Supplementary Material
Electrochemical Control Experiments

Five cyclic voltamograms were obtained to ensure that the shift in flavin redox potential was due to specific hydrogen bonding interactions with the colloid bound diaminopyridines. The observed redox comples for each of the following five solutions (all solutions are distilled/Ar purged CH_2Cl_2 with 0.1 M tetra-*n*-butyl ammonium perchlorate as the electrolyte and 0.05 mM ferrocene (Fc) as an internal reference) are summed up in the table:

Solution 1: 0.05 mM **Fl_{ox}**
Solution 2: 0.05 mM **$MeFl_{ox}$**
Solution 3: 0.05 mM **Fl_{ox}**, 0.3 mM **DAP-Au** (2.5 mM effective diaminopyridine concentration)
Solution 4: 0.05 mM **Fl_{ox}**, 0.3 mM **C8-Au**
Solution 5: 0.05 mM **$MeFl_{ox}$**, 0.3 mM **DAP-Au** (2.5 mM effective diaminopyridine concentration)

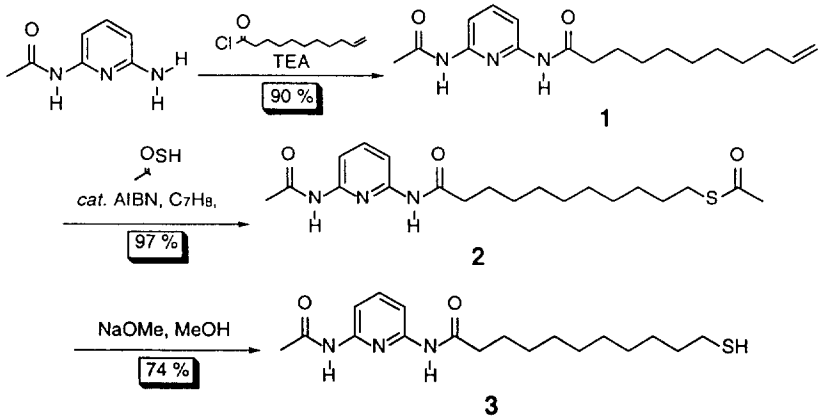
Table of redox potentials

Solution	$E_{1/2}$(mV) Fc	$E_{1/2}$(mV) flavin	$E_{1/2}$(mV) flavin, Fc=0
1	320	-978	-1298
2	282	-1056	-1338
3	289	-945	-1243
4	292	-994	-1286
5	285	-1048	-1333

X-Ray Photoelectron Spectroscopy(XPS)

XPS spectra were recorded by drop casting thin films of the colloid from CH_2Cl_2 solution on to Indium-Tin Oxide coated glass slides. Spectra were then recorded using a Physical Electronics model 5100 ESCA spectrometer, exciting with Mg Kα X-rays.

Experimental Section



Synthetic Scheme

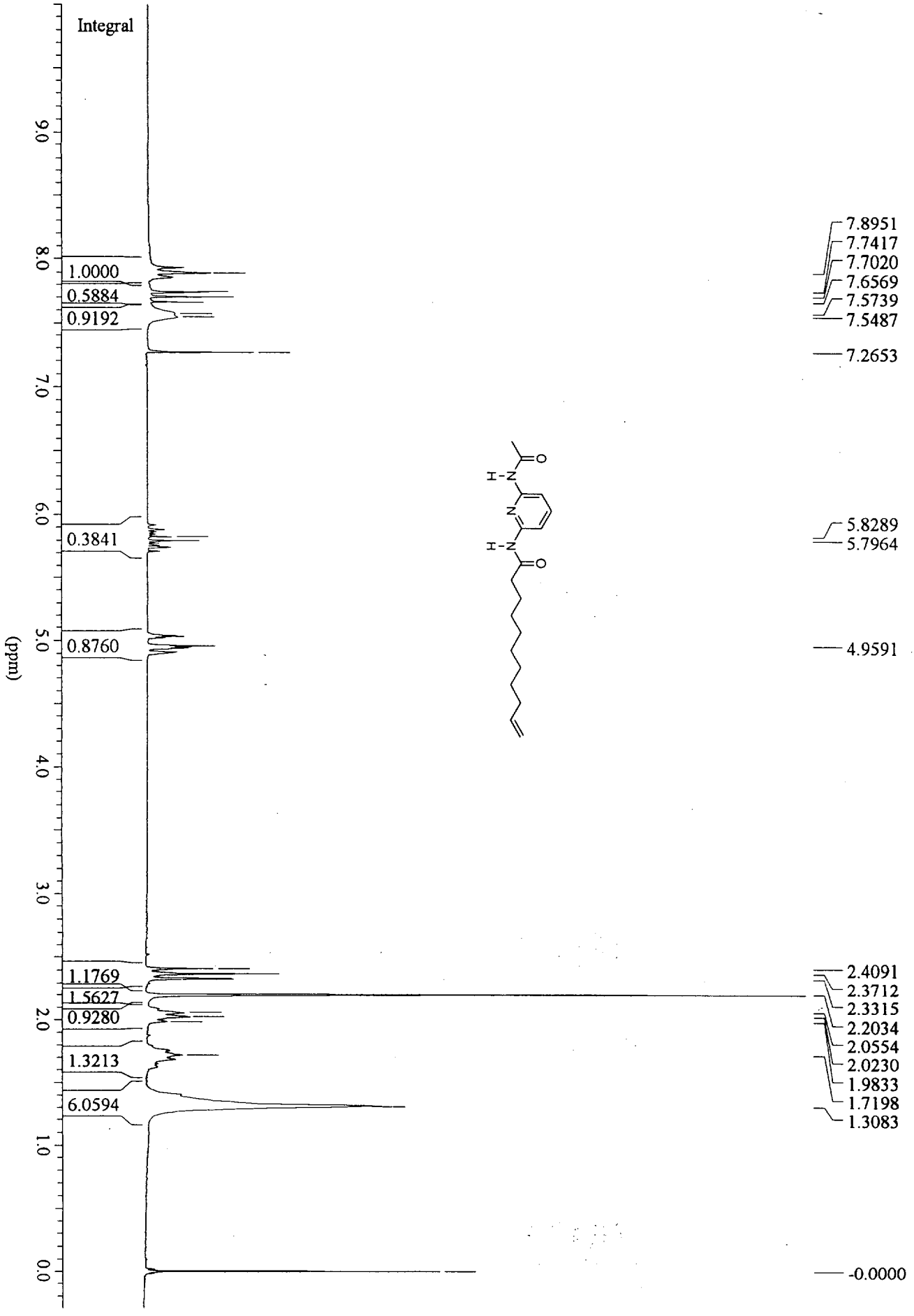
General. 2-amino-6-acetylamidopyridine (Bernstein, J., *et. al. J. Am. Chem. Soc.*, **1947**, *69*, 1151), flavin and N(3)-methyl flavin (Breinlinger, E., *et. al. J. Am. Chem. Soc.*, **1995**, *117*, 5379.), and octanethiol SAM on colloidal gold (Brust, M., *et. al. J. Chem. Soc. Chem. Com.*, **1994**, 801) were prepared according to literature methods. Toluene and CH_2Cl_2 were distilled from CaH_2 under argon. All reactions were carried out in oven or flame dried glassware under an atmosphere of argon. ^1H NMR spectra were recorded in $CDCl_3$ (purchased from Cambridge Isotope Labs, Inc.) at 200 MHz and referenced internally to TMS at 0.0 ppm. NMR spectra involving colloids were taken in $CDCl_3$ that had been stirred over K_2CO_3 for at least 24 hours prior to use since it was found that residual acid caused rapid decomposition of colloids. All reagents and other solvents were used as received from commercial sources. NMR and electrochemical titrations were run as previously described. (Breinlinger, E.; Niemz, A.; Rotello, V. *J. Am. Chem. Soc.*, **1995**, *117*, 5379.)

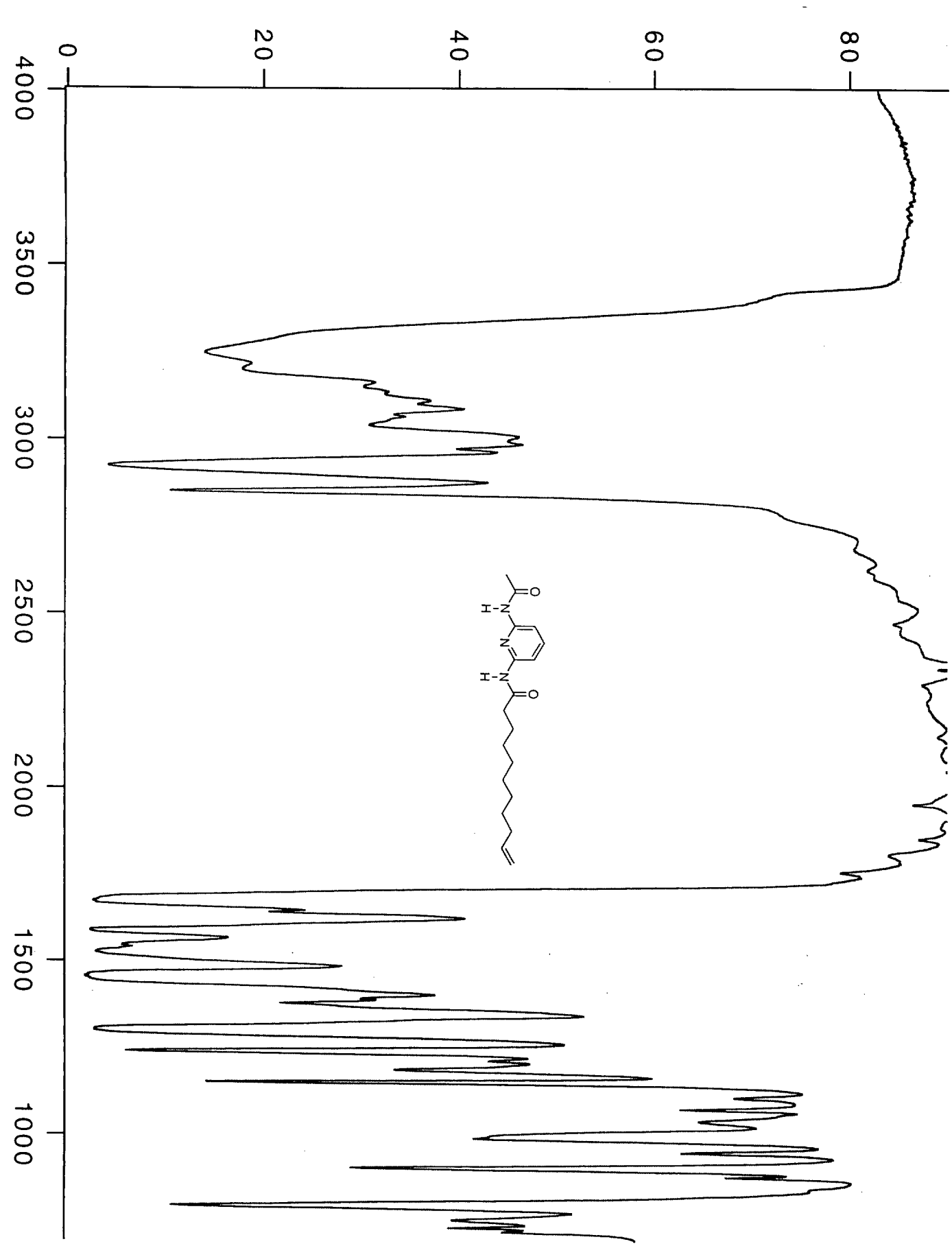
Diacyldiaminopyridine 1. In a 100 mL round bottom flask, monoacyldiaminopyridine (700 mg, 4.63 mmol) and triethylamine (470 mg, 0.7 mL, 4.63 mmol) are dissolved in 40 mL CH_2Cl_2. 10-Undecenoyl chloride (938 mg, 1.0 mL, 4.63 mmol) was then added dropwise, and the turbid solution stirred overnight. The reaction was transferred to a separatory funnel, washed once each with a saturated aqueous $NaHCO_3$ and NaCl solutions, and dried over $MgSO_4$. Solvent removal yielded a yellow solid which was chromatographed (SiO_2; 1:1 ethyl acetate : hexanes) to give the product as a white solid, 1.32 g (90% yield) ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.89 (m, 2H); 7.70 (t, 1H, J = 7.96 Hz); 7.52 (bs, 2H); 5.81 (m, 1H); 4.96 (m, 2H); 2.37 (t, 2H, J = 7.96 Hz); 2.01 (m, 2H); 1.72 (m, 2H); 1.31 (m, 12H). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max} 3255, 3014, 2922, 2845, 1672, 1581, 1514, 1452, 1295, 1247, 1152, 985, 904, 794 cm^{-1}. Anal. Calcd. for $C_{18}H_{27}N_3O_2$: C, 68.11; H, 8.57. Found: C, 68.16; H, 8.61.

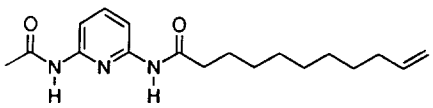
Thiolacetate 2. In a 50 mL round bottom flask, **1** (500 mg, 1.6 mmol), thiolacetic acid (250 mg, 0.25 mL, 3.2 mmol), and AIBN (50 mg) were dissolved in 15 mL toluene. Argon was bubbled through the solution for 15 minutes, and the reaction was then refluxed for 90 minutes, giving a yellow solution. The reaction was cooled, washed once each with a saturated aqueous $NaHCO_3$ and NaCl solutions, and dried over $MgSO_4$. Solvent removal yielded a yellow solid which was chromatographed (SiO_2; 1:1 ethyl acetate:hexanes) to give the product as a white solid, 600 g (97% yield) ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.89 (m, 2H); 7.70 (t, 1H, J = 7.94 Hz); 7.54 (bs, 2H); 2.86 (t, 2H, J = 6.86 Hz); 2.38 (t/s, 5H); 2.20 (s, 3H); 1.60 (m, 4H); 1.28 (m, 12H). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max} 3295, 2924, 2856, 1680, 1587, 1509, 1450, 1289, 1245, 1147, 948, 791, 148, 690 cm^{-1}. Anal. Calcd. for $C_{20}H_{31}N_3O_3S$: C, 61.04; H, 7.94. Found: C, 60.96; H, 7.84.

Thiol 3. In a 25 mL round bottom flask, **2** (170 mg, 0.43 mmol) is dissolved in 10 mL MeOH. NaOMe (0.75 mL of a 30% weight solution in MeOH, 4.3 mmol) is then added and argon is bubbled through the solution for 60 minutes before the reaction is stirred overnight. The colorless solution is quenched by the dropwise addition of an excess of a saturated aqueous NH_4Cl solution, and the methanol removed on the rotovap. The residue is dissolved in EtOAc/H_20, the organic portion washed twice with water, once with a saturated aqueous NaCl solution, and dried over $MgSO_4$. Solvent removal yielded a yellow solid which was chromatographed (SiO_2; 1:9 ethyl acetate:CH_2Cl_2) to give the product as a white solid, 600 g (97% yield) ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.89 (m, 2H); 7.70 (t, 1H, J = 7.93 Hz); 7.53 (bs, 2H); 2.52 (apr. q, 2H, J = 7.22 Hz); 2.34 (t, 2H, J = 6.86 Hz); 2.20 (s, 3H); 1.65 (m, 4H); 1.29 (m, 12H). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max} 3285, 2924, 2851, 1682, 1588, 1510, 1449, 1297 cm^{-1}. Anal. Calcd. for $C_{18}H_{29}N_3O_2S$: C, 61.50; H, 8.32. Found: C, 61.43; H, 8.50.

DAP-Au. In a 25 mL round bottom flask, octane thiol covered colloidal gold (105 mg, assuming octane thiol is *ca.* 30 % of the weight then for octane thiol: 31.5 mg, 0.215 mmol) and **3** (19 mg, 0.054 mmol) were dissolved in 10 mL CH_2Cl_2. Argon is bubbled thought the solution for 20 minutes, and the dark brown solution is then stirred for 24 hours under argon. Solvent removal yielded a dark brown solid which was washed extensively with EtOH and redissolved in CH_2Cl_2. Three cycles of solvent removal and ethanol washing gave 75 mg of **DAP-Au** free of unbound thiols (determined by NMR spectroscopy- lack of sharp resonances). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.99 (vbs), 7.87 & 7.60 (bs, 1.48 H), 2.34 & 2.13 & 1.25 & 0.881 (mbs, 71 H). IR (thin film from CH_2Cl_2 on NaCl plate) ν_{max} 3294, 2923, 2856, 1692, 1579, 1517, 1450, 1296, 1234, 1162, 1085, 1023, 801, 724 cm^{-1}.







MICROANALYSIS LABORATORY

boala@chem.umass.edu
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Telephone: (413)545-0045

P.O. _____

A.) Fill in items # 1 - 15.
B.) This form must be signed by department head or advisor.
C.) A **minimum** of 5 mg. of sample per element is required.
D.) Sample **must** be neatly **labeled** and **numbered.**
E.) **SUBMITEE MUST PICK UP SAMPLE WHEN DATA IS COMPLETE**

1.) Sa # ABL-54 2.) Date 28 27 jan 99 3.) Submitted by Andy Boal 4.) Dept chem

5.) M.P. or B.P. _____ 6.) Authorized by Y. ROTELLO 7.) Bldg/Rm# LGRT/303

8.) Analysis requested C,H 9.) Univ or College UMass

10.) Tele.# 5-4865 11.) Single ✓ Duplicate _____

12.) Compound formula $C_{18}H_{27}N_3O_2$ 13.) Theoretical % of ea. element C: 68.11% H: 8.57%

14.) Properties — (Air, Moist, or Tem. Sens.) 15.) * Further notes or other problems with sa.

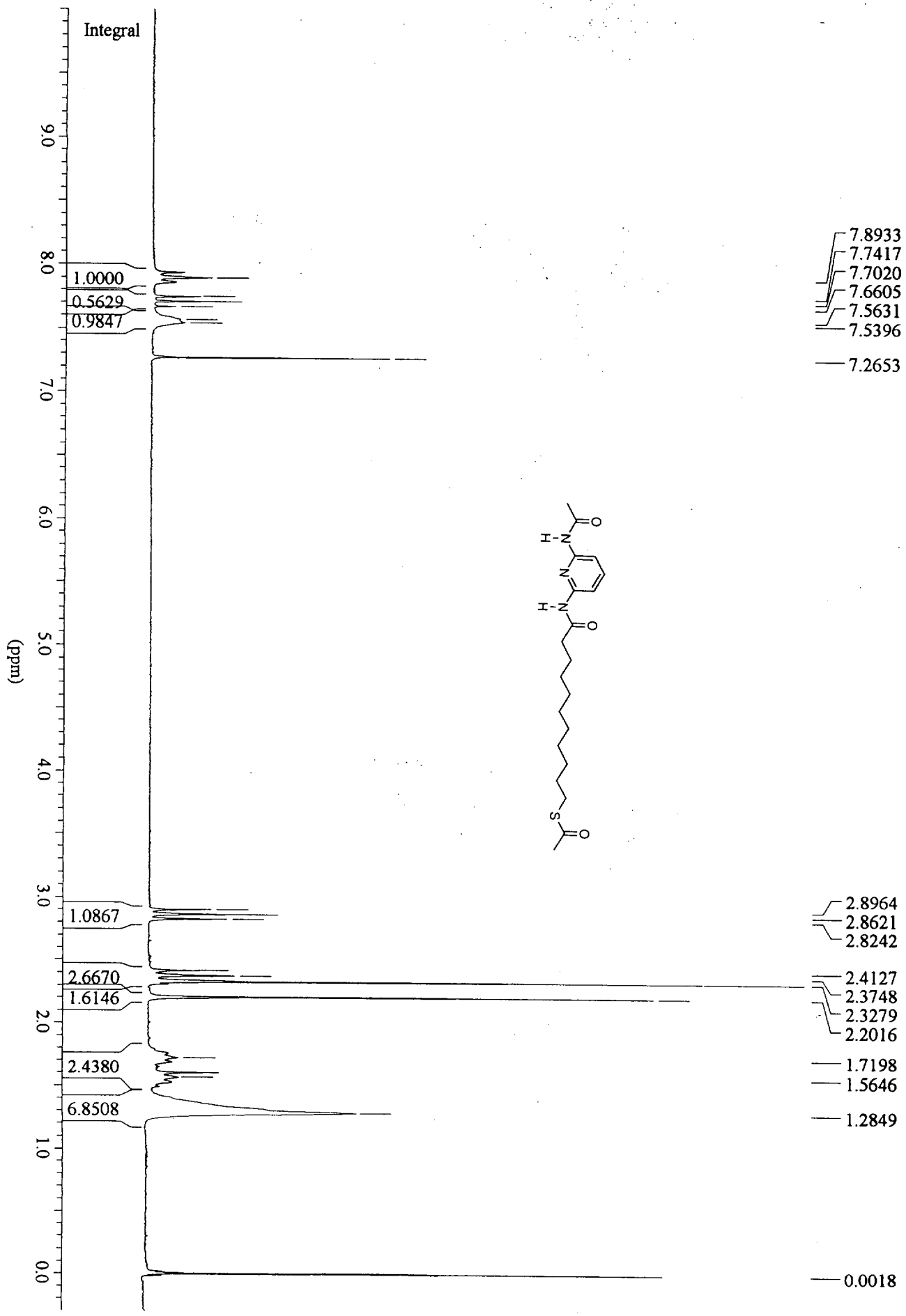
* Describe: _____

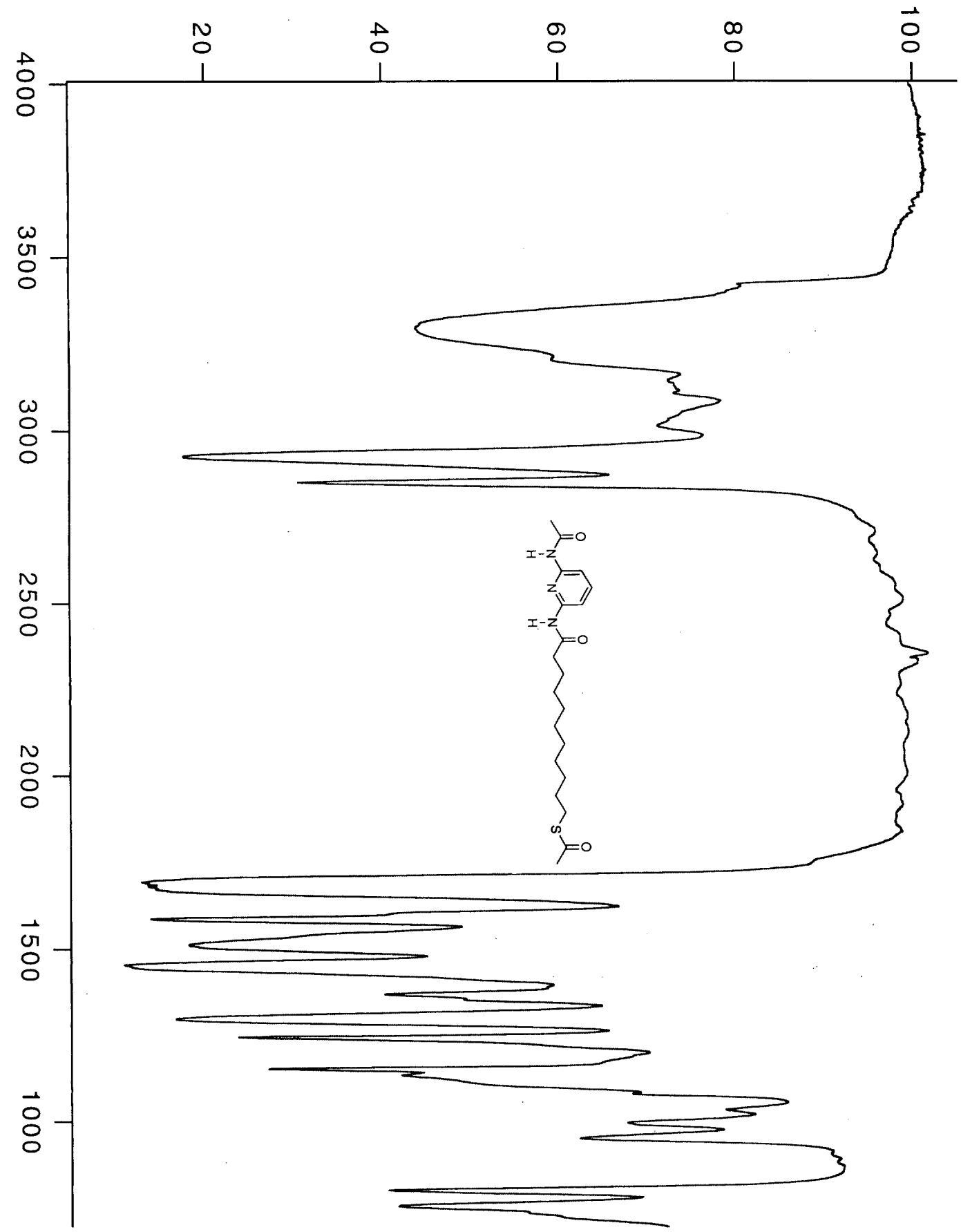
DO NOT WRITE IN BOX BELOW

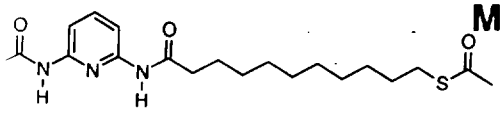
Routine analyses as weight %		*Other analyses as specified below*	
Carbon	68.16	Metal [ ]	
Hydrogen	8.61	Water (by Karl Fischer)	
Nitrogen		Sample Drying	
Halogen [ ]		Special Weighing	
Sulfur		Other [ ]	
Phosphorus			
Ash		Total $	

Comments _____

Date Completed 1/28/99 *Signature, Microanalyst* _____







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D.) Sample **must** be neatly **labeled** and **numbered.**
E.) **SUBMITEE MUST PICK UP SAMPLE WHEN DATA IS COMPLETE**

1.) Sa # ABI-62 2.) Date 2/1/99 3.) Submitted by Andy Boal 4.) Dept chem

5.) M.P. or B.P. _____ 6.) Authorized by V. ROTELLO 7.) Bldg/Rm# LGRT1303

8.) Analysis requested C, H 9.) Univ or College UMass

10.) Tele.# 5-4865 11.) Single ✓ Duplicate _____

12.) Compound formula $C_{20}H_{31}N_3O_3S$ 13.) Theoretical % of ea. element C: 61.04% H: 7.94%

14.) Properties — (Air, Moist, or Tem. Sens.) 15.) * Further notes or other problems with sa.

* Describe: _____

DO NOT WRITE IN BOX BELOW

Routine analyses as weight %

Carbon 60.96
Hydrogen 7.84
Nitrogen _____
Halogen _____
Sulfur _____
Phosphorus _____
Ash _____

Other analyses as specified below

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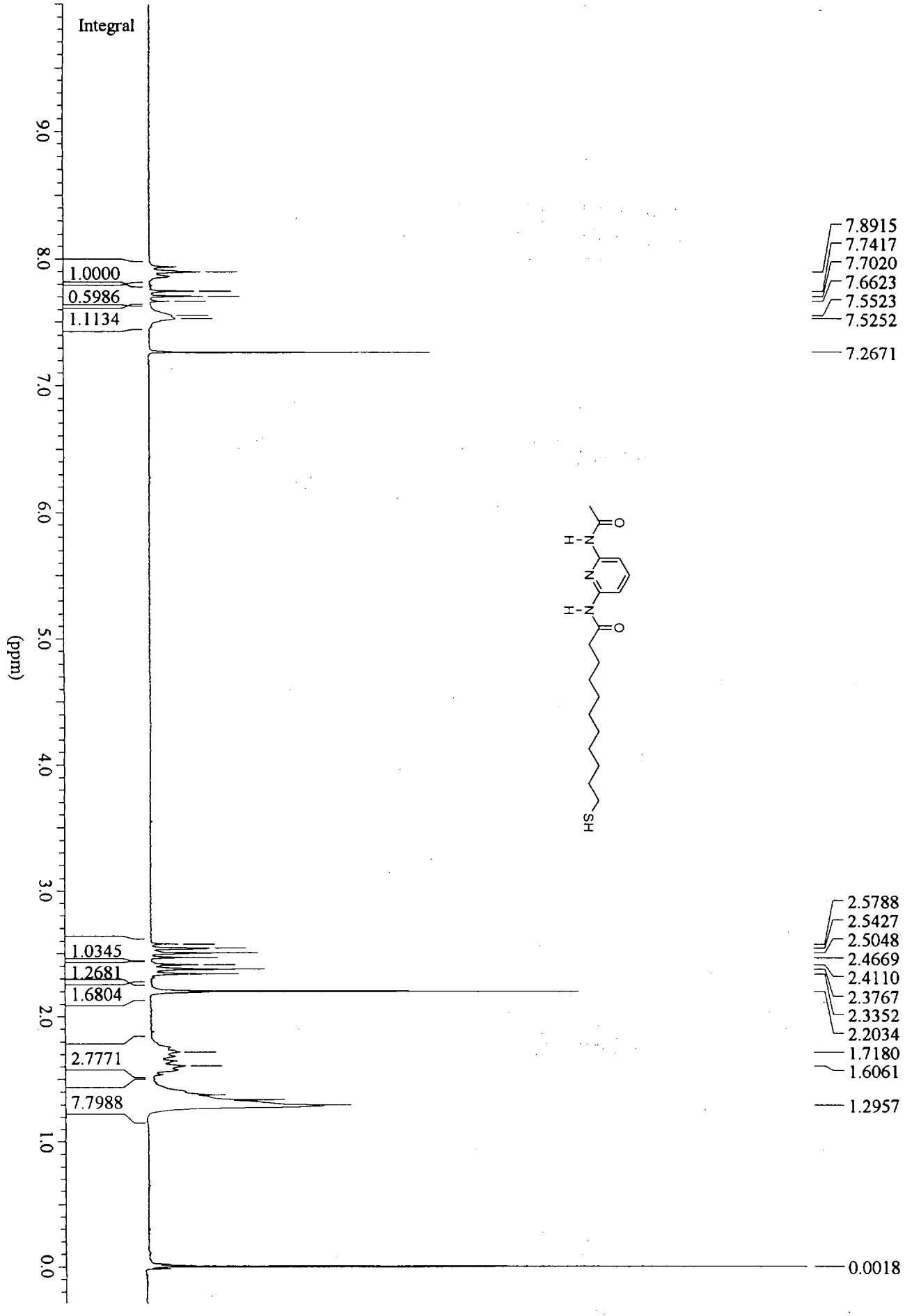
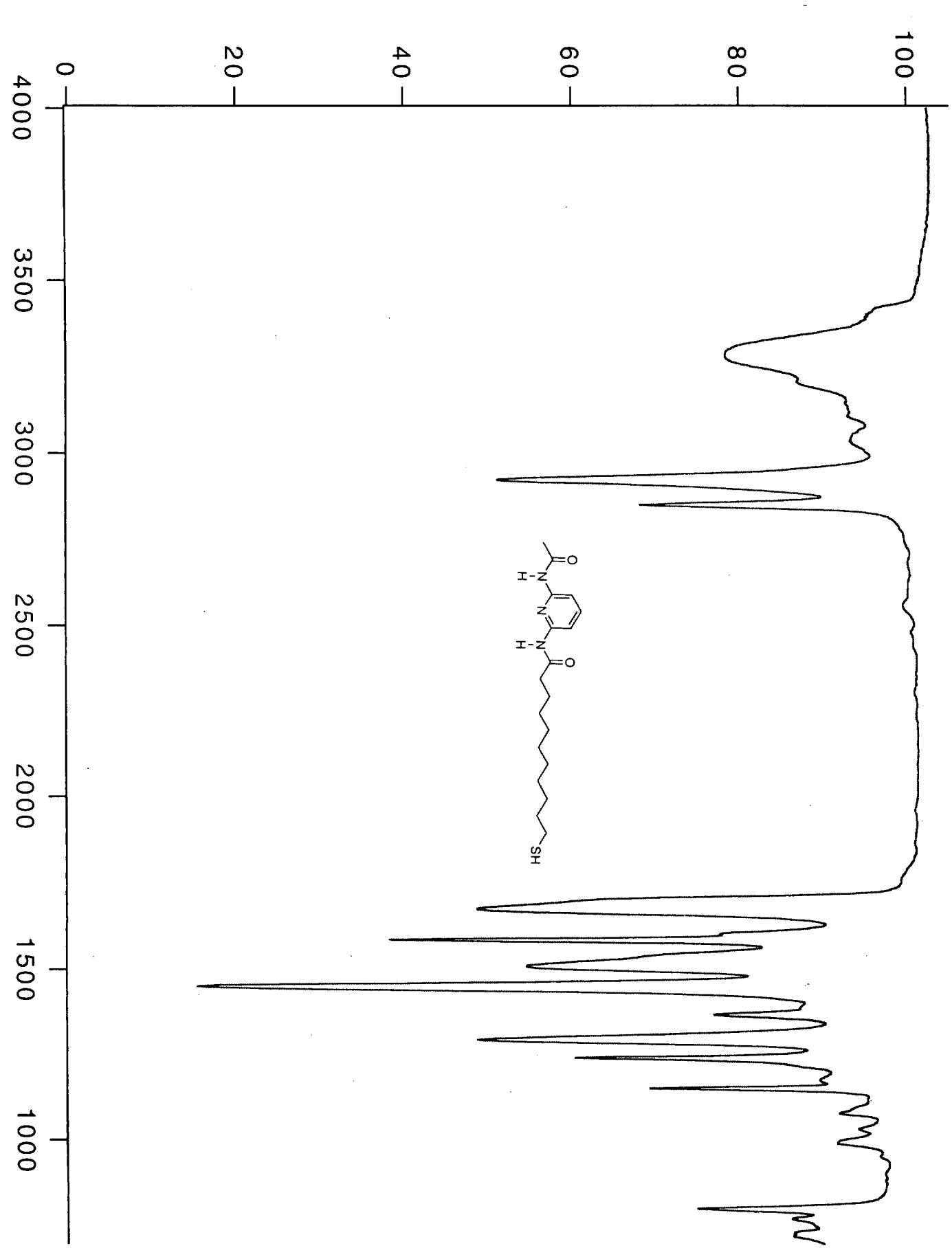
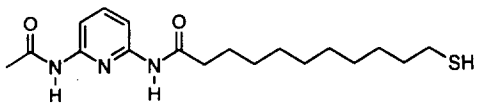
Sample Drying _____
Special Weighing _____
Other _____
Total $ _____

Comments Pan

Date Completed 2/2/99 *Signature Microanalyst* [signature]







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D.) Sample **must** be neatly **labeled** and **numbered.**
E.) **SUBMITEE MUST PICK UP SAMPLE WHEN DATA IS COMPLETE**

1.) Sa # ABI-116 2.) Date 28-27 jan 99 3.) Submitted by Andy Boal 4.) Dept chem

5.) M.P. or B.P. _____ 6.) Authorized by V. ROTELLO 7.) Bldg/Rm# LGRT/303

8.) Analysis requested C,H 9.) Univ or College UMass

10.) Tele.# 5-4865 11.) Single ✓ Duplicate _____

12.) Compound formula $C_{18}H_{29}N_3O_2S$ 13.) Theoretical % of ea. element C: 61.50% H: 8.32%

14.) Properties — (Air, Moist, or Tem. Sens.) 15.) * Further notes or other problems with sa.

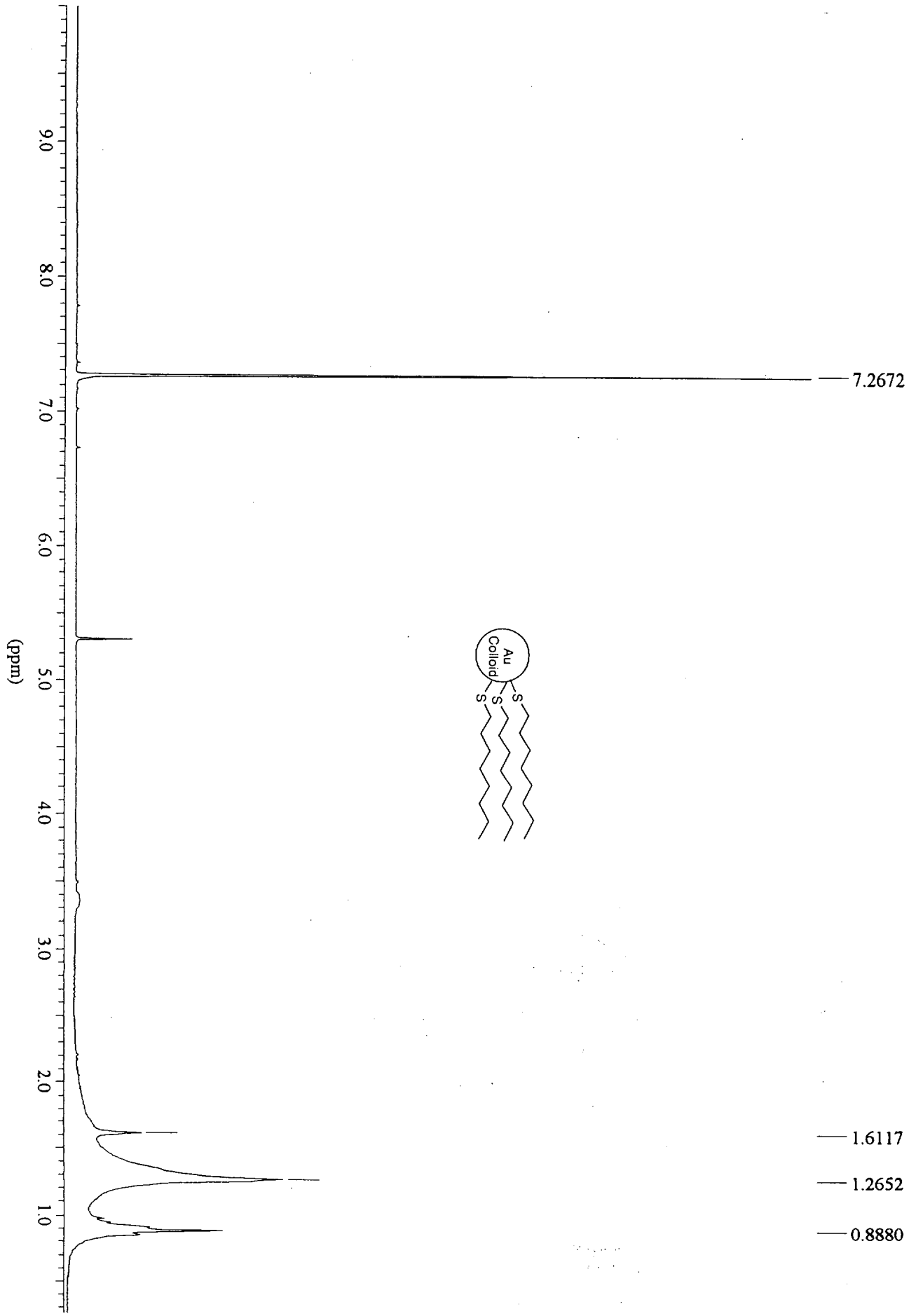
* Describe: _____

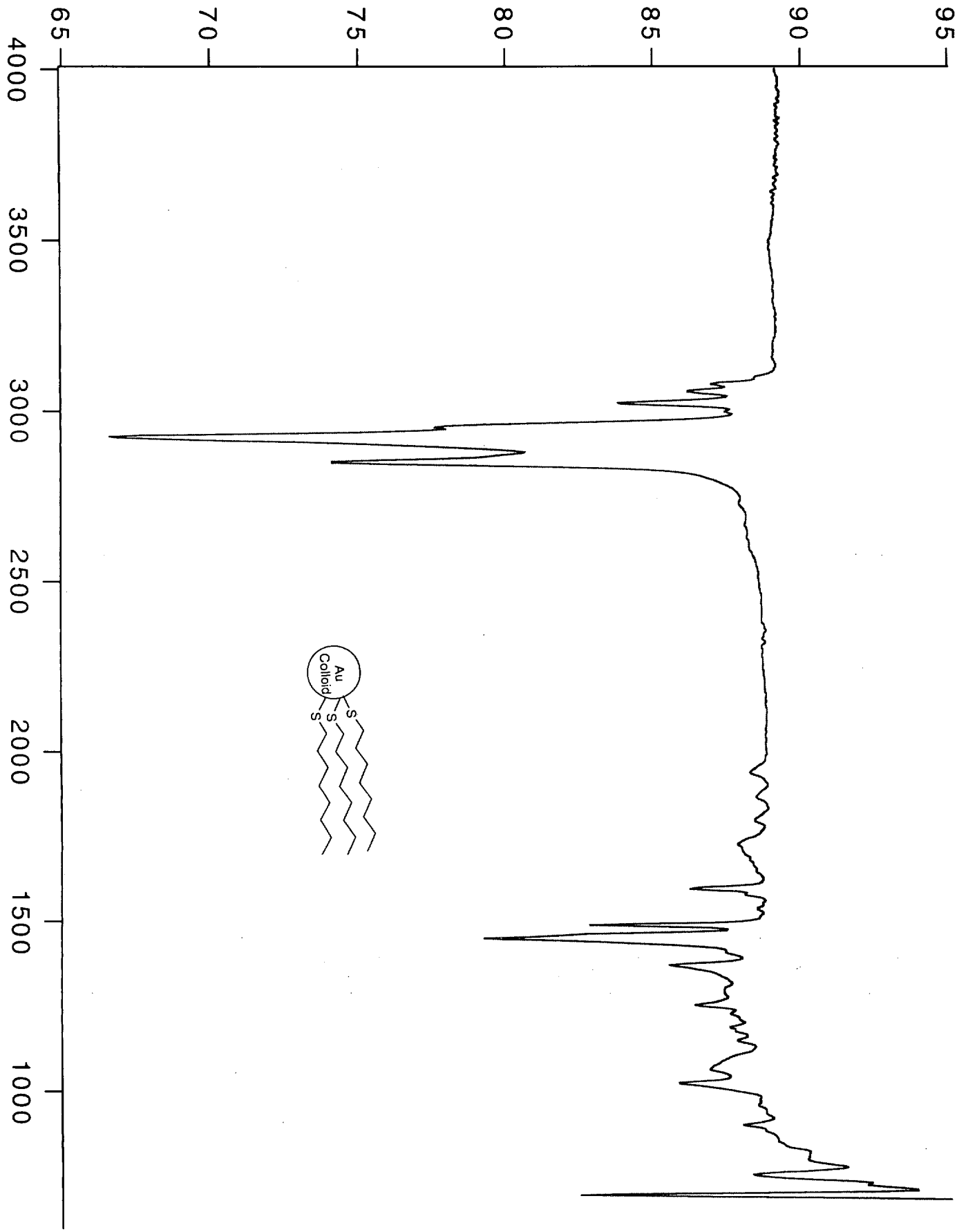
DO NOT WRITE IN BOX BELOW

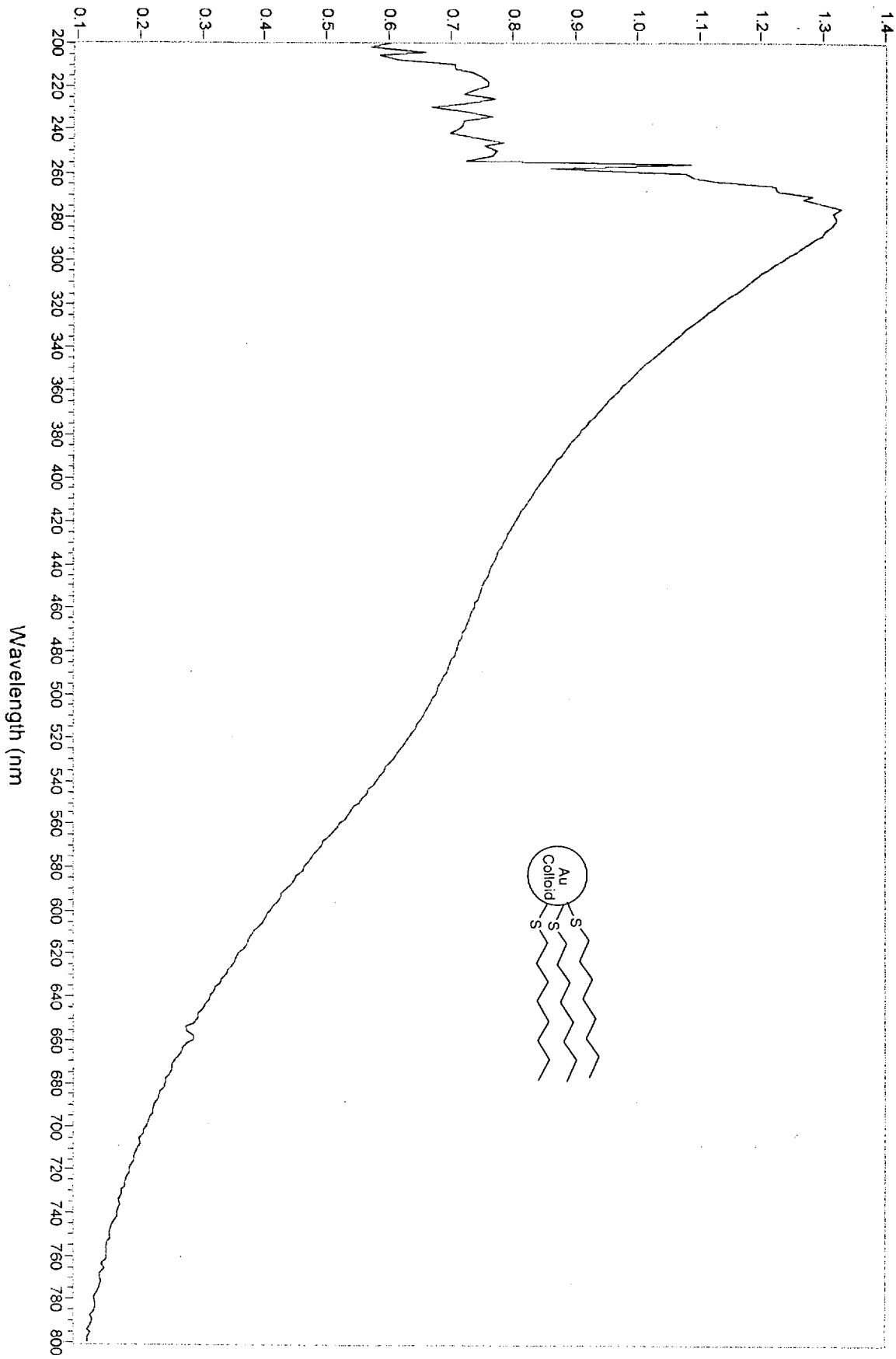
Routine analyses as weight %		*Other analyses as specified below*	
Carbon	61.43	Metal [ ]	
Hydrogen	8.50	Water (by Karl Fischer)	
Nitrogen		Sample Drying	
Halogen [ ]		Special Weighing	
Sulfur		Other [ ]	
Phosphorus			
Ash		Total $	

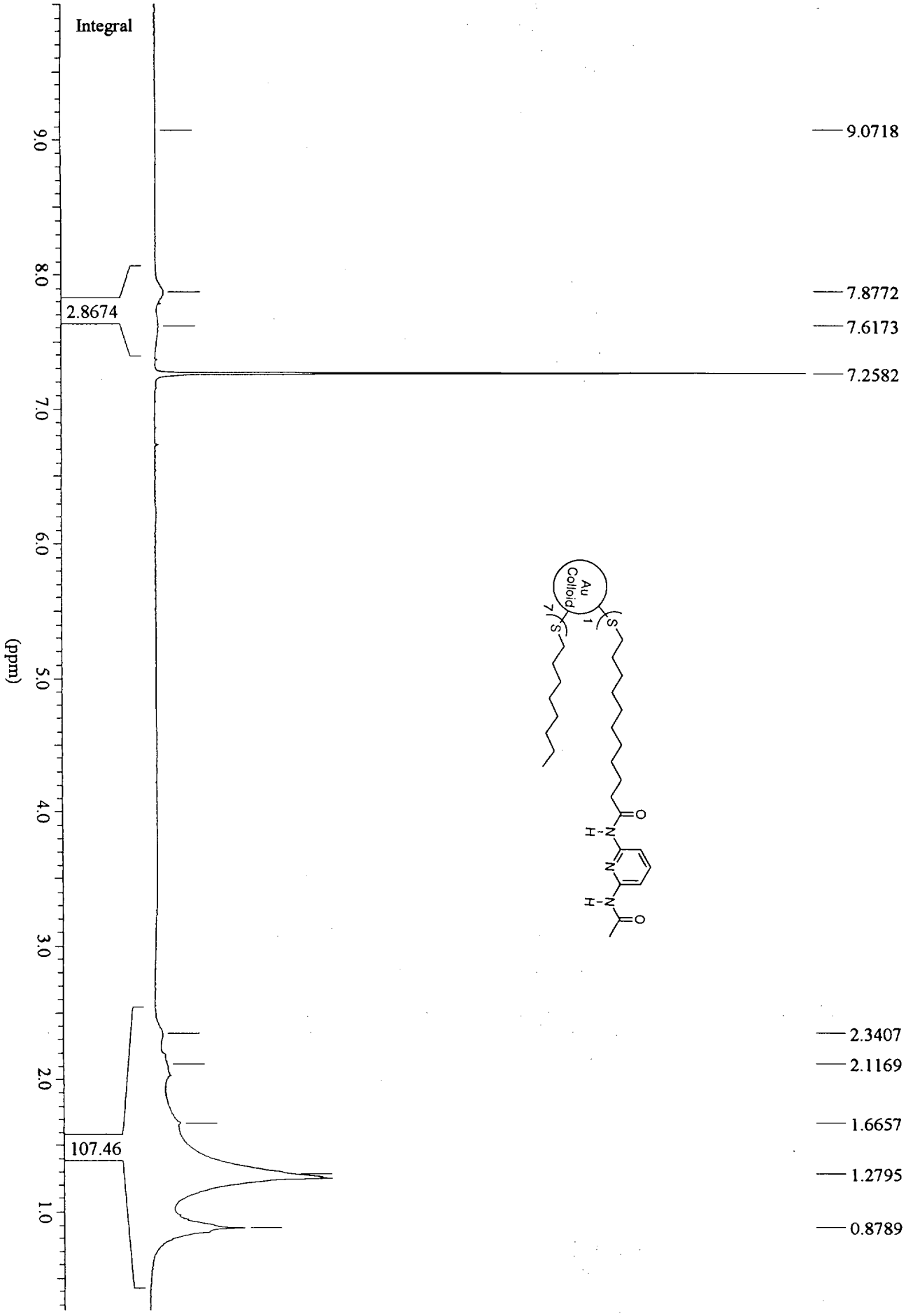
Comments _____

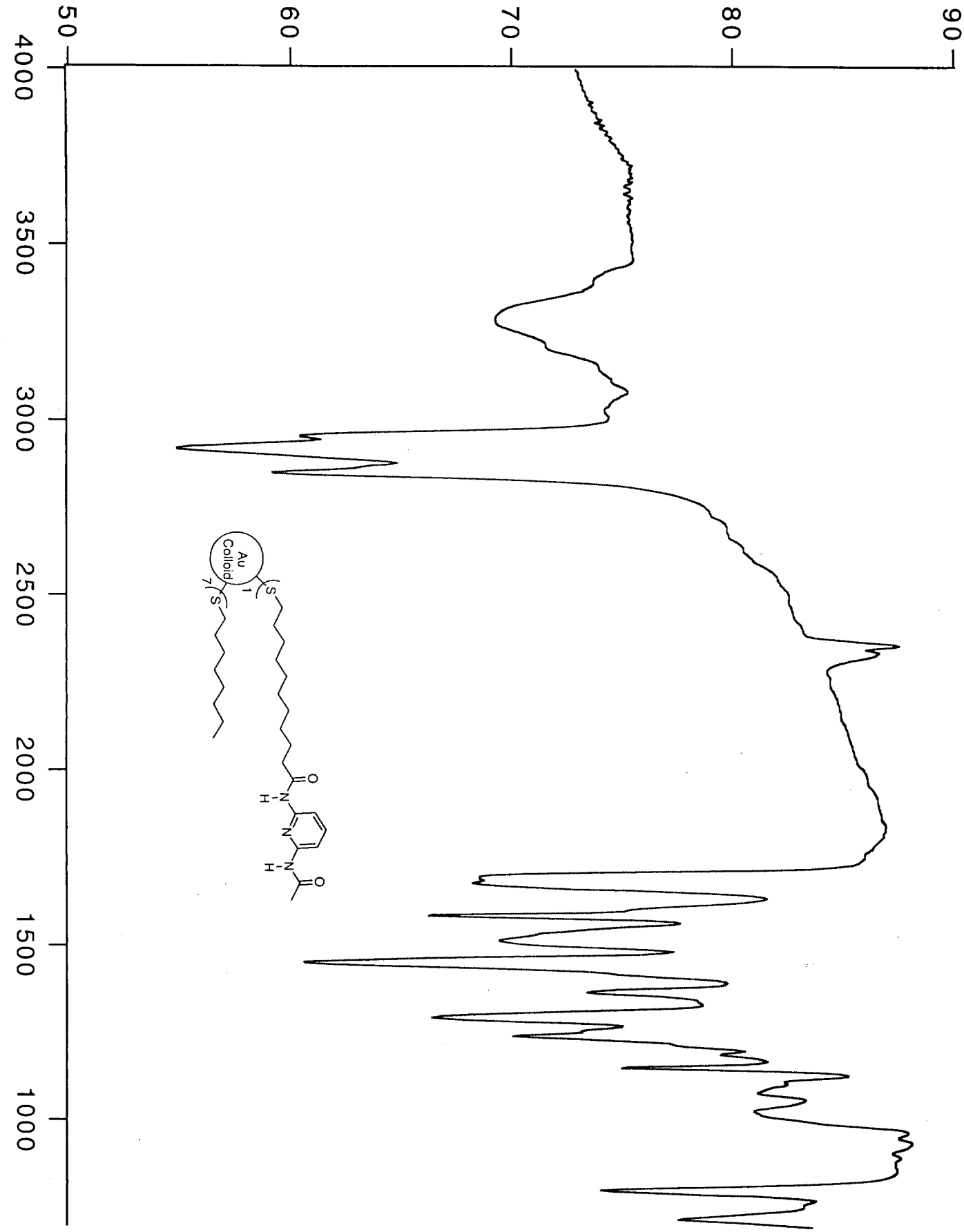
Date Completed 1/28/99 *Signature,Microanalyst* _____

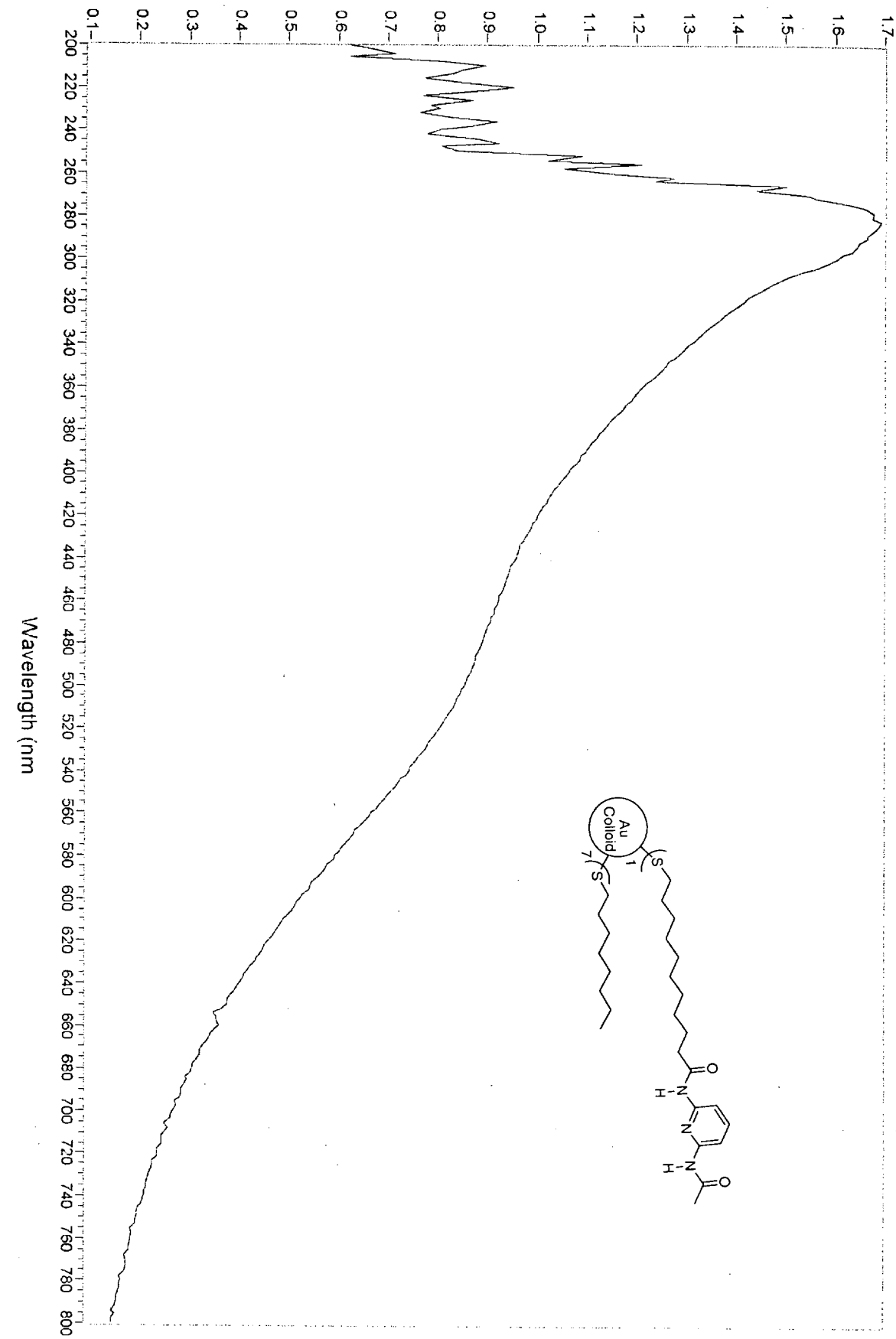


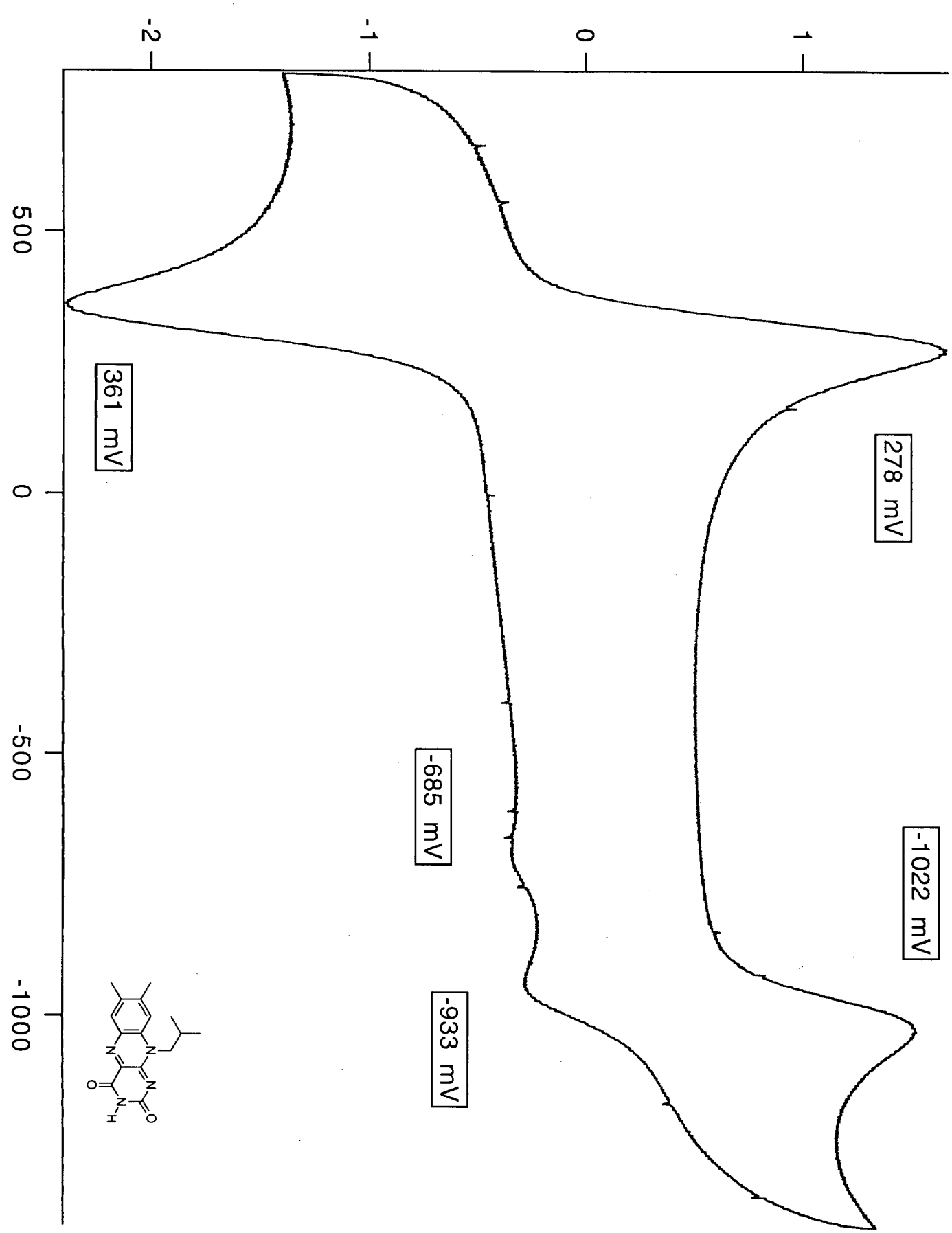


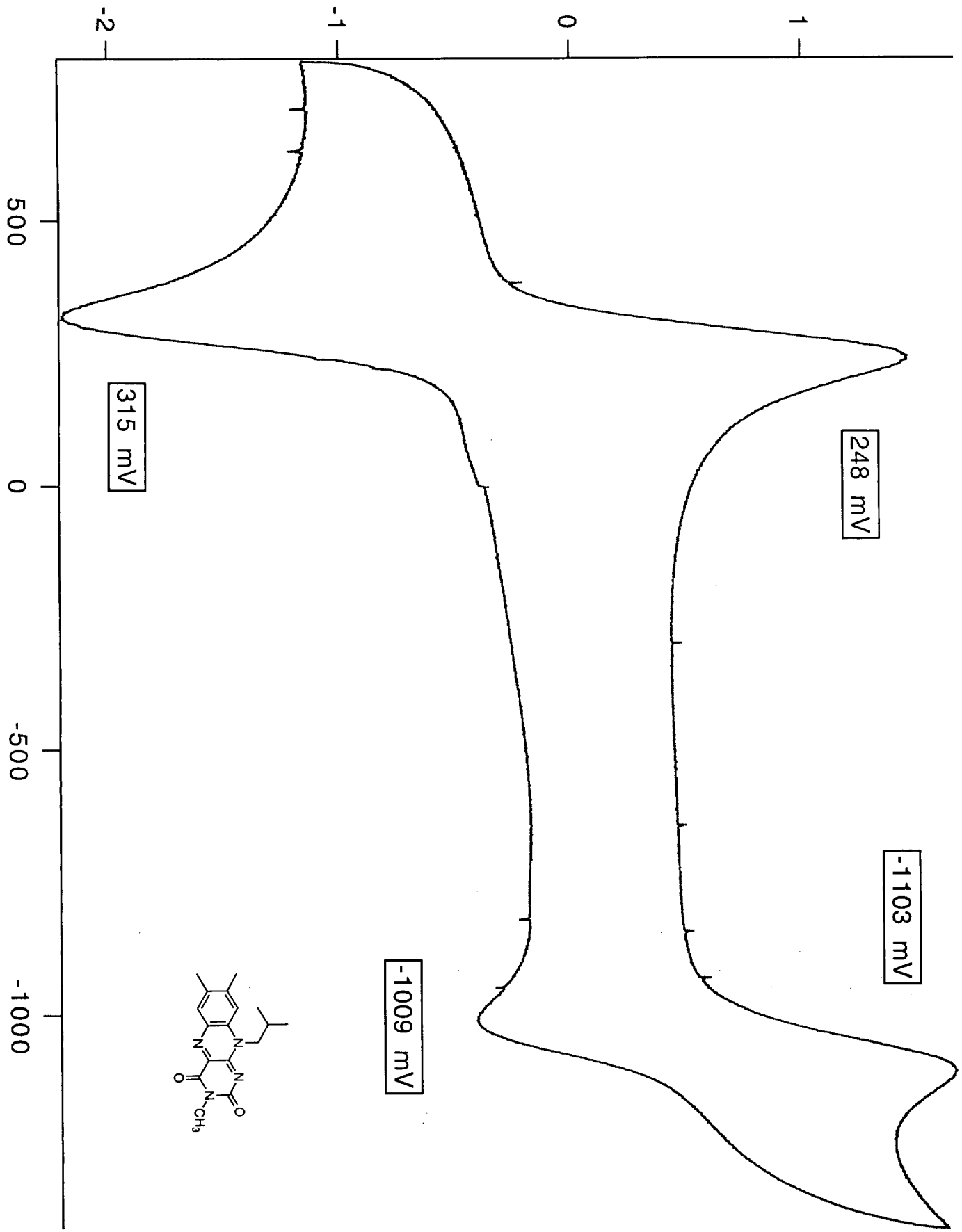


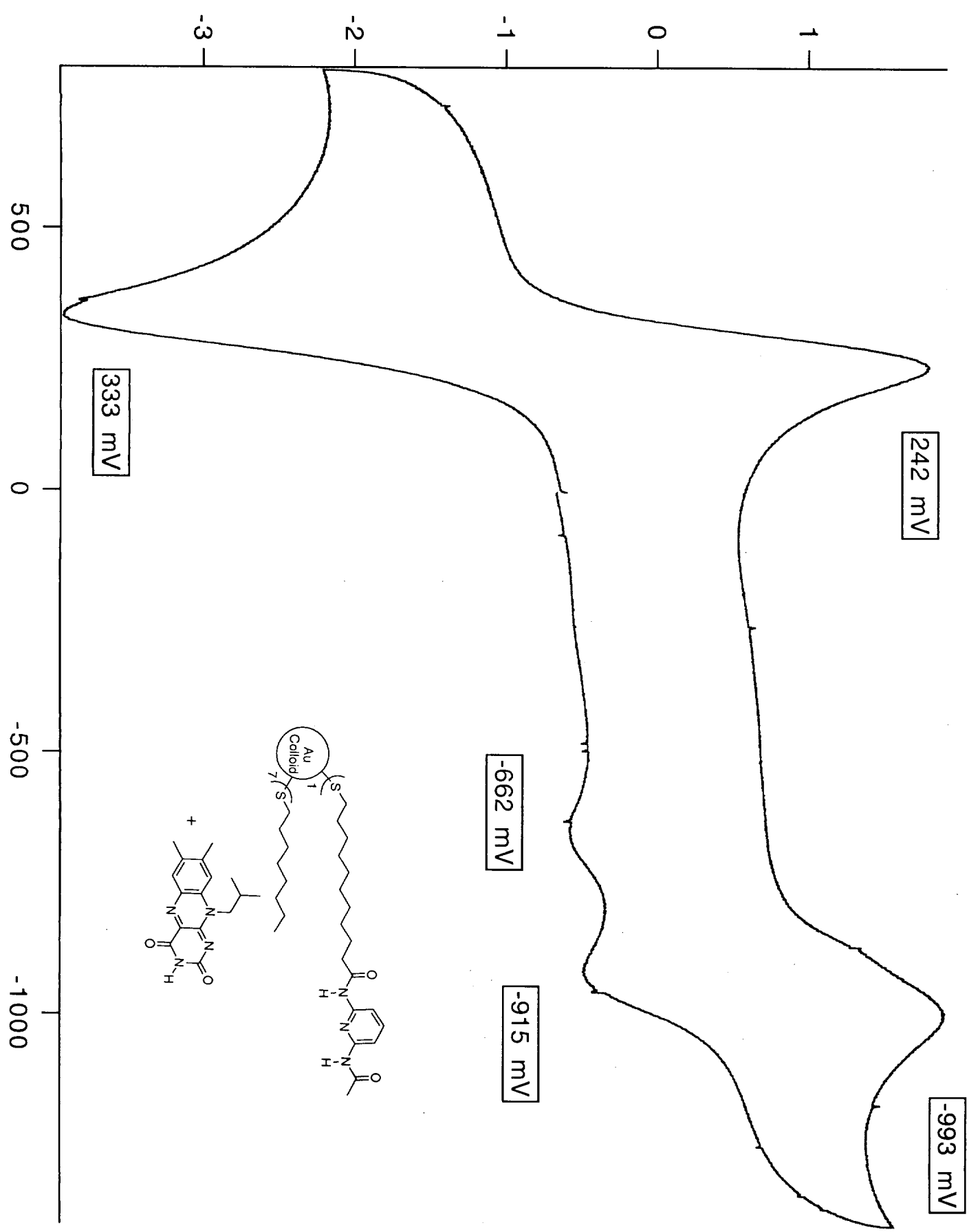


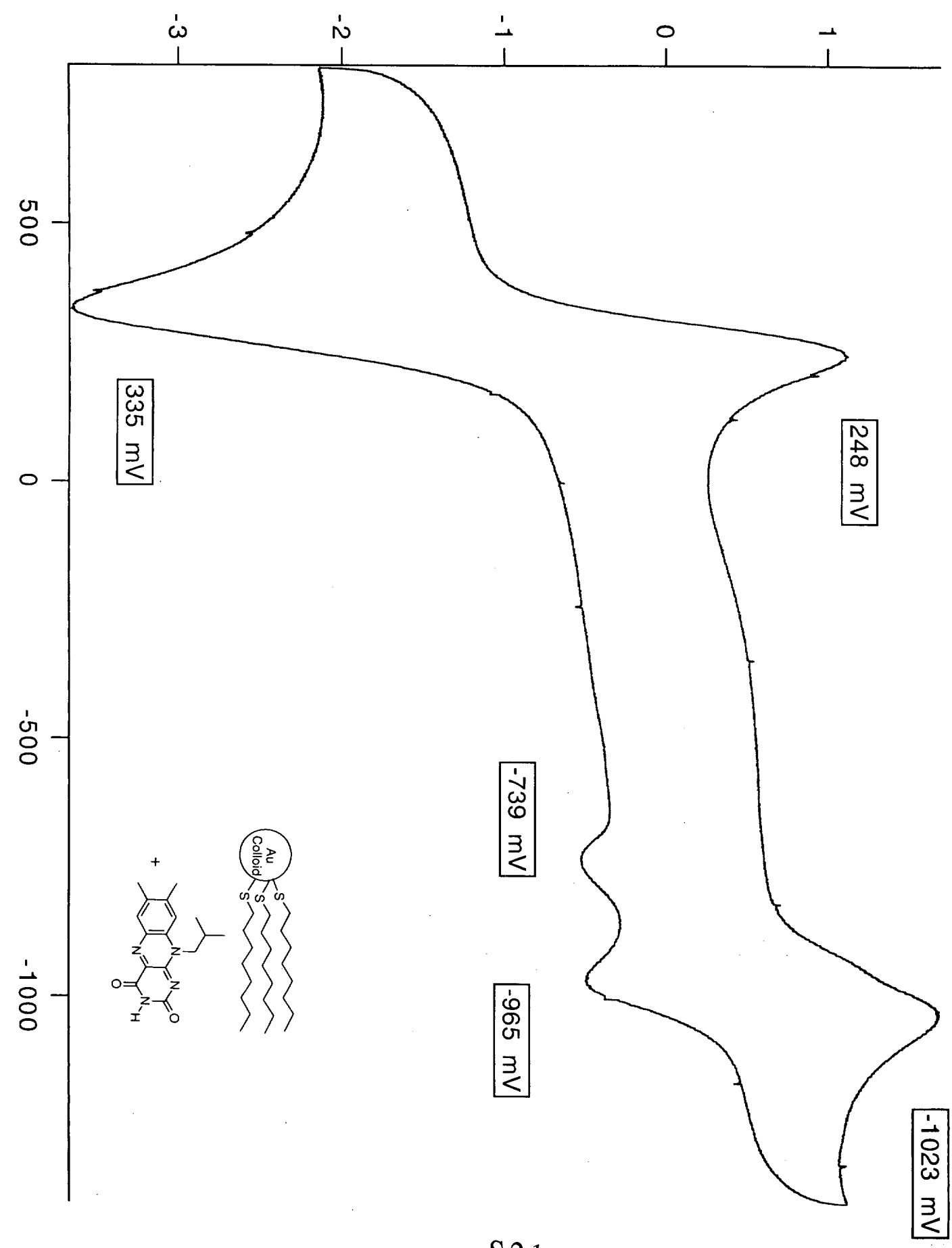


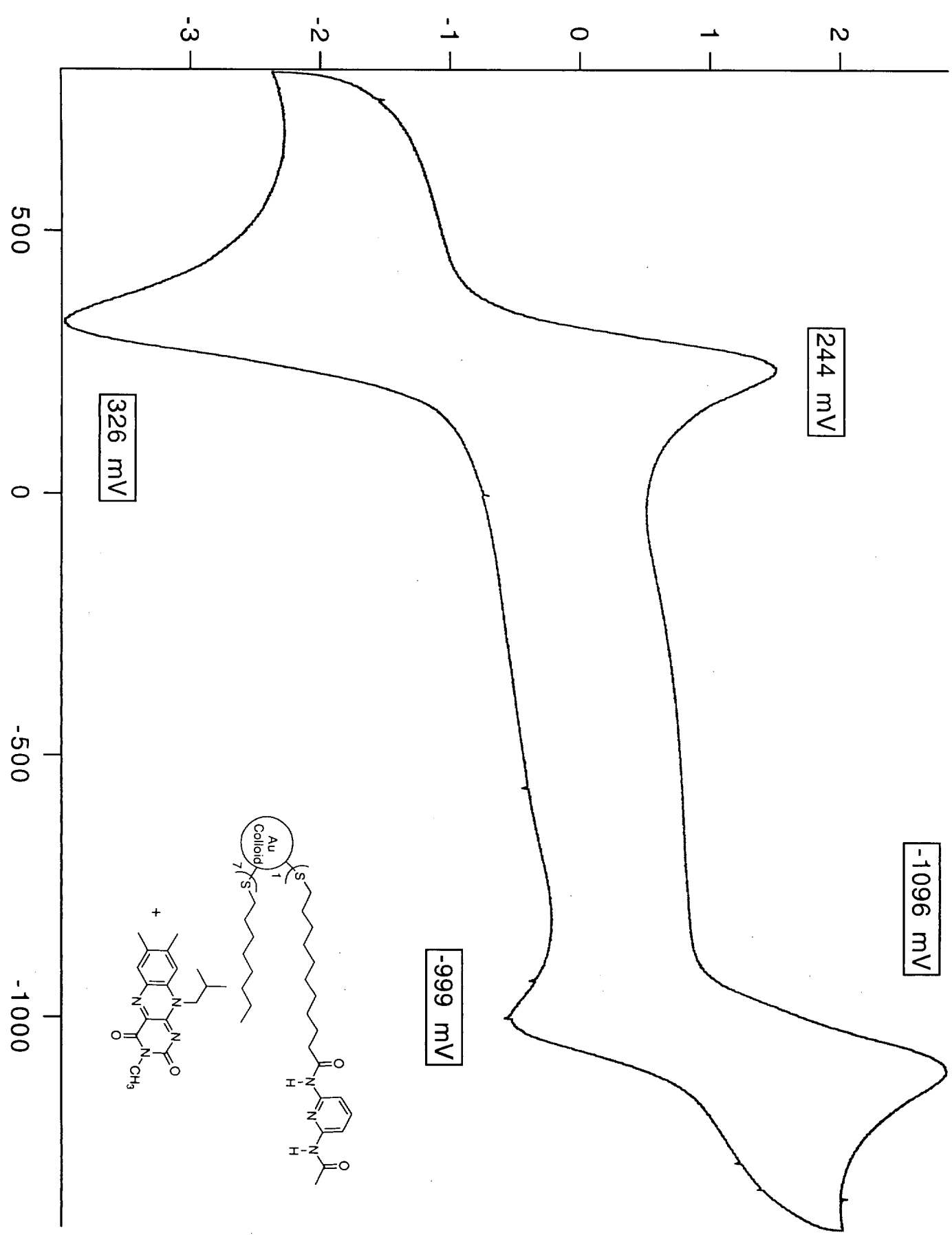


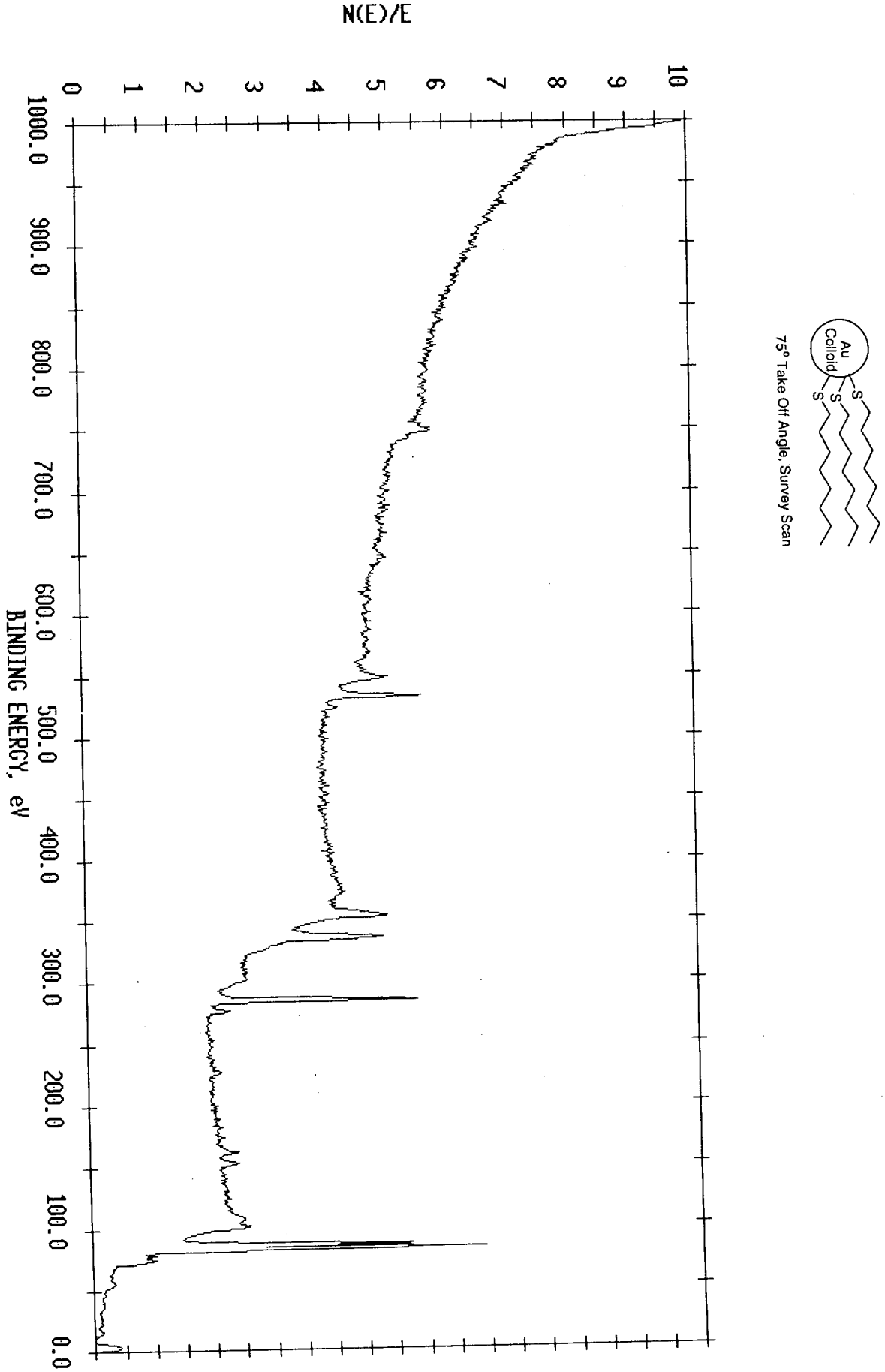


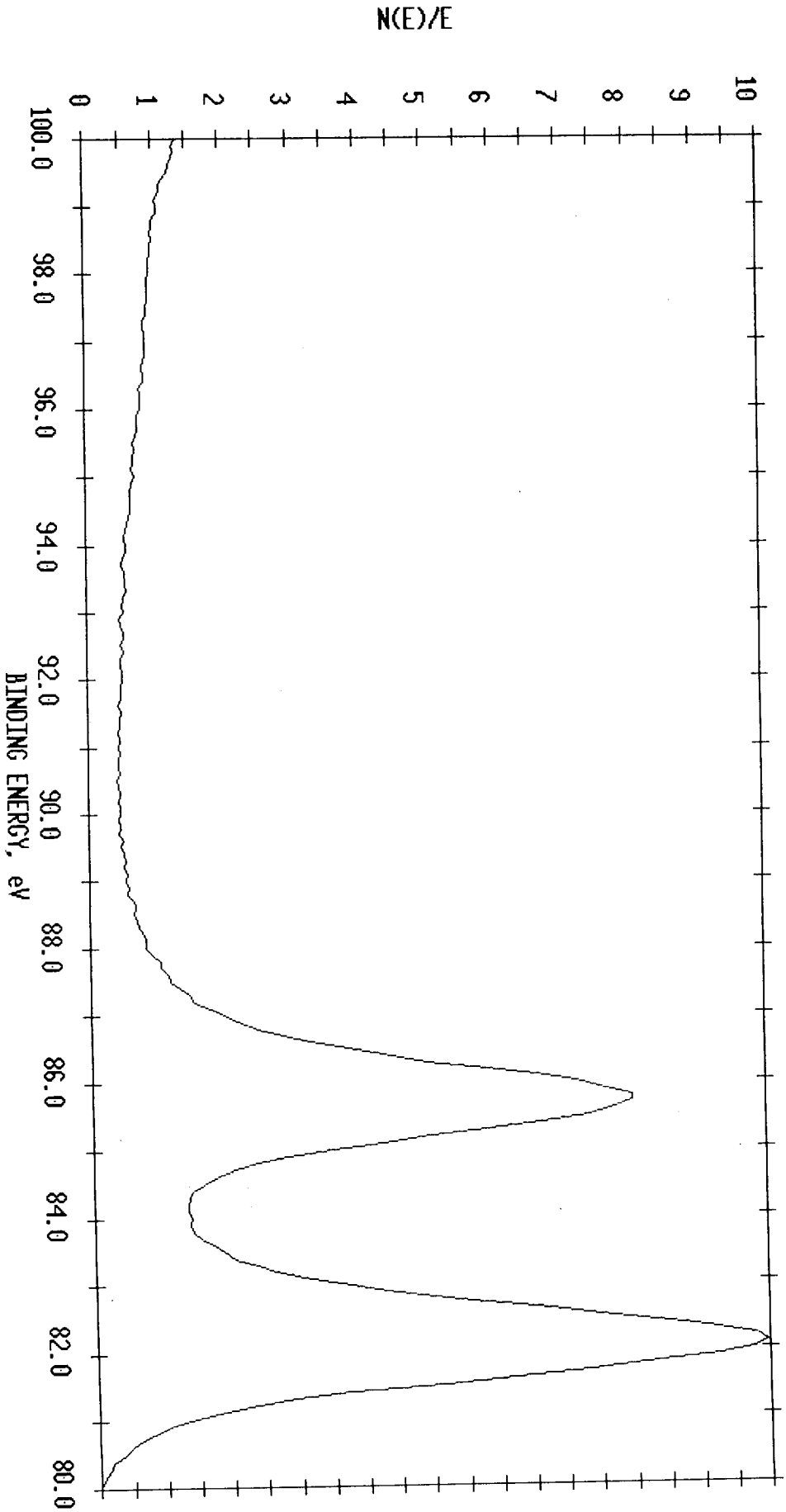


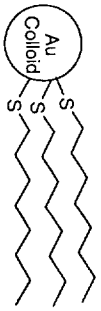












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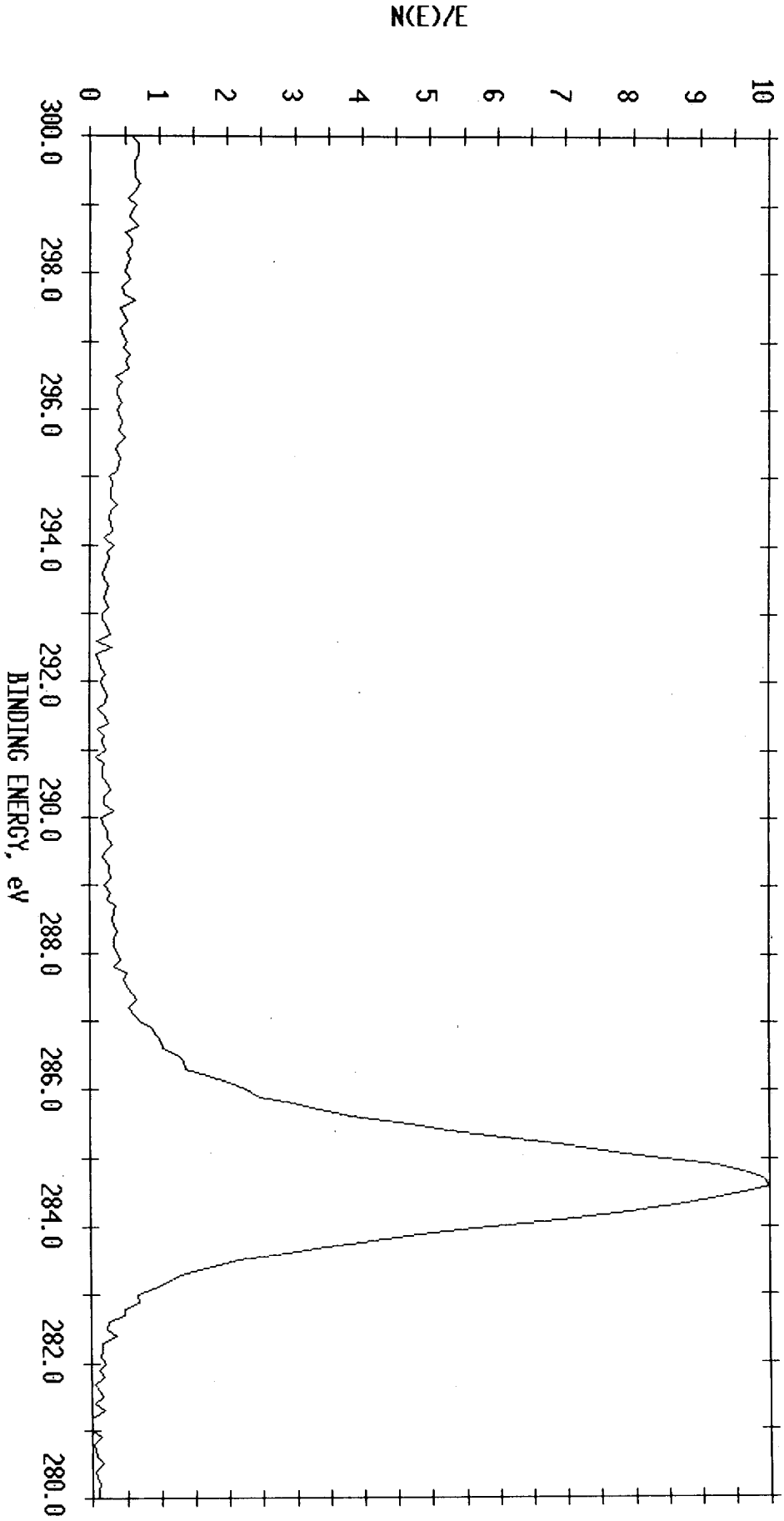

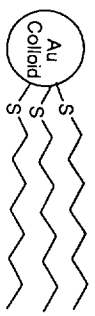

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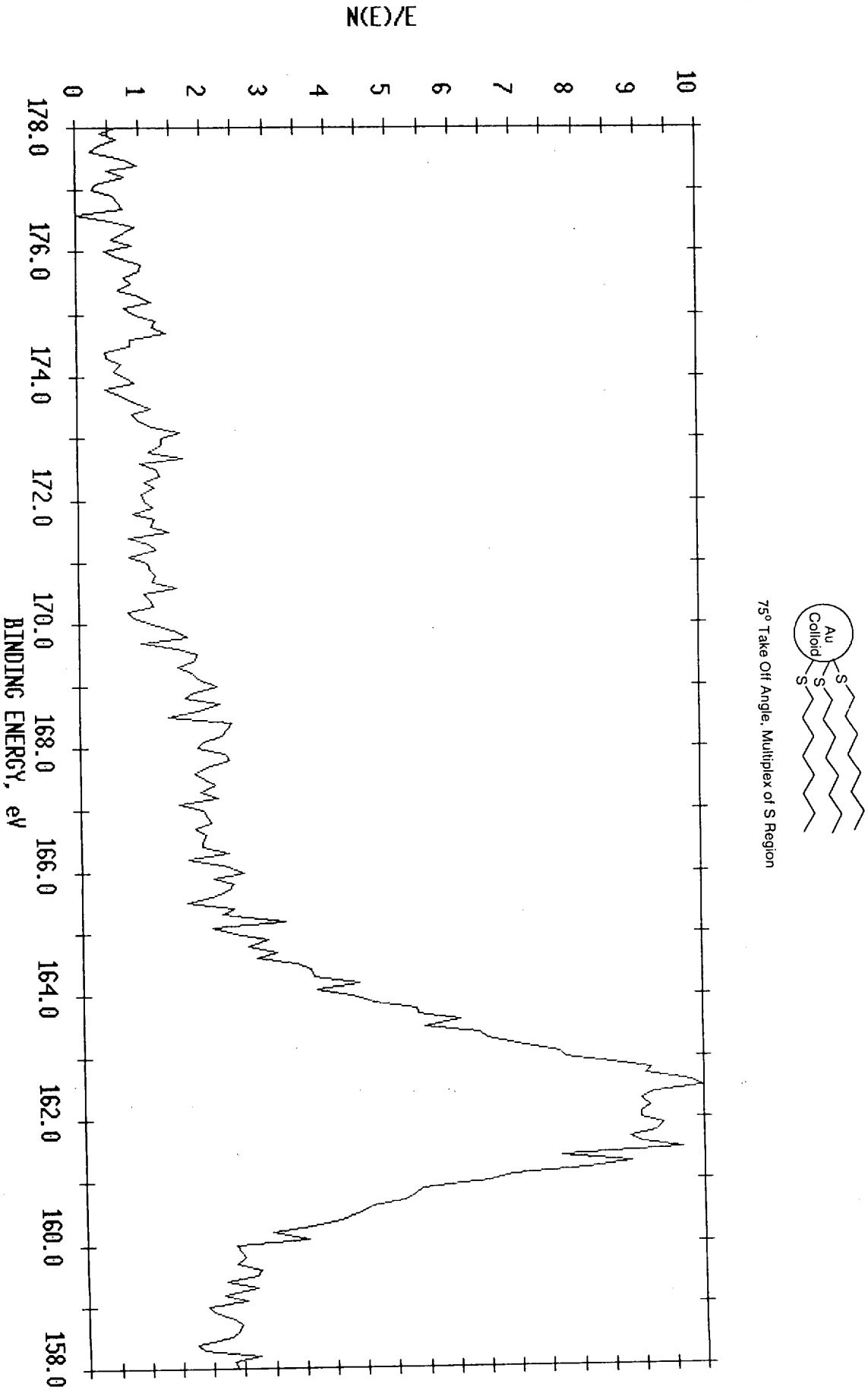
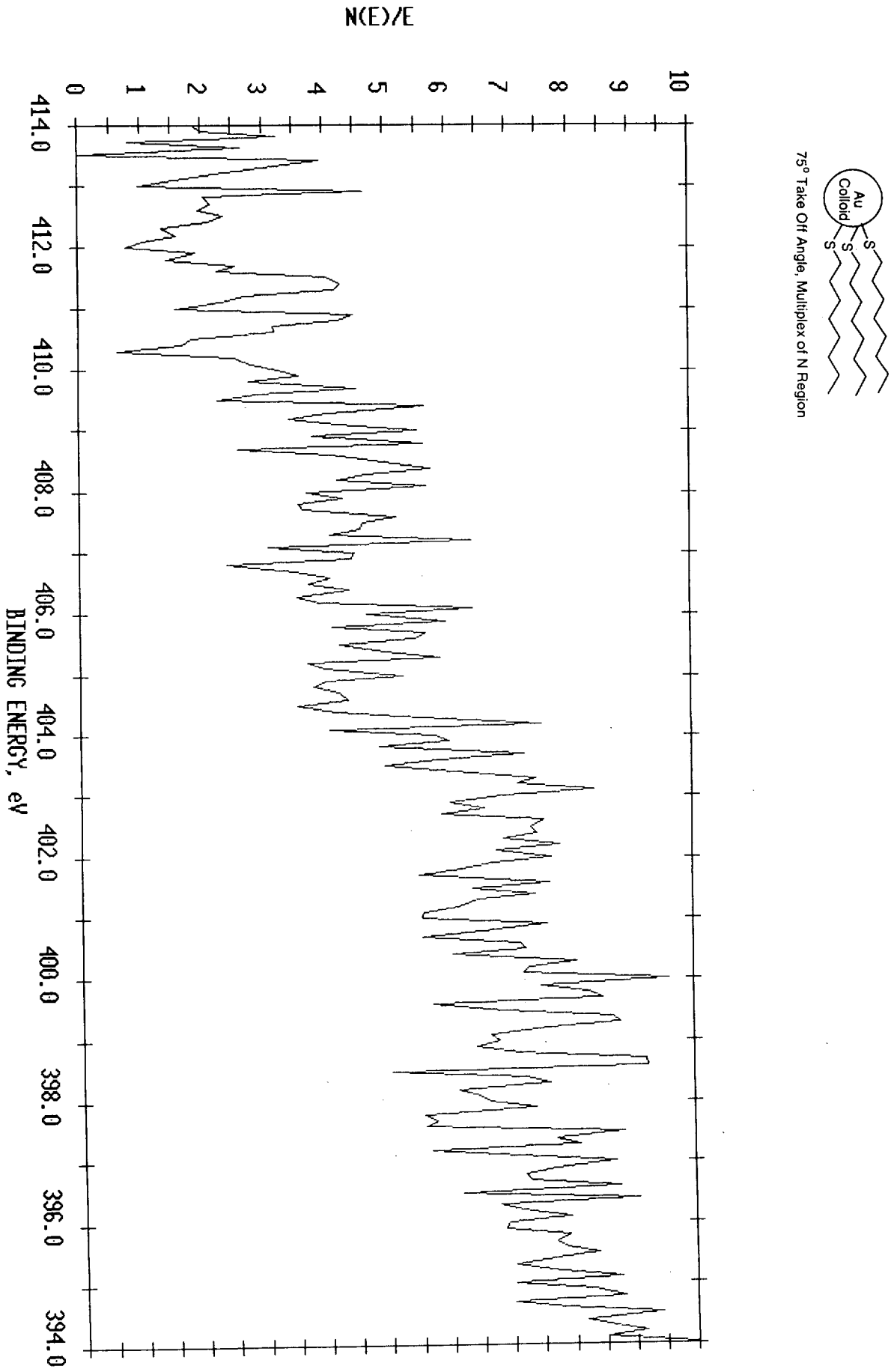
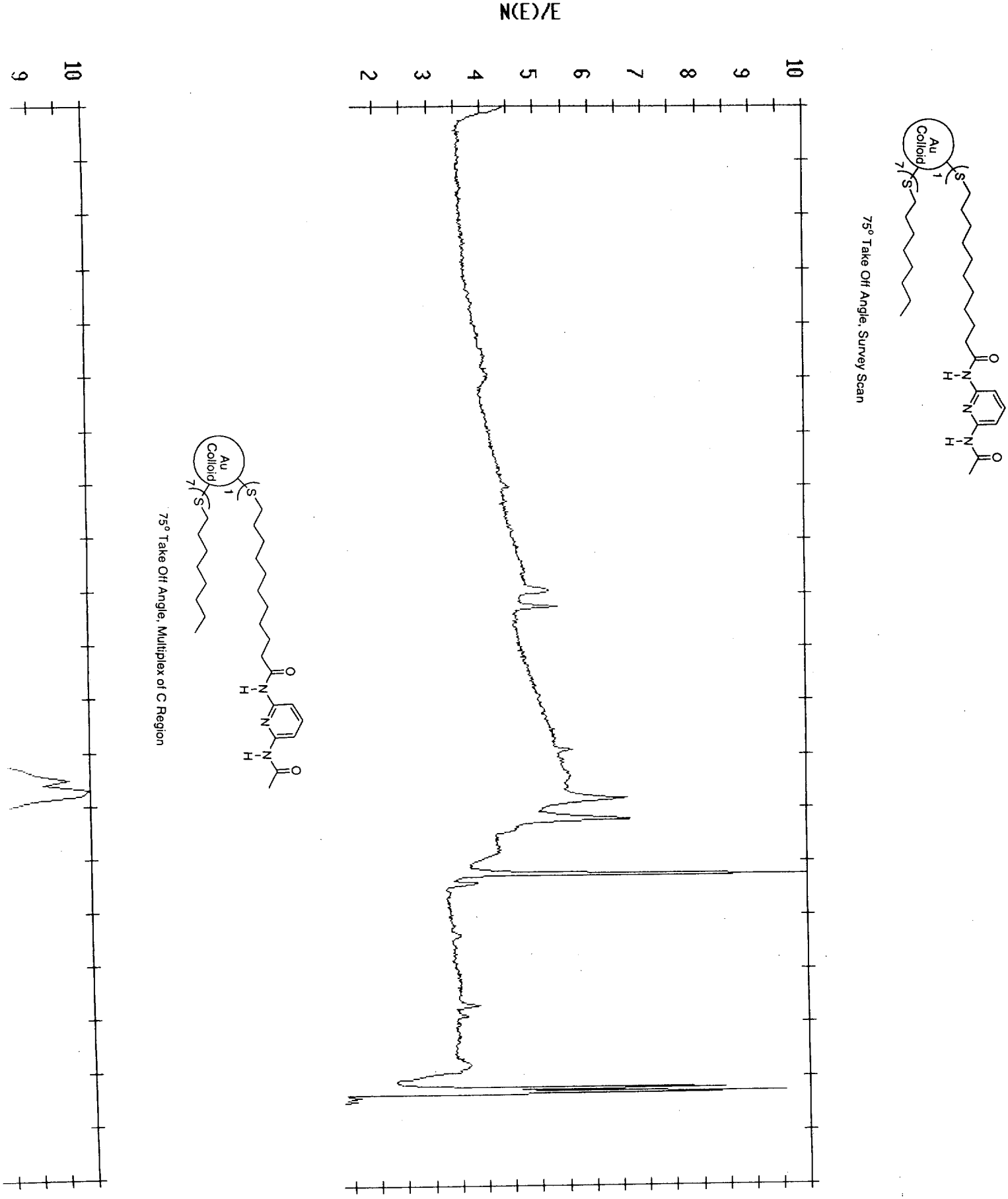
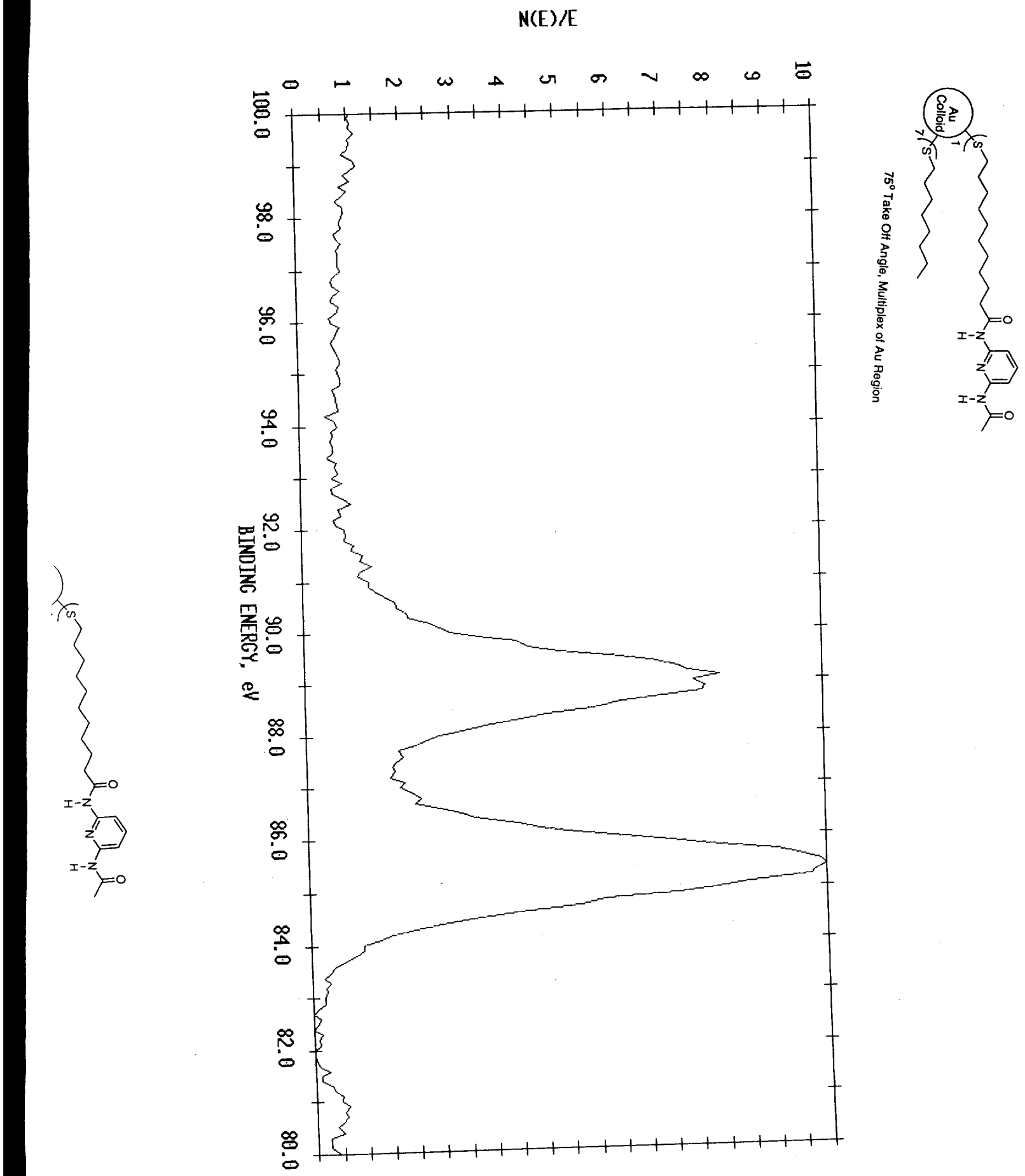
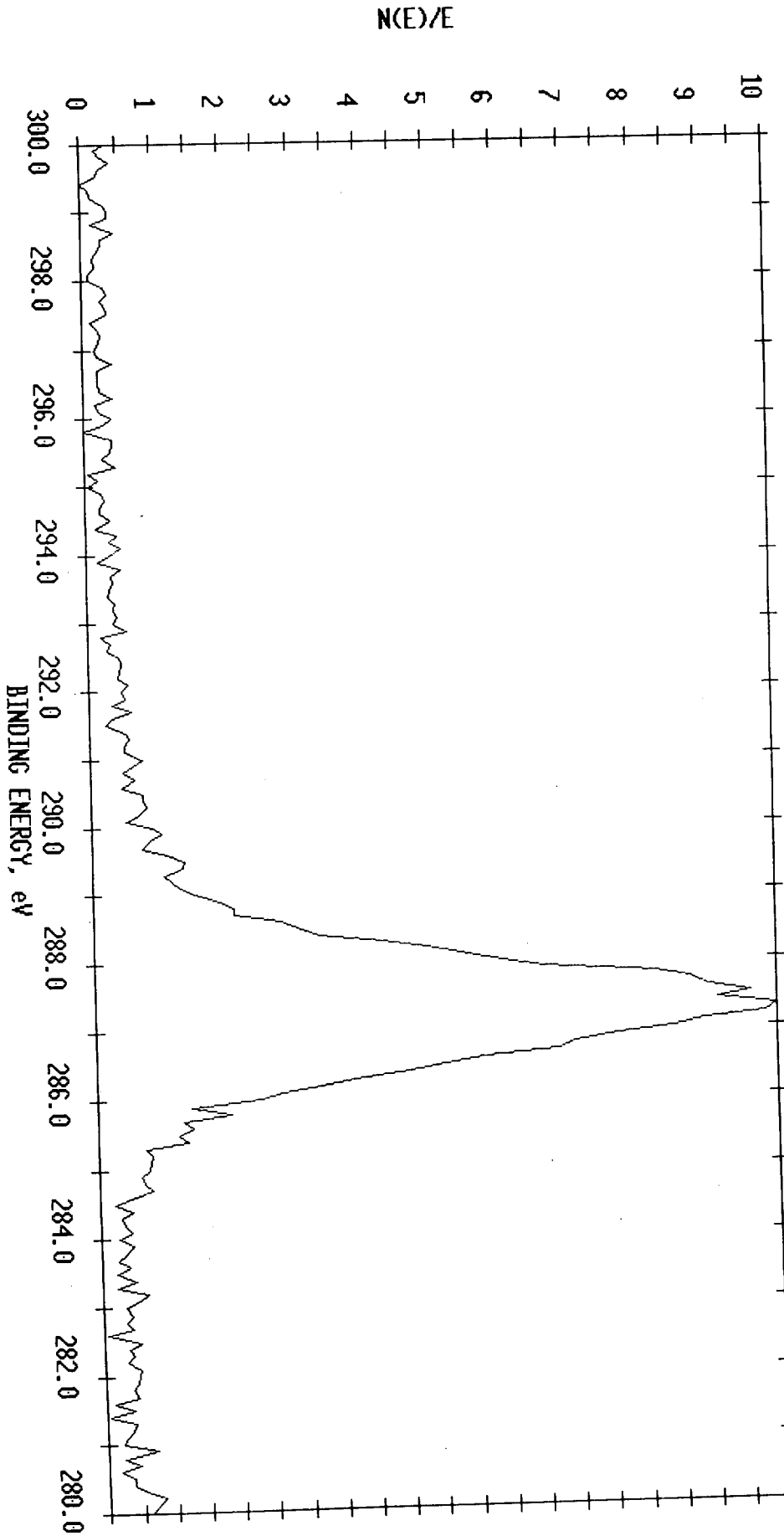
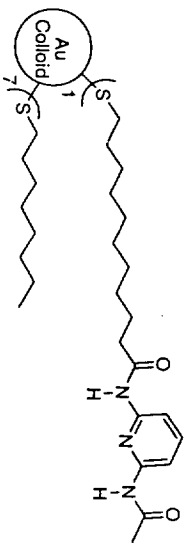




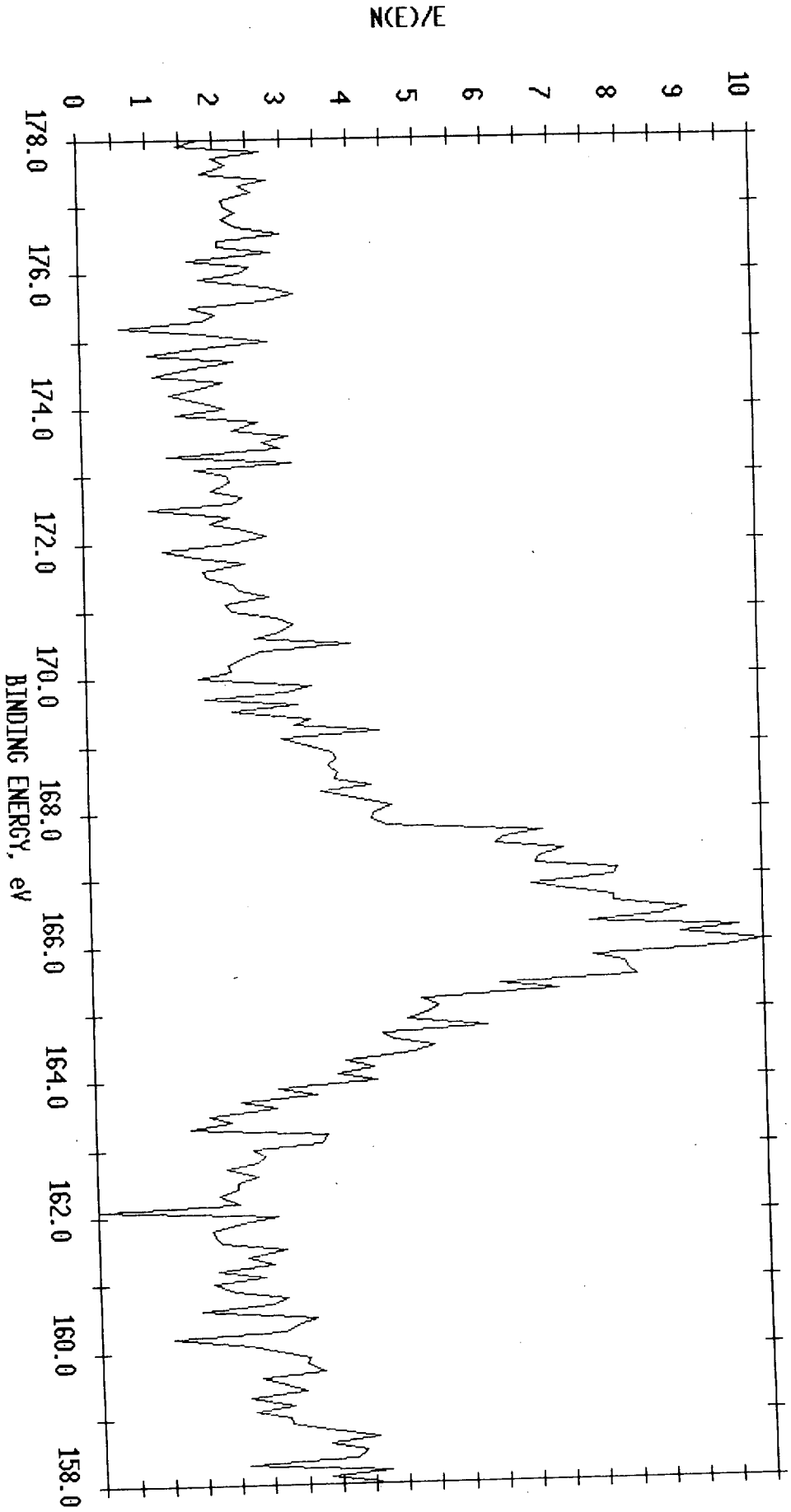


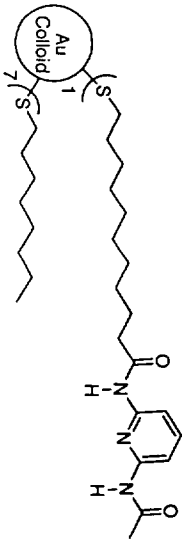






75° Take Off Angle, Multiplex of C Region





75° Take Off Angle, Multiplex of S Region