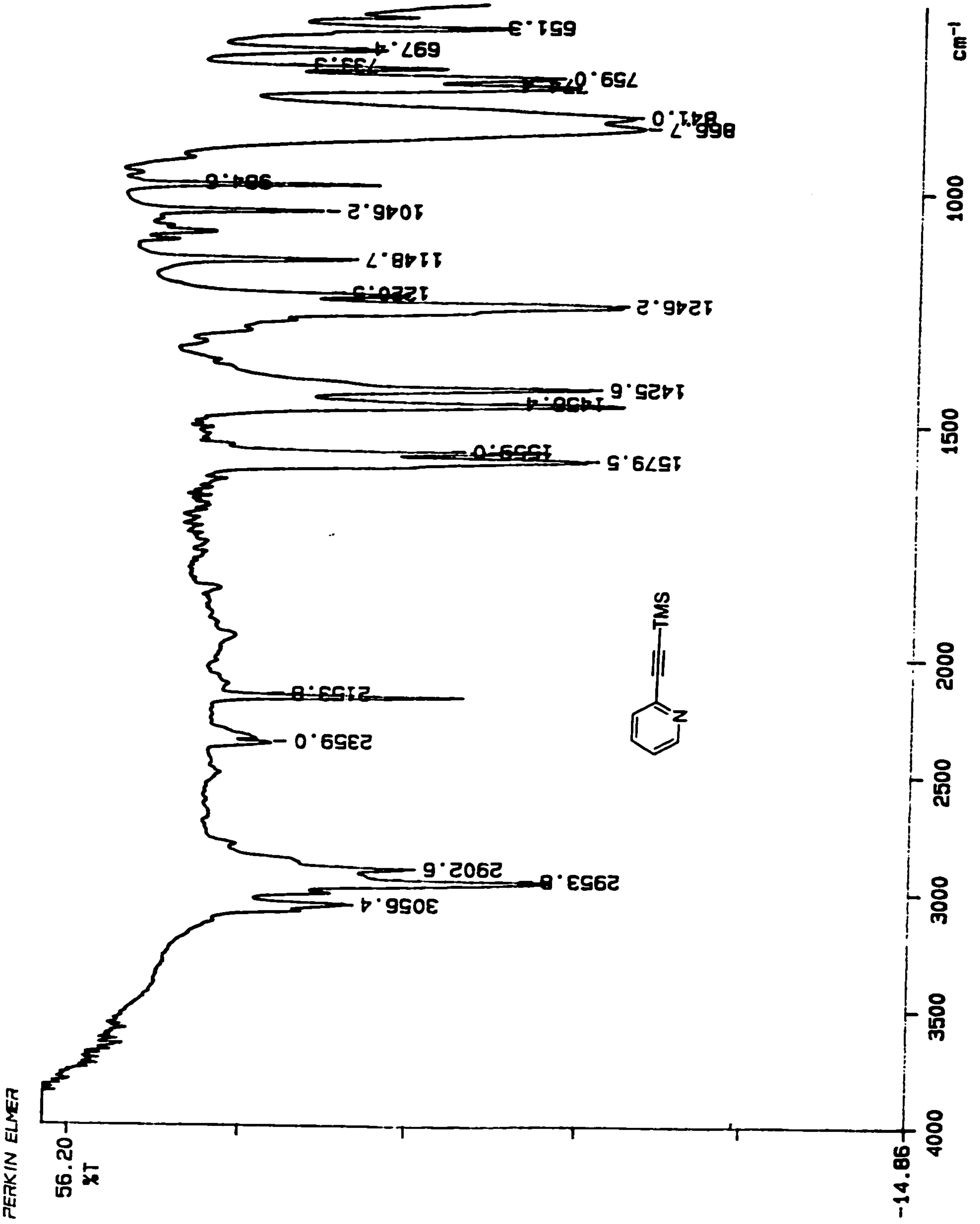
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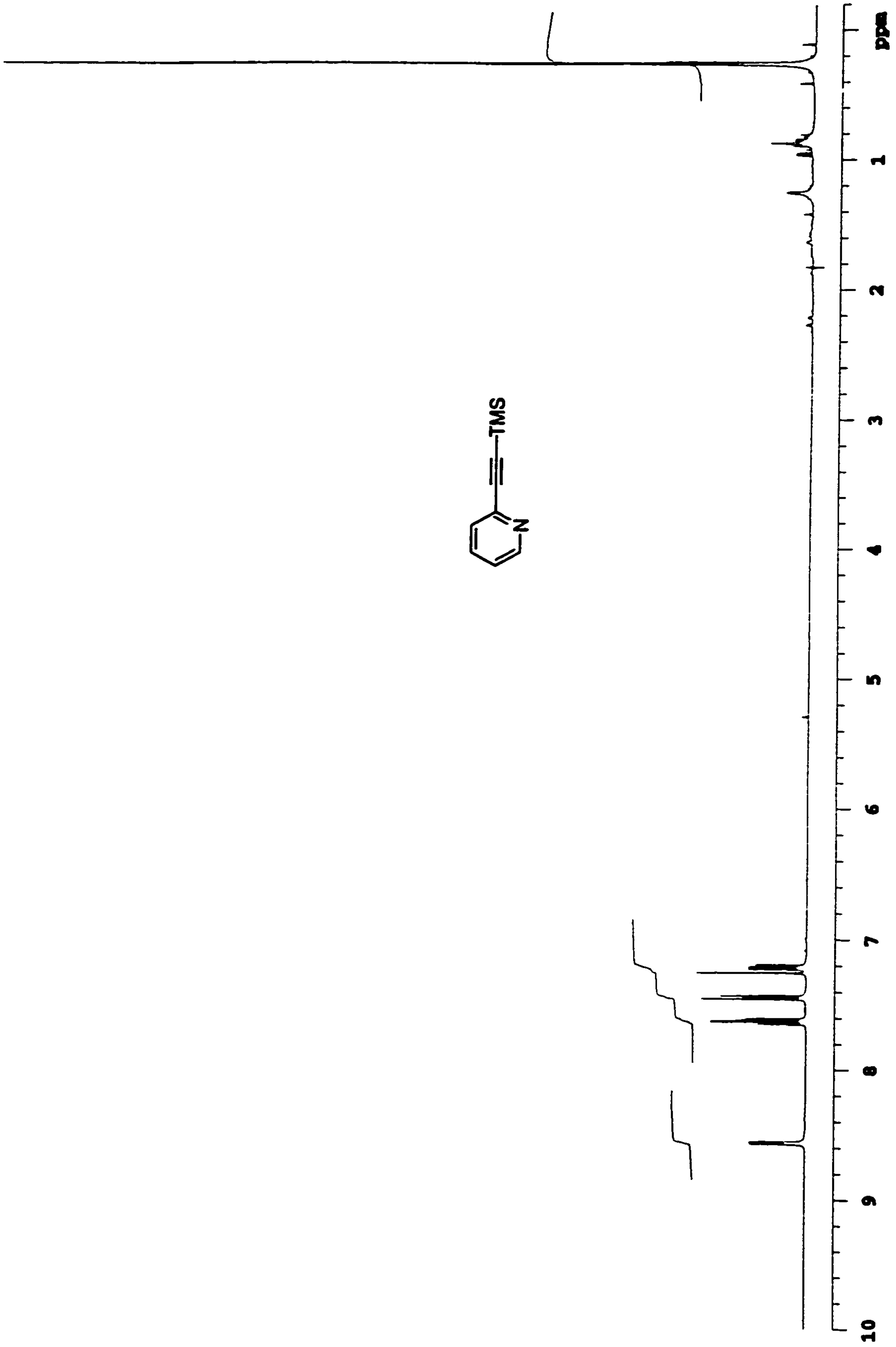
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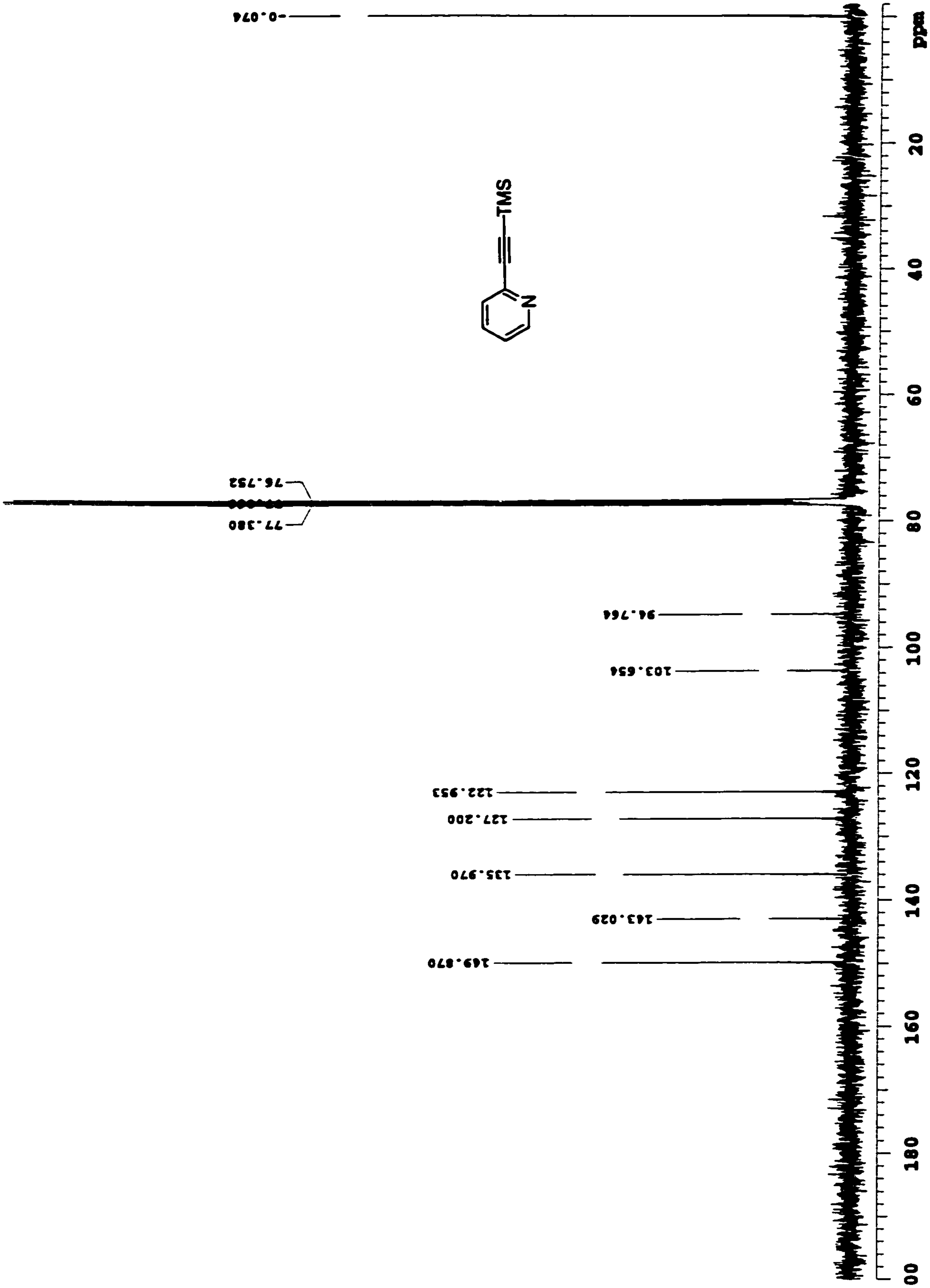
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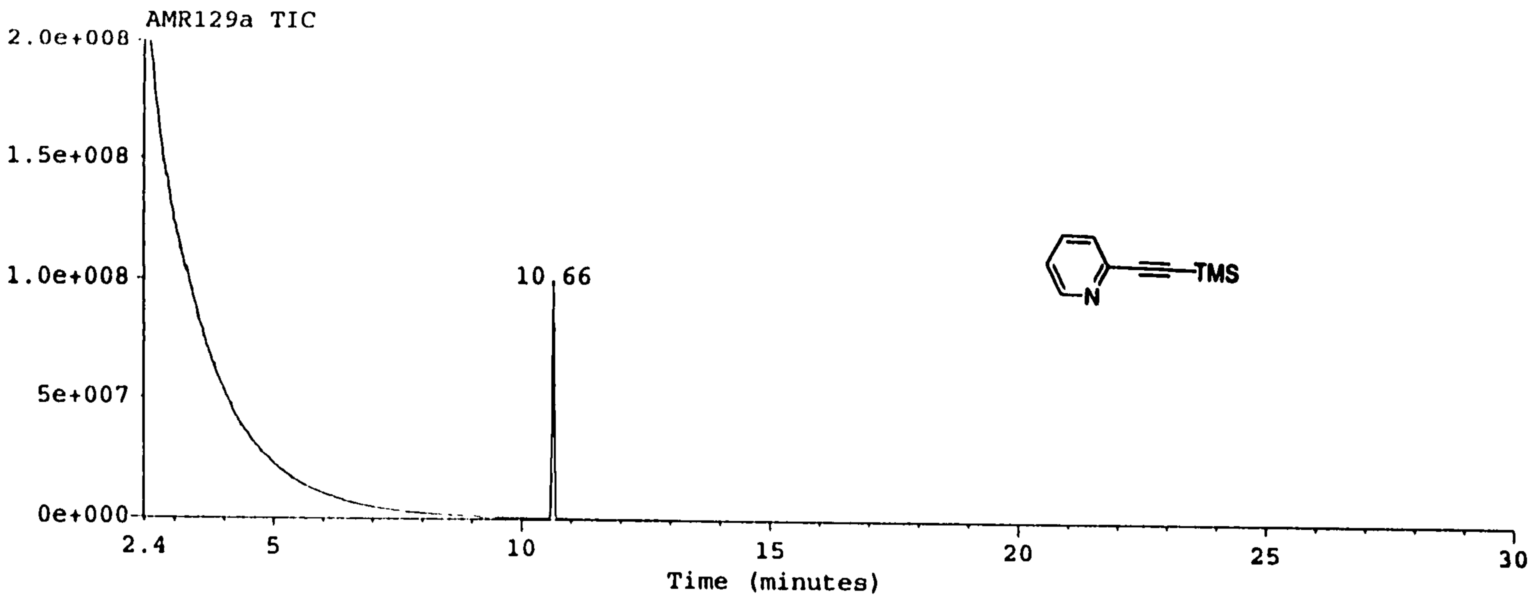

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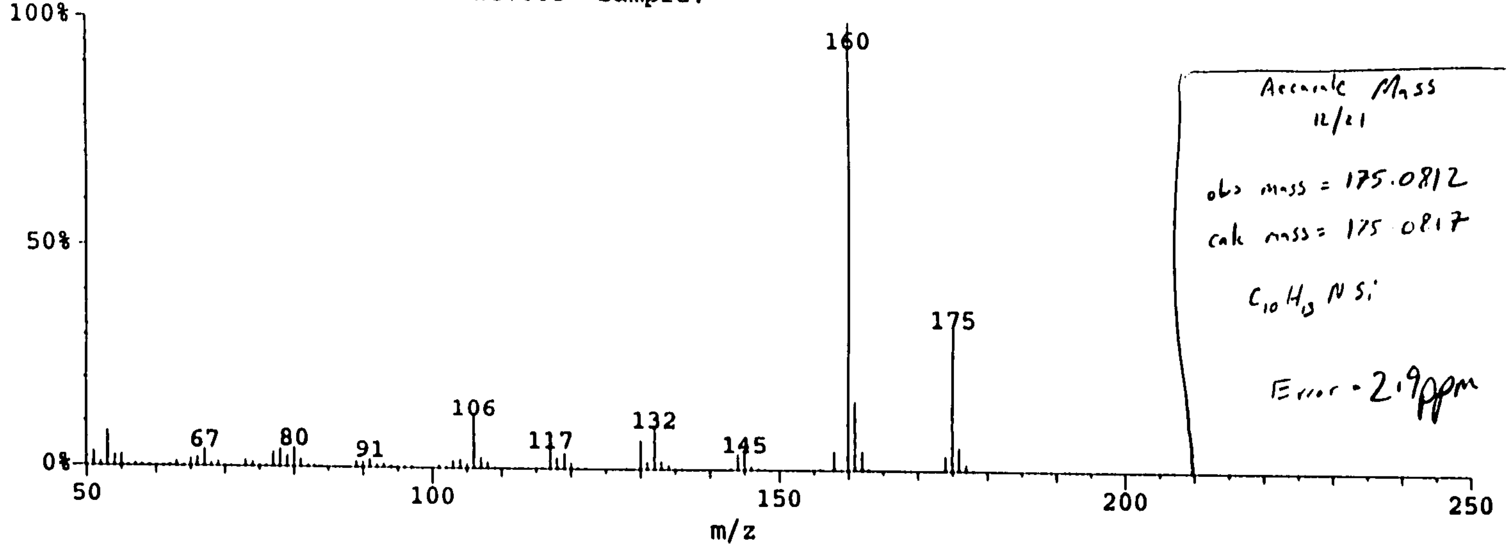

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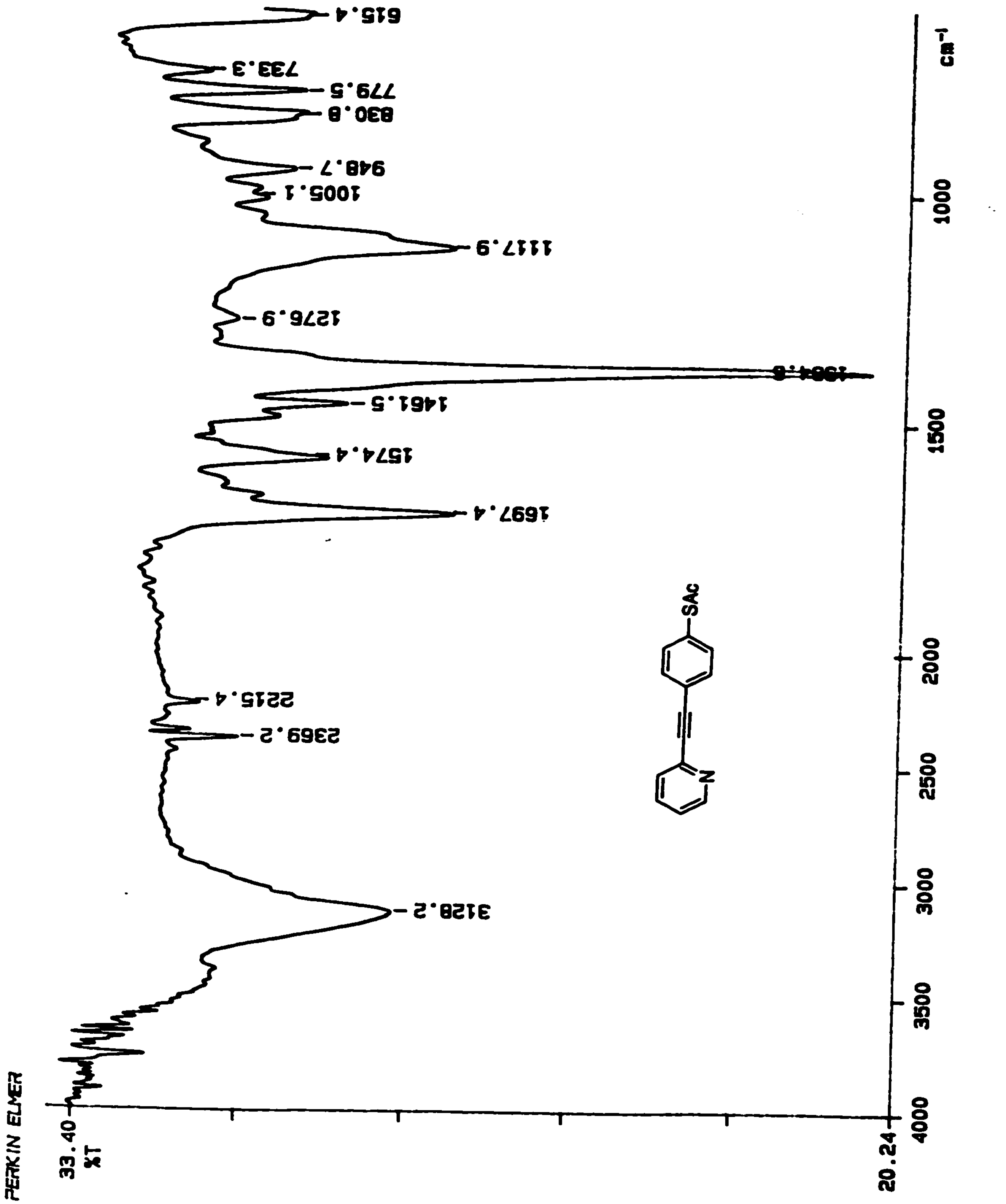
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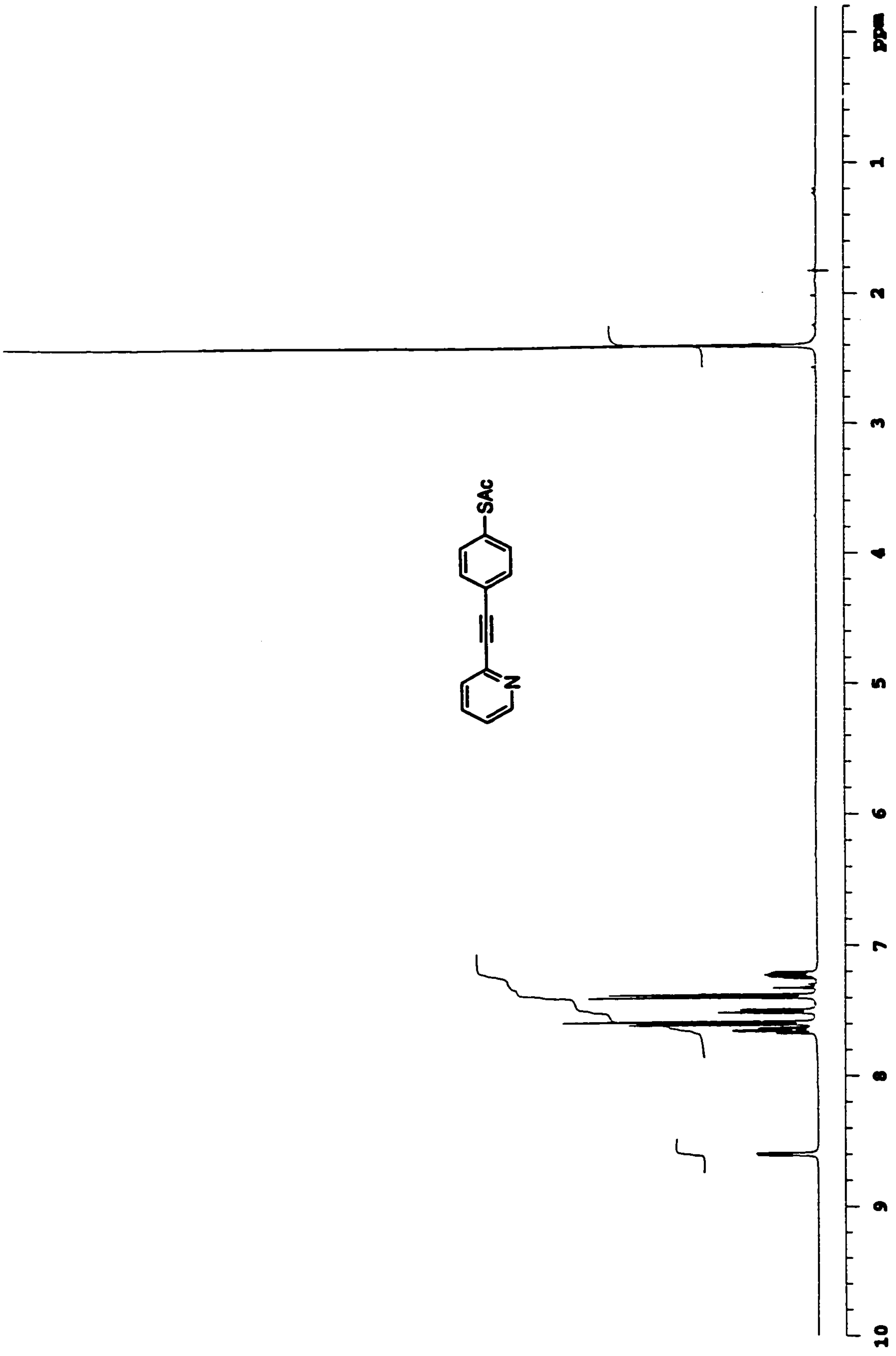
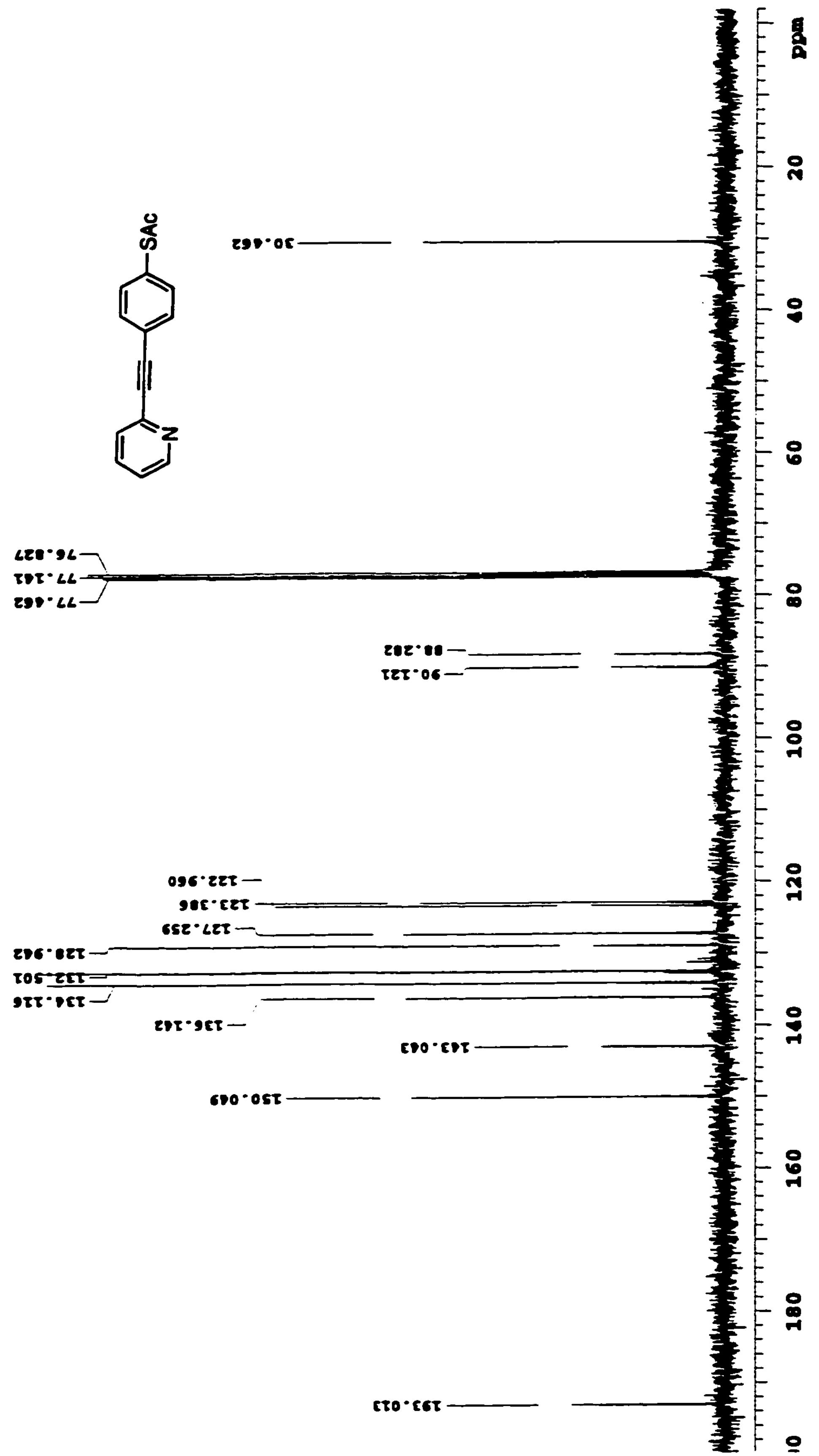
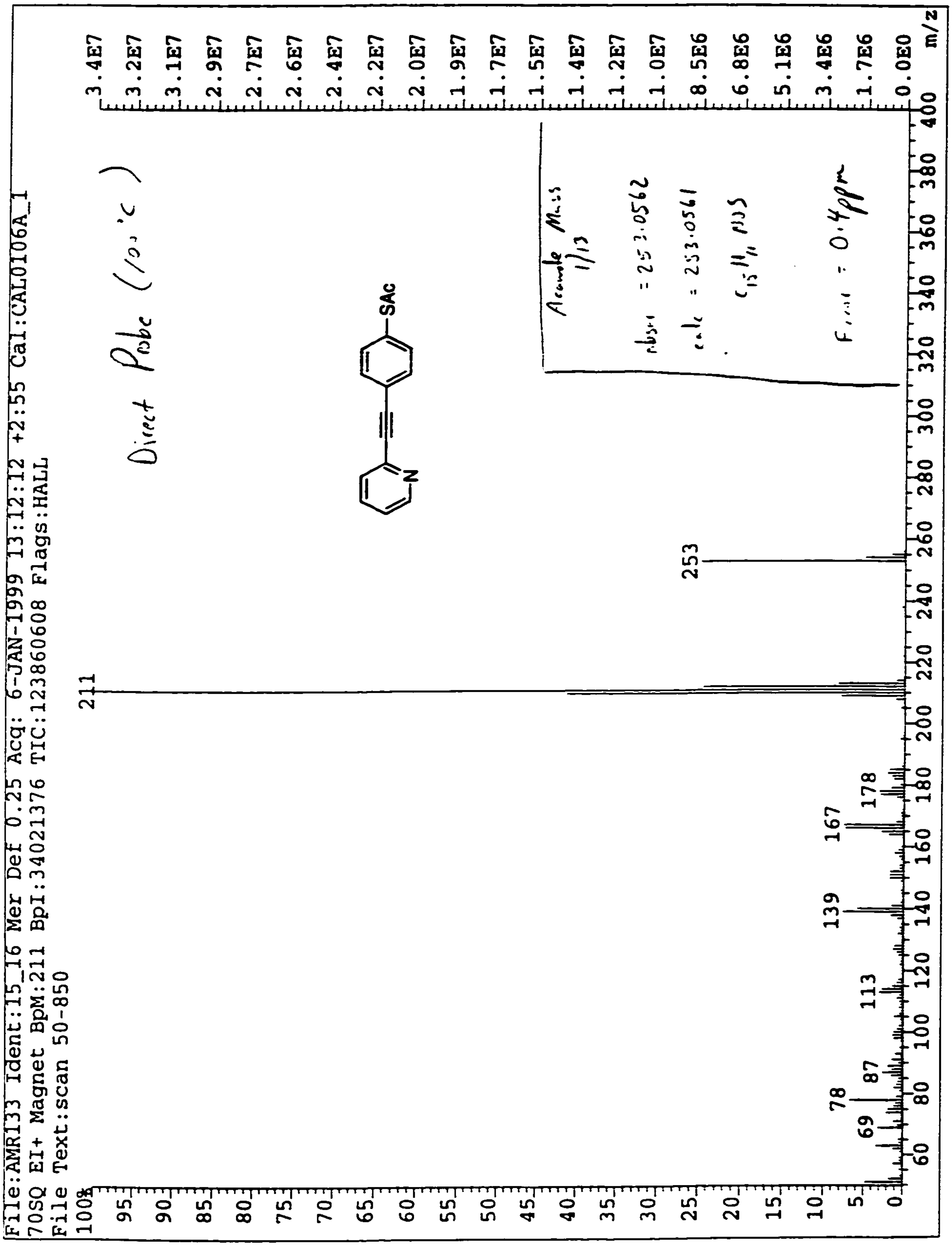
1384.6
1276.9
1117.9
1005.1
948.7
830.8
779.5
733.3
615.4
N
SAc


SAc
N
ppm
1
2
3
4
5
6
7
8
9
10


SAc
N
30.462
76.827
77.141
77.462
88.282
90.121
122.960
123.386
127.259
128.942
132.501
134.116
136.142
143.043
150.049
193.013
ppm
20
40
60
80
100
120
140
160
180



Direct Probe (100 °C)

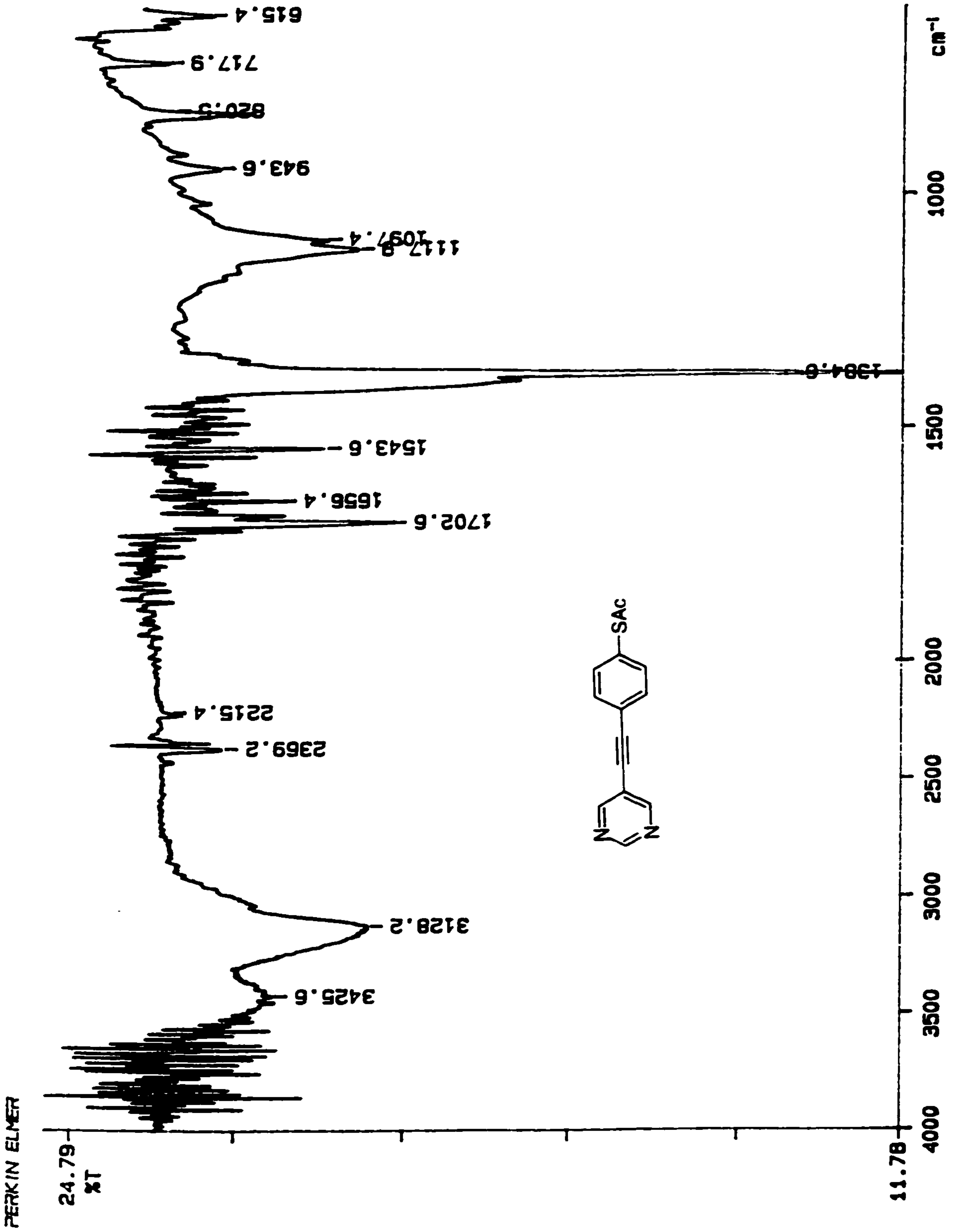
Accurate Mass
11/13

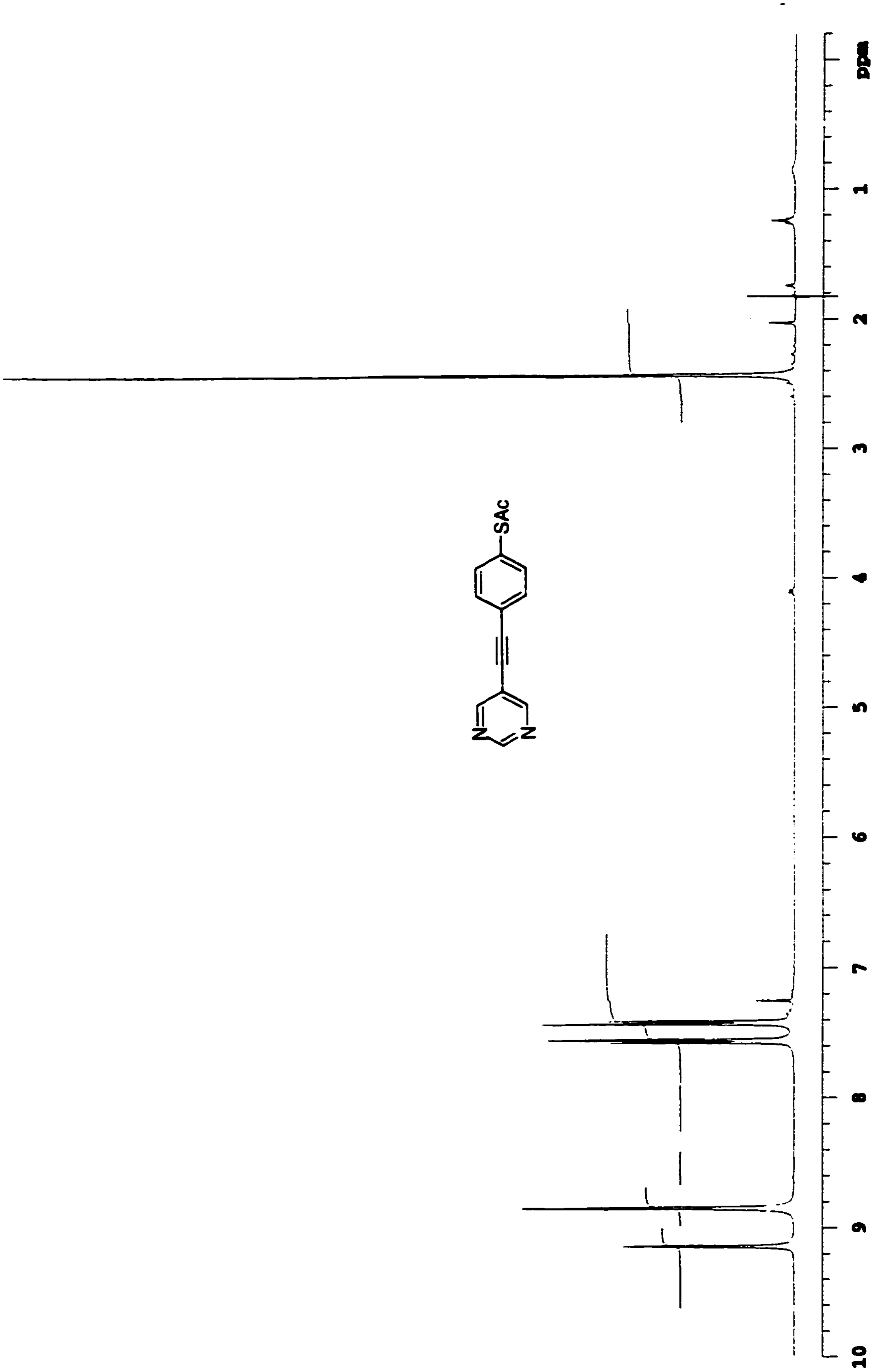
obsd = 253.0562

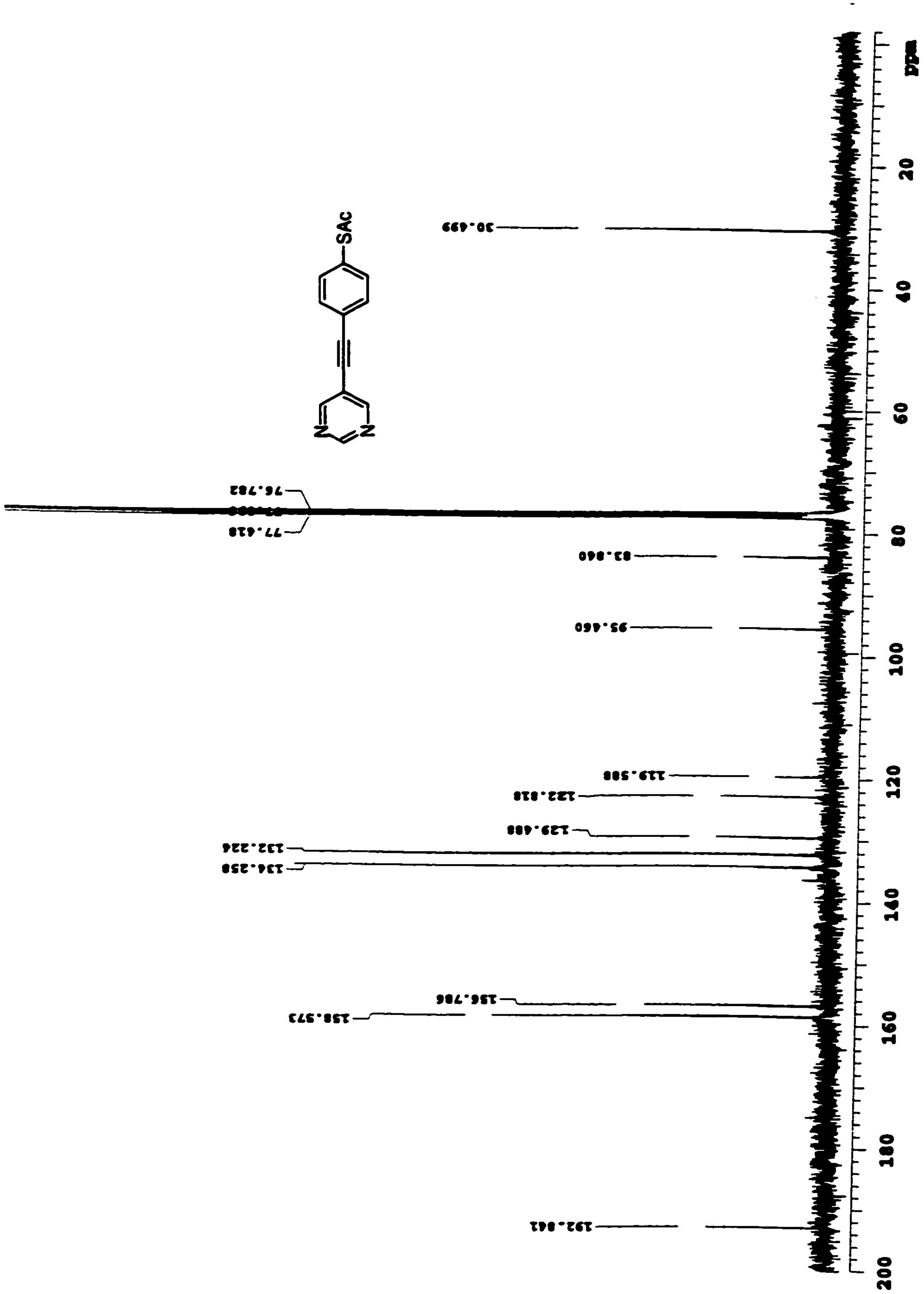
calc = 253.0561

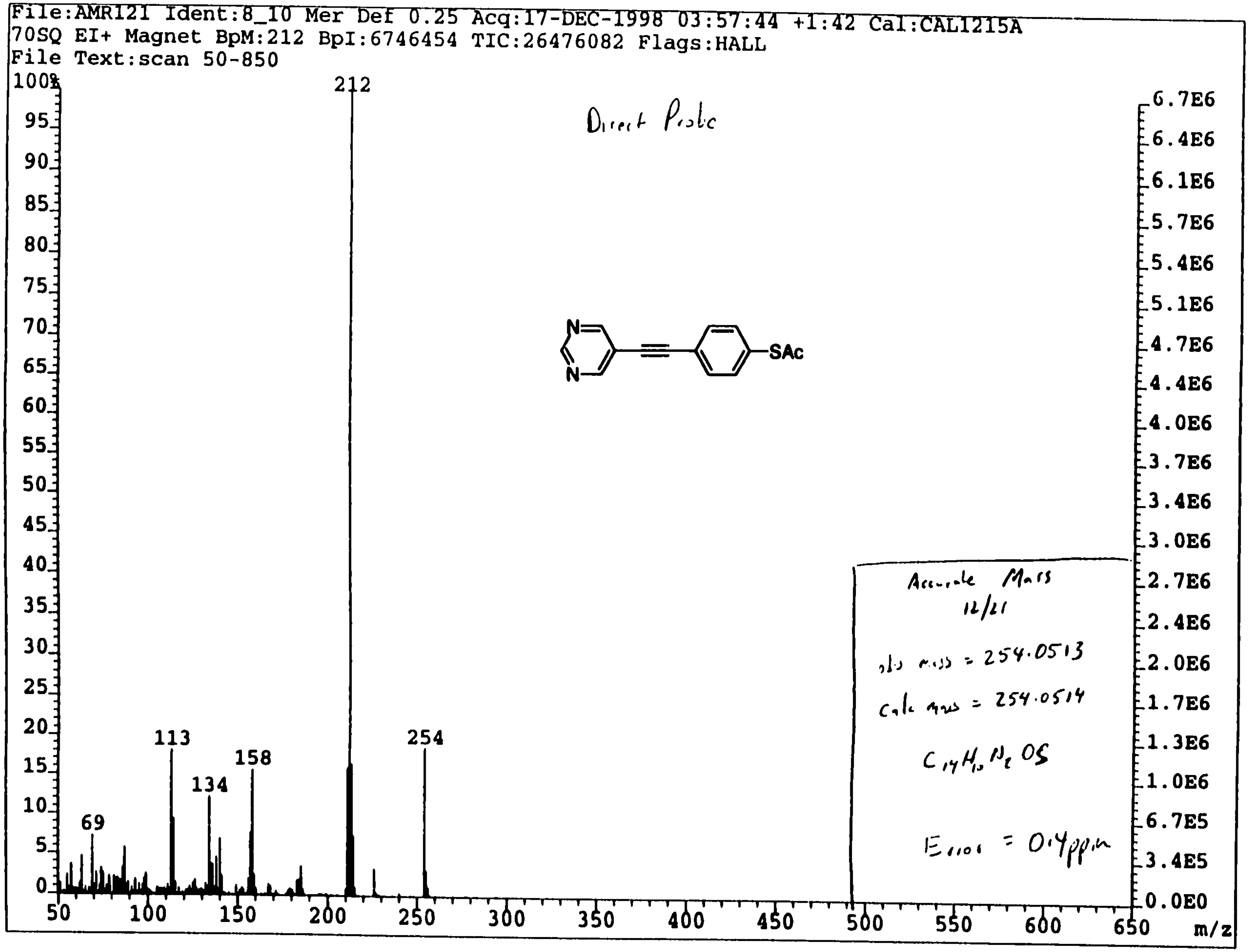
$C_{15}H_{11}NOS$

Error = 0.4 ppm


PERKIN ELMER
24.79
%T
11.78
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
3425.6
3128.2
2369.2
2215.4
1702.6
1656.4
1543.6
1384.6
1117.8
1097.4
943.6
820.5
717.9
615.4
SAc
N
N


SAc
N
N
ppm
1
2
3
4
5
6
7
8
9
10


SAc
N
N
30.499
76.782
77.000
77.418
83.840
95.460
119.588
122.818
129.488
132.224
134.258
156.786
158.573
192.842
ppm
20
40
60
80
100
120
140
160
180
200



File:AMRI21 Ident:8_10 Mer Def 0.25 Acq:17-DEC-1998 03:57:44 +1:42 Cal:CAL1215A
70SQ EI+ Magnet BpM:212 BpI:6746454 TIC:26476082 Flags:HALL
File Text:scan 50-850

Direct Probe

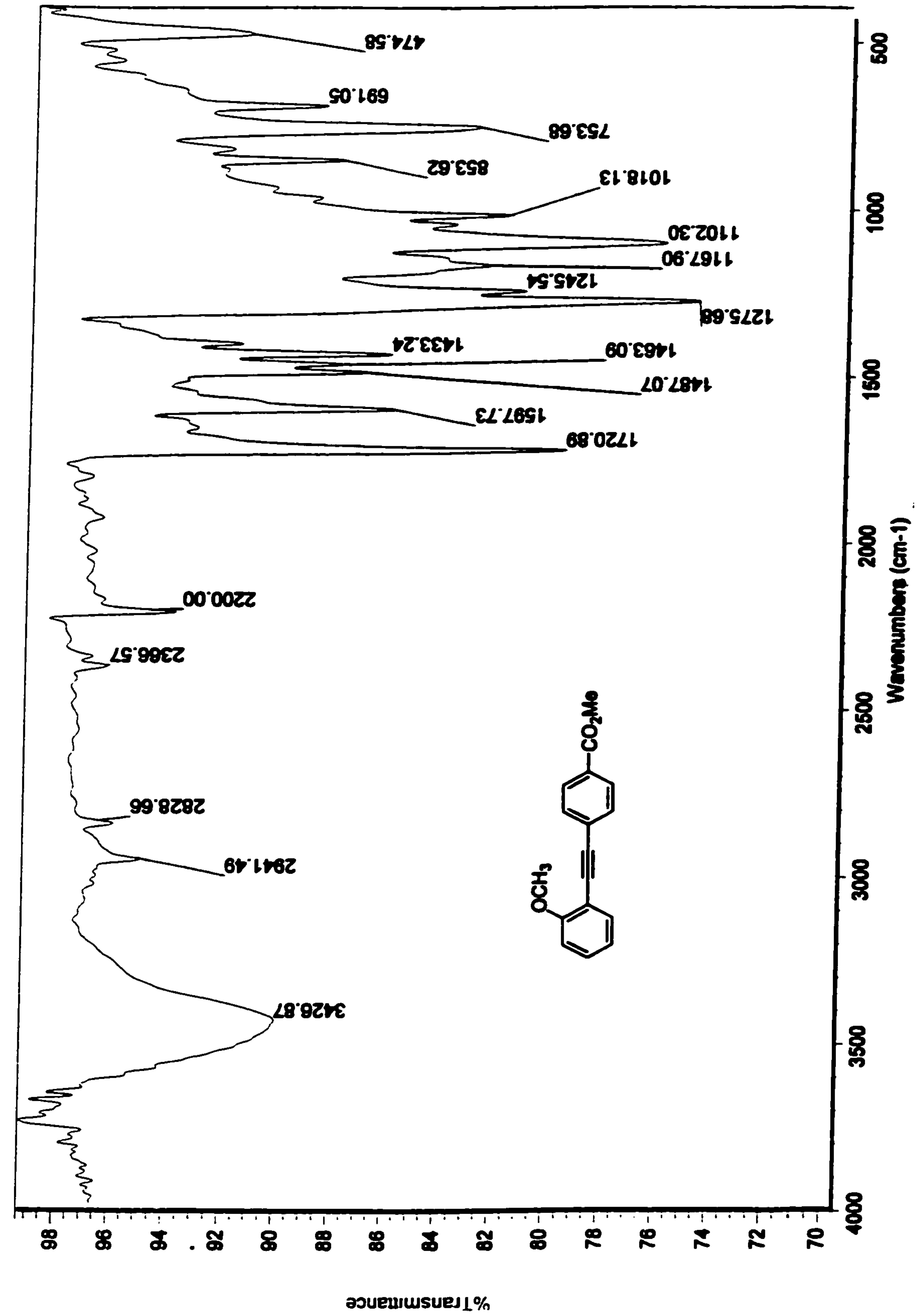
Accurate Mass
12/21

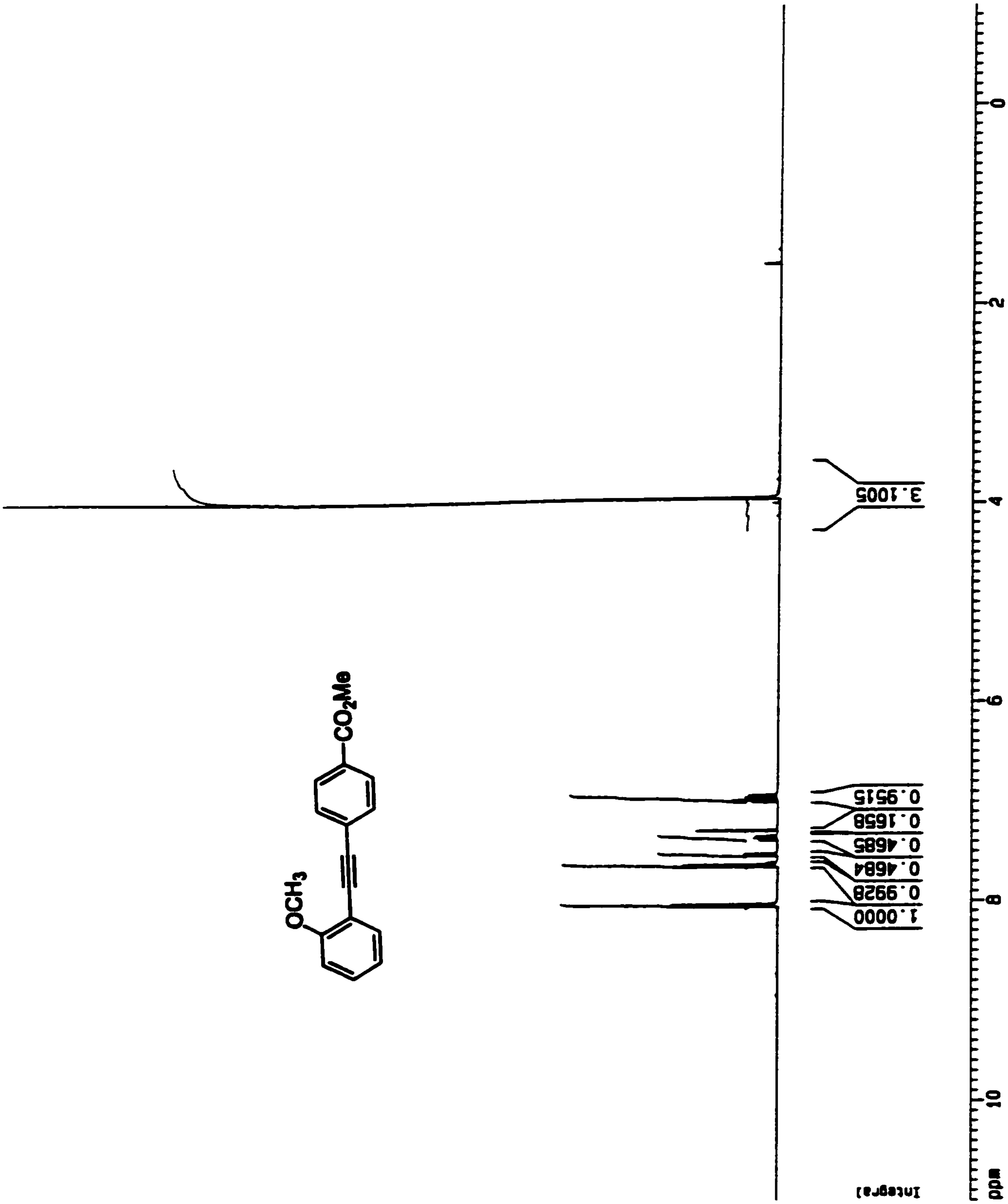
obs mass = 254.0513

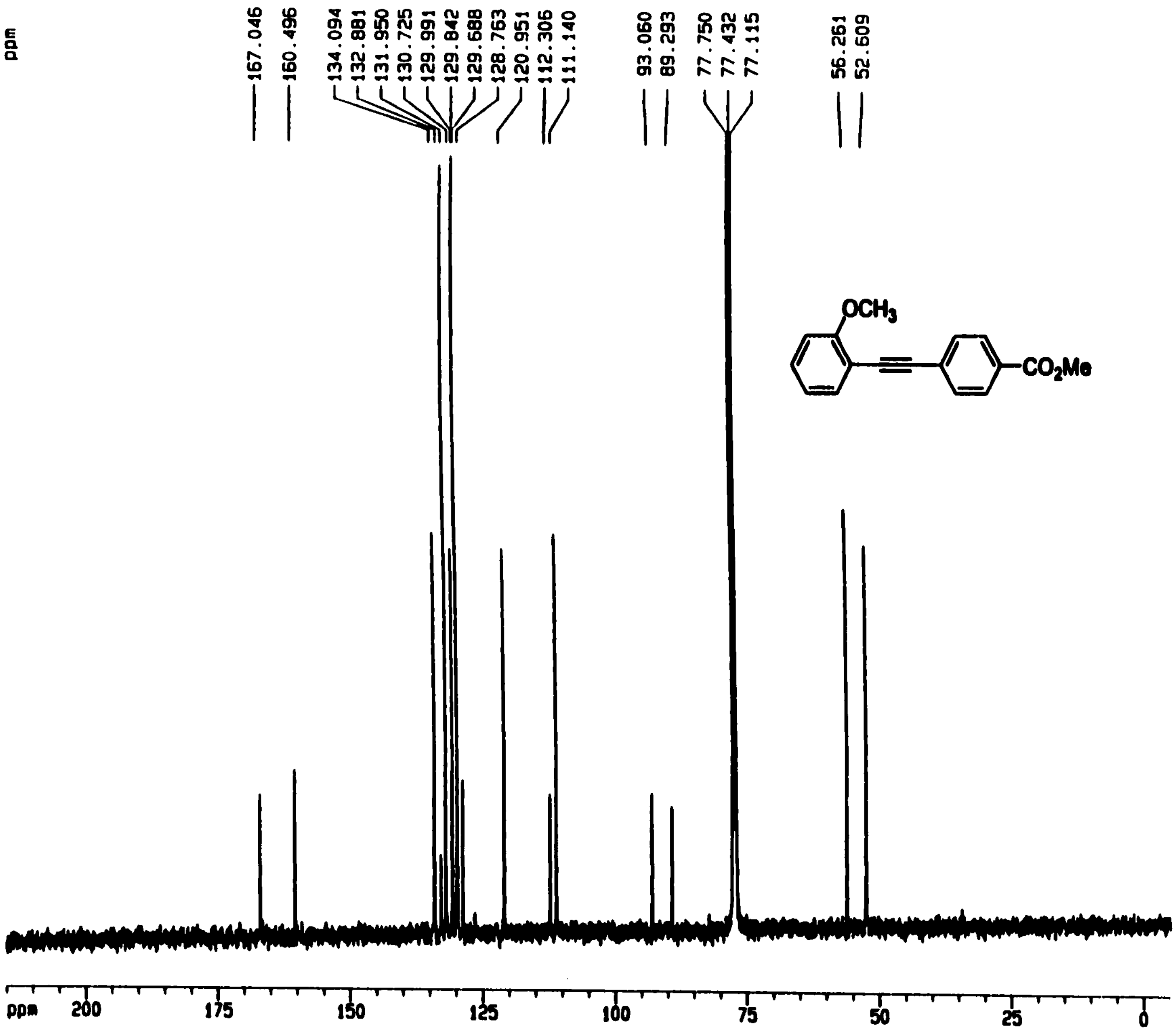
calc mass = 254.0514

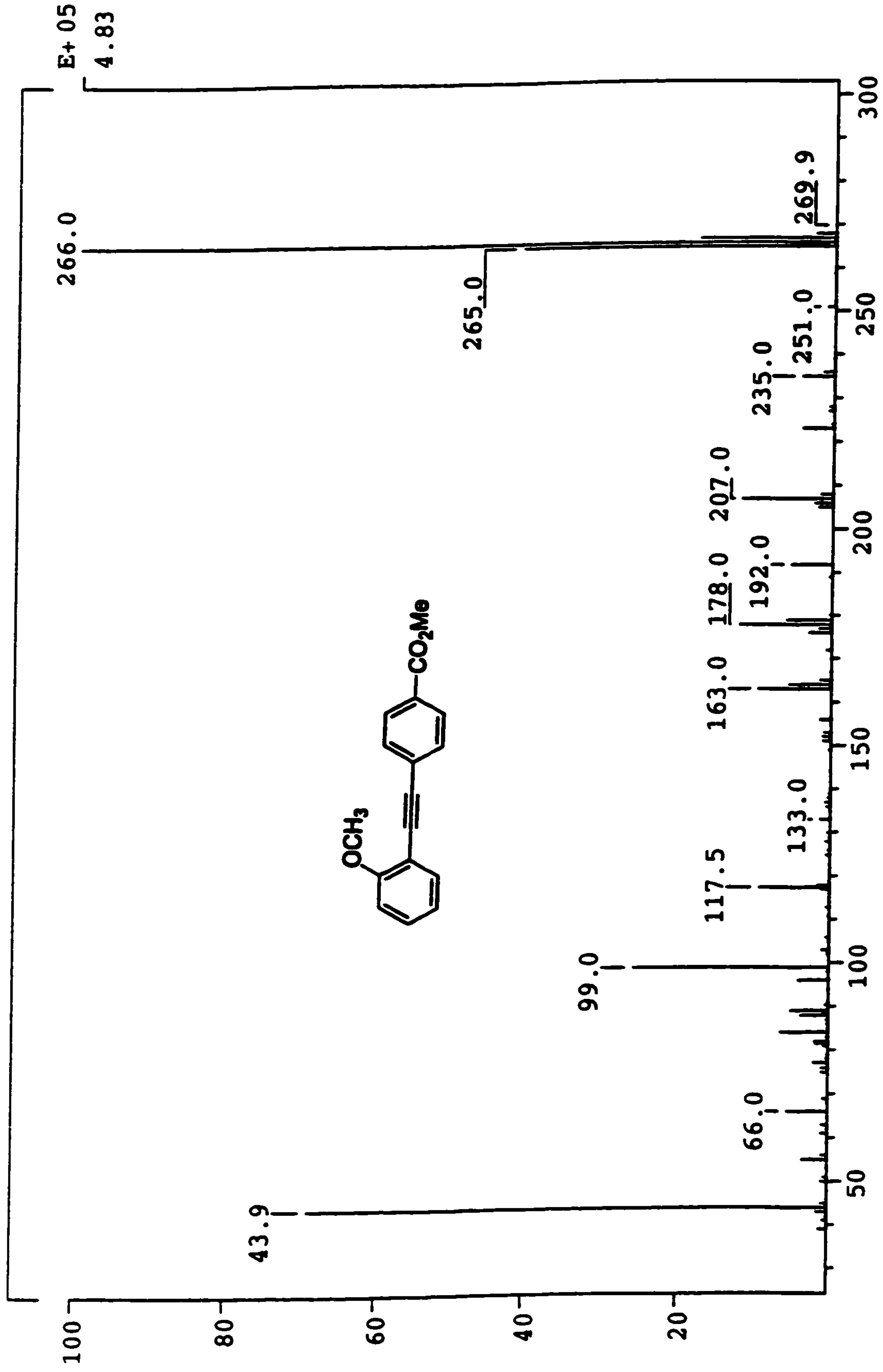
$C_{14}H_{10}N_2OS$

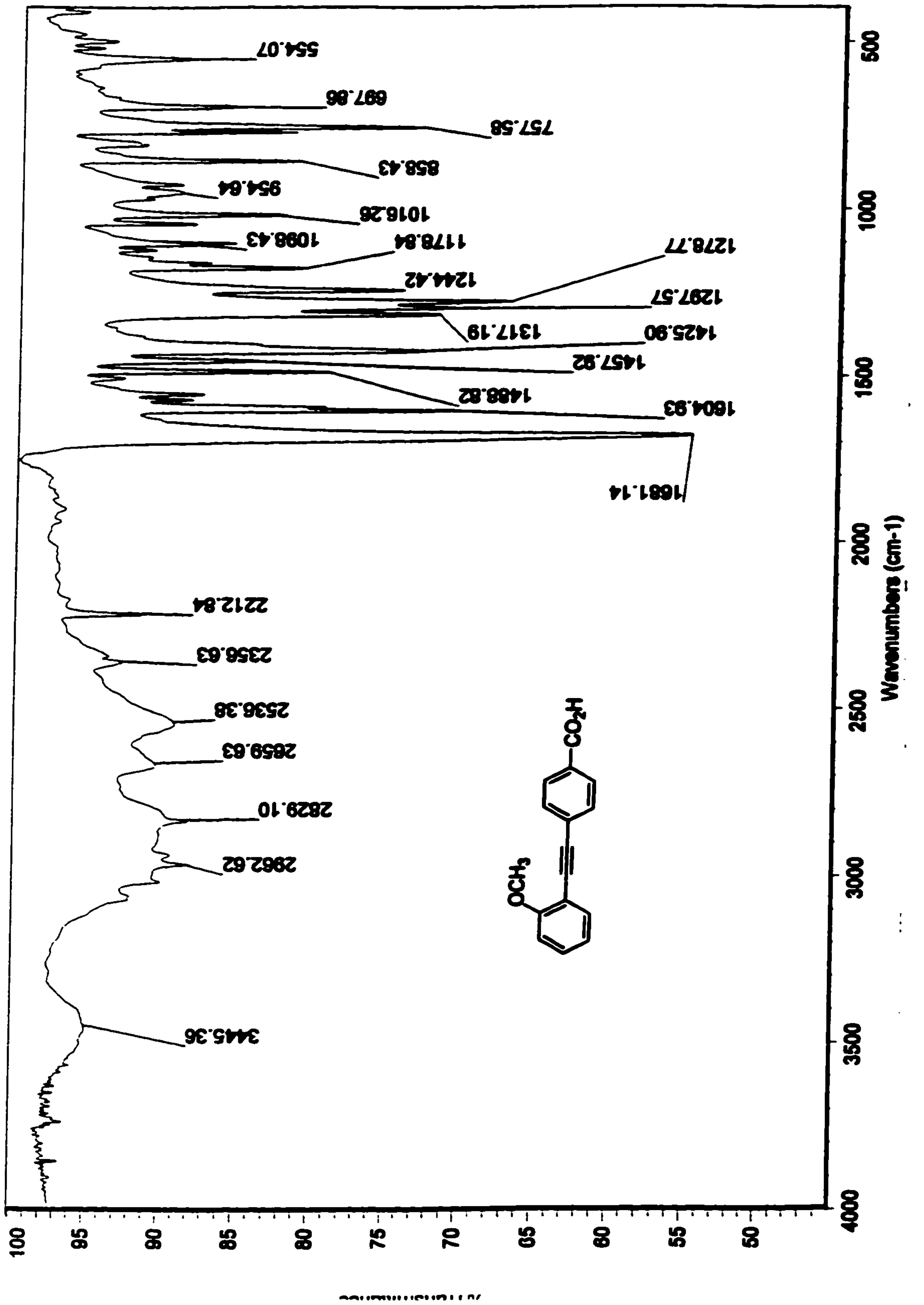
Error = 0.4ppm

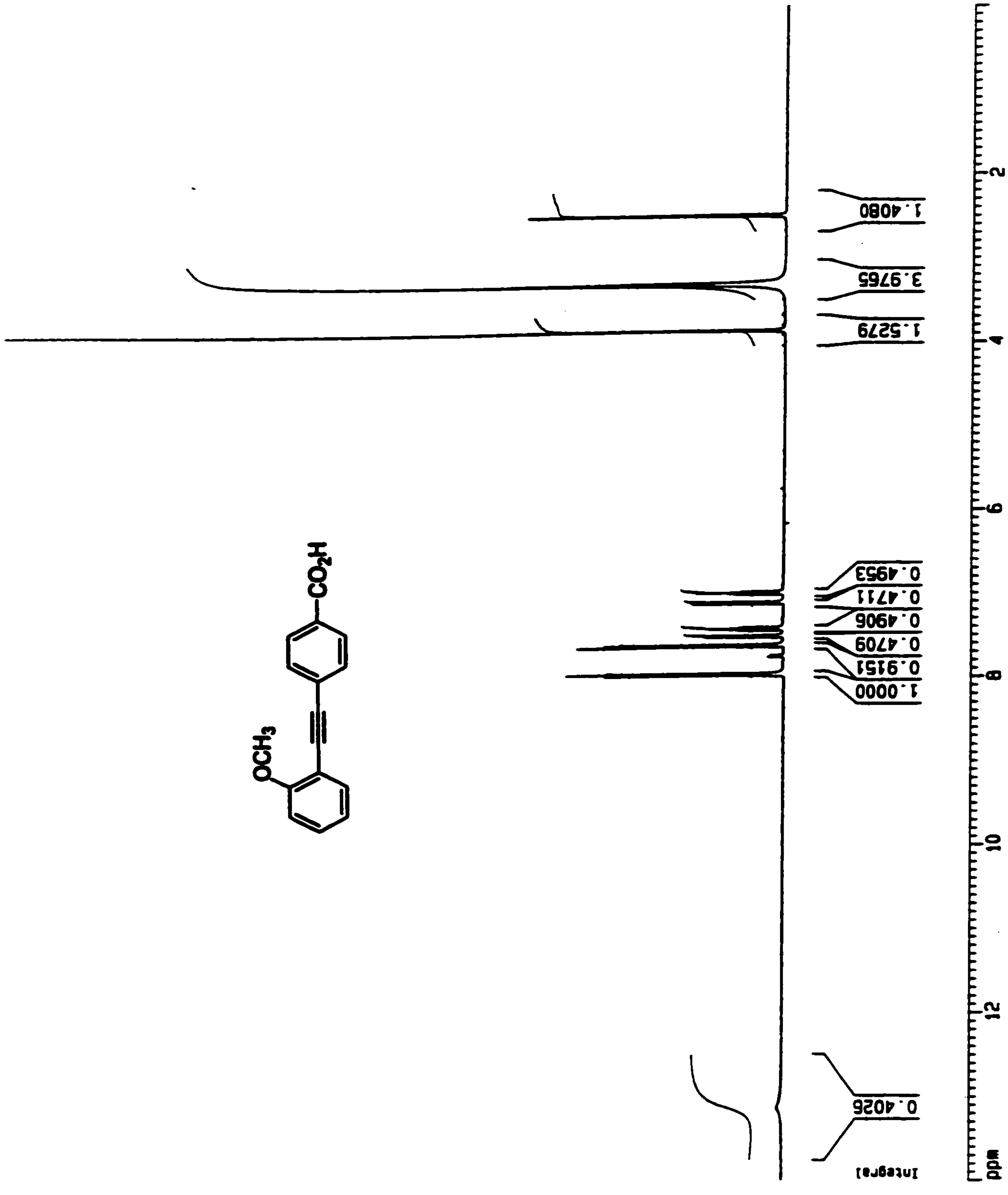

474.58
691.05
753.68
853.62
1018.13
1102.30
1167.90
1245.54
1275.68
1433.24
1463.09
1487.07
1597.73
1720.89
2200.00
2366.57
2828.66
2941.49
3426.87
OCH3
CO2Me
%Transmittance
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500

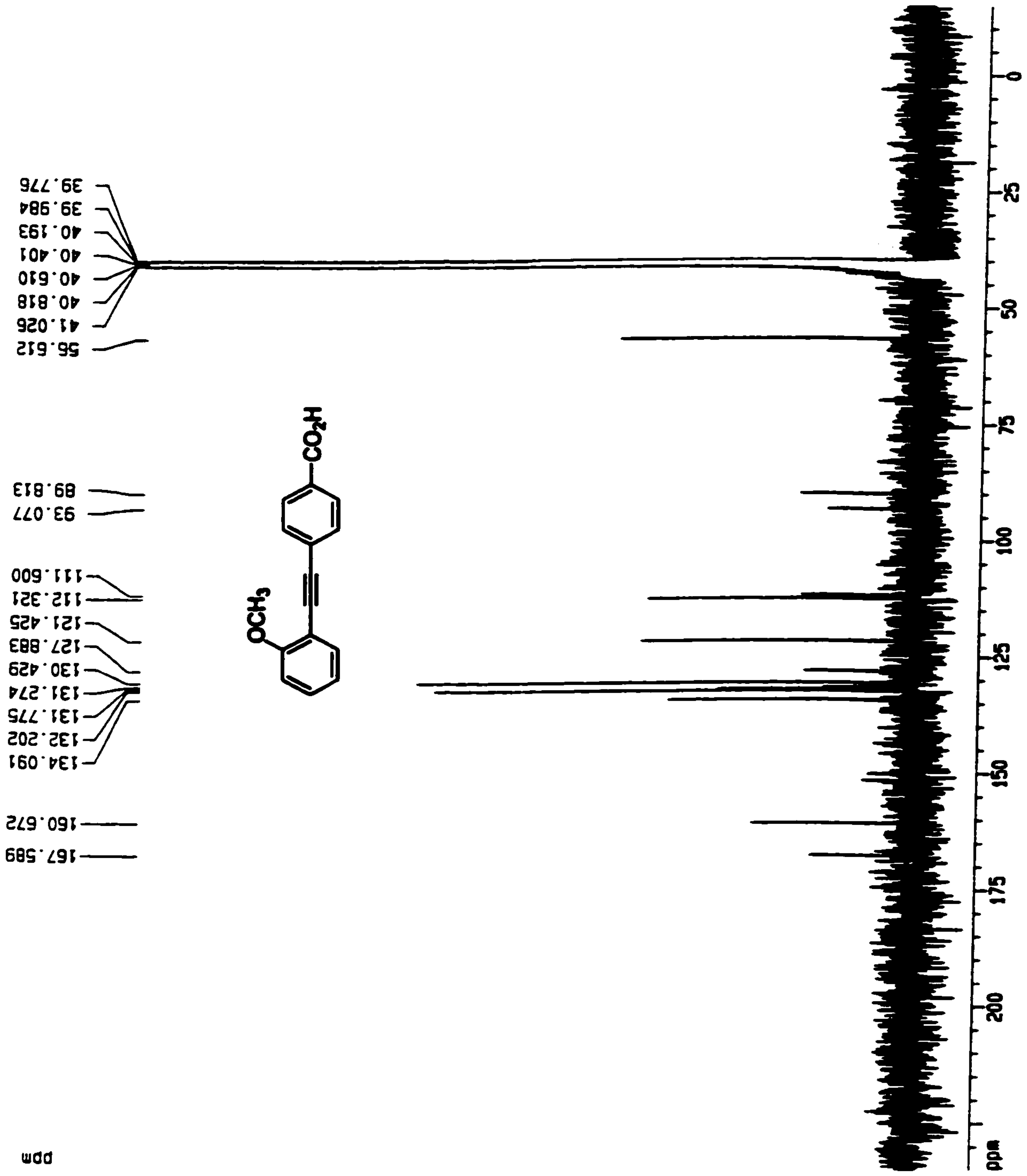

OCH$_3$
CO$_2$Me
3.1005
0.9515
0.1658
0.4685
0.4684
0.9928
1.0000
Integral
ppm
0
2
4
6
8
10

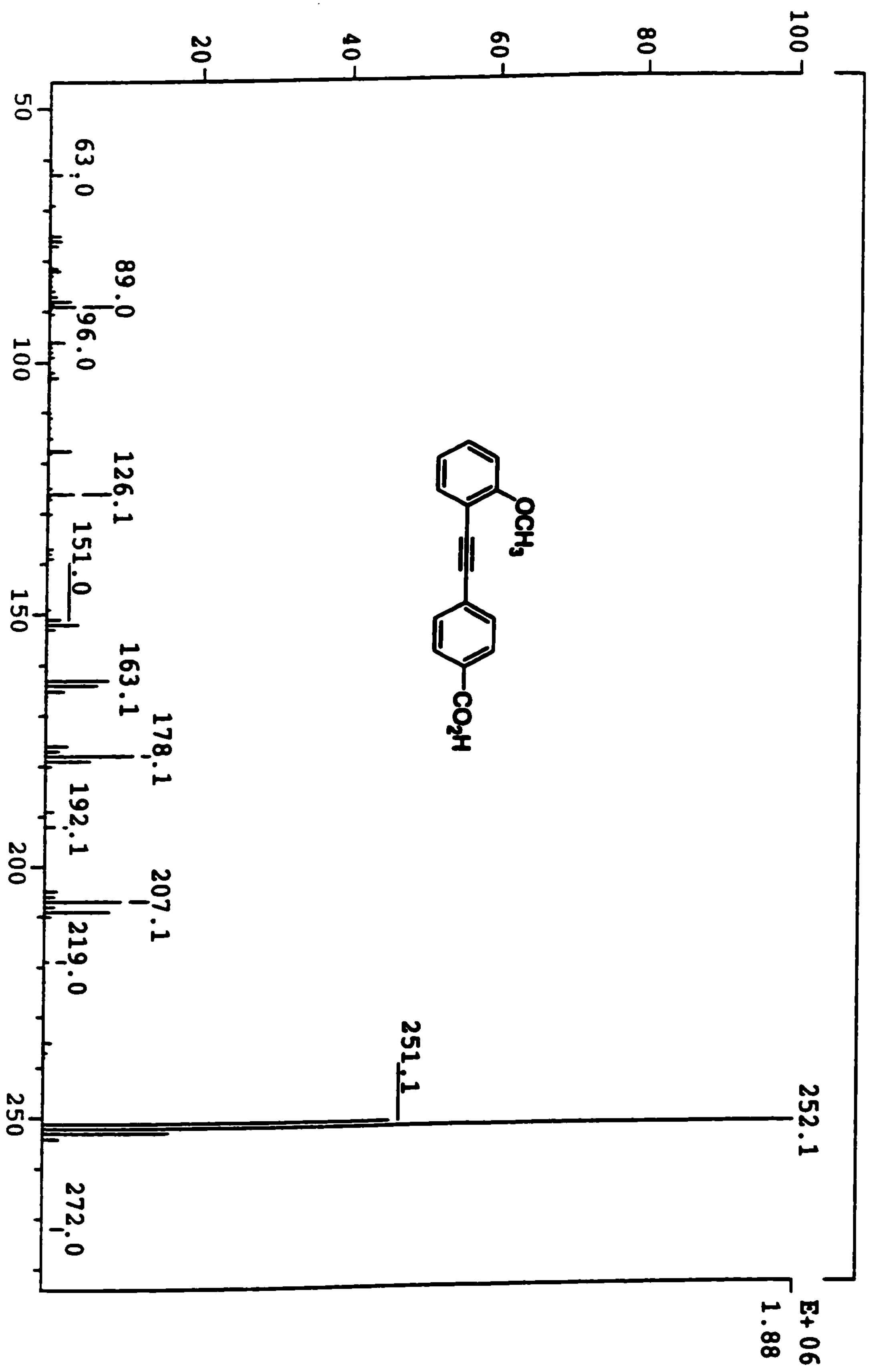

ppm
167.046
160.496
134.094
132.881
131.950
130.725
129.991
129.842
129.688
128.763
120.951
112.306
111.140
93.060
89.293
77.750
77.432
77.115
56.261
52.609
OCH3
CO2Me
ppm
200
175
150
125
100
75
50
25
0


E+ 05
4.83
266.0
265.0
269.9
251.0
235.0
207.0
192.0
178.0
163.0
133.0
117.5
99.0
66.0
43.9
50
100
150
200
250
300
100
80
60
40
20
OCH3
CO2Me


554.07
697.86
757.58
858.43
954.64
1016.26
1098.43
1178.84
1278.77
1244.42
1297.57
1317.19
1425.90
1457.92
1488.82
1604.93
1681.14
2212.84
2356.63
2536.38
2659.63
2829.10
2962.62
3445.36
OCH3
CO2H
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
100
95
90
85
80
75
70
65
60
55
50
%Transmittance


OCH3
CO2H
1.4080
3.9765
1.5279
0.4953
0.4711
0.4906
0.4709
0.9151
1.0000
0.4026
Integral
2
4
6
8
10
12
ppm


39.776
39.984
40.193
40.401
40.610
40.818
41.026
56.612
89.813
93.077
111.600
112.321
121.425
127.883
130.429
131.274
131.775
132.202
134.091
160.672
167.589
ppm
OCH$_3$
CO$_2$H
0
25
50
75
100
125
150
175
200
ppm


100
80
60
40
20
50
100
150
200
250
63.0
89.0
96.0
126.1
151.0
163.1
178.1
192.1
207.1
219.0
251.1
252.1
272.0
E+ 06
1.88
OCH$_3$
CO$_2$H