



# Synthesis and Characterization of the First Liquid Single Source Precursors for the Deposition of Ternary Chalcopyrite (CuInS<sub>2</sub>) Thin Film Materials

Kulbinder K. Banger  
Ohio Aerospace Institute, Brook Park, Ohio

Jonathan Cowen  
Cleveland State University, Cleveland, Ohio

Aloysius F. Hepp  
Glenn Research Center, Cleveland, Ohio

## The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

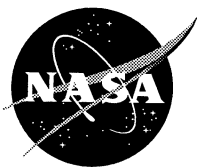
- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized data bases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to [help@sti.nasa.gov](mailto:help@sti.nasa.gov)
- Fax your question to the NASA Access Help Desk at 301-621-0134
- Telephone the NASA Access Help Desk at 301-621-0390
- Write to:  
NASA Access Help Desk  
NASA Center for Aerospace Information  
7121 Standard Drive  
Hanover, MD 21076



# Synthesis and Characterization of the First Liquid Single Source Precursors for the Deposition of Ternary Chalcopyrite (CuInS<sub>2</sub>) Thin Film Materials

Kulbinder K. Banger  
Ohio Aerospace Institute, Brook Park, Ohio

Jonathan Cowen  
Cleveland State University, Cleveland, Ohio

Aloysius F. Hepp  
Glenn Research Center, Cleveland, Ohio

National Aeronautics and  
Space Administration

Glenn Research Center

## Acknowledgments

We thank NASA for financial support under cooperative agreement NCC3-817, Daniel Scheimen for assistance with TGA/DSC experiments, Dr. David Hehemann, Dr. Stan Duraj, and Dr. Alan Riga for laboratory resources.

Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Available from

NASA Center for Aerospace Information  
7121 Standard Drive  
Hanover, MD 21076

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22100

Available electronically at <http://gltrs.grc.nasa.gov/GLTRS>

# Synthesis and Characterization of the First Liquid Single Source Precursors for the Deposition of Ternary Chalcopyrite (CuInS<sub>2</sub>) Thin Film Materials

Kulbinder K. Banger  
Ohio Aerospace Institute  
Brook Park, Ohio 44142

Jonathan Cowen  
Cleveland State University  
Cleveland, Ohio 44115

Aloysius F. Hepp  
National Aeronautics and Space Administration  
Glenn Research Center  
Cleveland, Ohio 44135

The fabrication of polycrystalline chalcopyrite CIS absorber layers for thin film solar cells have received considerable interest due to their potential as the next generation of photovoltaic devices.<sup>1</sup> Chalcopyrite materials are highly appealing given their bandgaps are near optimum for either implementation in space, (AM0) or terrestrial applications, (AM1.5). For example a Cu(In,Ga)Se<sub>2</sub> based thin film solar cell has been reported to display an AM1.5 conversion of 18.8 percent.<sup>2</sup> A further challenge for space applications is the optimization of mass specific power to minimize power system launch costs. This requirement necessitates the use of lightweight substrates such as metal foils, or polymer substrates, which require the use of reduced-temperature processes, typically < 400 °C. Consequently, greater demand has been placed on the synthesis of new precursors capable of producing chalcopyrite materials at reduced temperatures. Clearly molecular engineering of MOCVD precursors plays a significant role and is receiving greater attention.<sup>3</sup> Ternary single source precursors, (type I-III-VI<sub>2</sub>) provide an attractive and clean approach, however very few are known, or have been tested.

In the course of our investigations for improved precursors for the CVD of chalcopyrite thin-films,<sup>4,6</sup> we have discovered new liquid single source precursors to the ternary semiconductor CuInS<sub>2</sub>, based on the [{PR<sub>3</sub>]<sub>2</sub>Cu(SR')<sub>2</sub>In(SR')<sub>2</sub>] architecture.<sup>7</sup> Manipulation of the steric and electronic properties of the neutral donor ligand and the thiol moiety, permits directed adjustment of the physical and thermal properties of the precursor. Use of extended alkyl groups resident either on the phosphine, or thiol groups affords the liquid derivatives, [{P(*n*-Bu)<sub>3</sub>]<sub>2</sub>Cu(SEt)<sub>2</sub>In(SEt)<sub>2</sub>] **1** and [{P(*n*-Bu)<sub>3</sub>]<sub>2</sub>Cu(S(*n*-Pr))<sub>2</sub>In(S(*n*-Pr))<sub>2</sub>] **2**, respectively.

The complexes are synthesised based on a modification of the procedure reported by Kanatzidis,<sup>7</sup> with the thiol derivative being generated *in situ* by reaction of the conjugate acid with NaOEt in methanol, thus producing no adverse side products, in addition to an "activated" NaSR'. The multi-stage synthesis yields the desired products in good yields, (> 65 percent) as opaque liquids that are stable in air for over 5 hrs, during normal handling.<sup>8</sup> One of the key

features of these new precursors is their liquid phase, which is remarkable considering their high molecular mass and stoichiometry, thus facilitating the possibility of a solvent free delivery and higher deposition rates during thin film fabrication. Needless to say, the precursors also display very high solubility in both polar and non-polar organic solvents, which may be attributed to their ionic character and to the non-polar alkyl groups resident on the phosphine.

Multinuclear NMR, low temperature Differential Scanning Calorimetry (DSC), and Thermogravimetric analyses (TGA) with evolved gas analysis, (EGA) were used to characterize and verify precursor formation and purity. NMR data demonstrated that **1** and **2** were free from any starting reagents (see supporting info). <sup>31</sup>P NMR spectra shows a shift for PBU<sub>3</sub>, from -32.50 to -19.2 for [{PBU<sub>3</sub>]<sub>2</sub>Cu{MeCN}<sub>2</sub>]+PF<sub>6</sub><sup>-</sup>, -22.4 for **1** and -22.5 ppm for **2**, which is indicative of ligand to metal co-ordination and hence complex formation.<sup>9</sup> Low temperature DSC provided information on the thermal stability and temperature dependent phase changes of the single source precursors. The samples were heated at a rate of 10 °C/min under a dinitrogen atmosphere, using hermetically sealed aluminum pans to eliminate weight loss associated with vaporization. The low temperature DSC profiles show an absence of an endotherm assignable to a melting phase transition, thus confirming their liquid phases at ambient temperatures (figure 1). The main exothermic events for **1** and **2** begin with onset temperatures of 258 °C and 225 °C with large exotherms of 220 J/g and 313 J/g, respectively, which can be assigned to the decomposition of the samples. The lower decomposition temperature of **2** is as expected, since an increase in chain length and/or steric "bulk" of the alkyl groups is reported to decrease stability.<sup>3c,10</sup>

Thermogravimetric analyses (TGA) were performed at ambient pressure in platinum pans, on samples of the liquid precursors. The samples were heated at a rate of 20 °C / min under a dinitrogen atmosphere to correlate with EGA. Weight loss was associated with decomposition of the complexes (figure 2). Calculation of the derivative maximum rate of weight loss (MRW, percent/°C), and step transition weight loss were used as a measure of relative

stability. The TGA curves show a smooth loss of mass over a temperature window of approximately 170 °C, accounting for a loss of 70 percent for **1** and 71 percent for **2**, of the original material where the MRW is found at 238 and 225 °C, respectively. The TGA profile for sample **1** and **2** indicate an initial weight loss, as low as 82 and 75 °C, whilst calculation of the extrapolated onset temperatures yields 189 and 171 °C, respectively. Calculation of the precursor efficiency for **1** and **2** to afford CuInS<sub>2</sub> as the final product, shows both samples to be within 1.5 percent based on the residual material from the TGA experiments. Preliminary Vacuum-TGA studies on **1**, shows the degradation temperature window to be as low as 100 to 160 °C, thus making these precursors ideal candidates for use in low temperature MOCVD on space qualified substrates such as Kapton™.

Interestingly, TGA data indicates that both precursors begin to decompose at lower temperatures than observed by DSC analysis. In order to resolve this issue, low temperature Modulated Differential Scanning Calorimetry, (MDSC) was undertaken, which provides information about the reversible, (heat capacity) and non-reversible, (kinetic) characteristics of thermal events, thereby providing greater sensitivity to deconvolute thermal phase transitions.<sup>11</sup> MDSC profiles for sample **1** and **2** show an onset for an endothermic phase transition occurring at approximately 80 and 75 °C, respectively, which may be correlated with the decomposition temperatures found in TGA, whilst the exothermic maxima, ( $T_{max}$ ) are of a magnitude constant with those found in the DSC experiments, (figure 3). Hence, MDSC supports the TGA decomposition data. A more thorough interpretation of the thermal properties of these materials is presented elsewhere.<sup>6</sup>

The mode of decomposition for the liquid precursors **1** and **2** was investigated by FTIR and mass spectroscopic EGA. The FTIR spectra for **1** (figure 4), show absorptions at approximately 3000, 1460, 1390, 1300 and 1250 cm<sup>-1</sup>, which are assignable to the initial expulsion of diethyl sulphide. Correlation with the mass spectra supports these findings on the basis of the library fit and from the assignment of the fragment and parent ions, ( $m/z = 90$ ). After approximately 15 minutes the intensity of the absorptions in the IR spectra due to diethyl sulphide decrease, however absorptions in the aliphatic regions are still evident. Comparison with the respective mass spectra allows for the assignment to the loss of PBU<sub>3</sub>, with a library fit of 92 percent and assignment of the parent ion ( $m/z = 202$ ). Importantly, mass spectroscopic EGA shows the absence of any fragment ions with an isotopic pattern associated with an indium derivative. In a similar experiment, EGA for the *n*-propyl derivative gave analogous results.

The ability of the new precursor to thermally decompose to yield single-phase CuInS<sub>2</sub> was investigated by powder X-ray diffraction (XRD) analysis and Energy Dispersive Spectroscopy, (EDS) on the non-volatile solids from the TGA experiments and vacuum pyrolysis, (5mmHg, 150 to 300 °C). XRD spectra for the non-volatile material produced from the pyrolysis of **1** confirmed it to be single-phase CuInS<sub>2</sub> (figure 5). Examination of the EDS spectra for the

same samples, shows predominant emissions due to Cu, In, and S edges, with the approximate percentage atomic composition of 27, 23 and 50 for **1** and 28, 23 and 49 for **2**, respectively, thus supporting the stoichiometric formation of CuInS<sub>2</sub>, albeit slightly copper rich.<sup>12</sup> The stoichiometry of CIS deposition is known to be temperature dependent,<sup>4c</sup> and so these initial results are very promising.

In summary we have produced the first known liquid single source precursors for the deposition of the ternary chalcopyrite CuInS<sub>2</sub>. Thermal analysis supports that selective adjustment of the sterically demanding groups either on the donor group, or chalcogenide, permits adjustment of the solid-state phase and stability of the precursor. Furthermore, the availability of a liquid phase precursor dramatically broadens the potential for a number of MOCVD processes, and may allow application to certain spin coating processes, fabrication of CuInS<sub>2</sub> quantum dots and impregnated CIS<sub>2</sub> polymer films.

## References

- (a) Basol, B.M.; *Thin Solid Films* **2000**, *361*, 514. (b) Klenk, M.; Schenker, O.; Alberts, V.; Bucher, E. *Thin Solid Films* **2001**, *387*, 47. (c) Harris, D.J.; Hehemann, D.G.; Cowen, J.E.; Hepp, A.F.; Raffaele, R.P.; Hollingsworth, J.A. *28th IEEE Photovoltaic Specialist Conference*, Anchorage, Alaska **2000**, 563.
- Contreras, M.; Egaas, B.; Ramanathan K. *Prog. Photovoltaics* **1999**, *7*, 311.
- (a) Schulz, S.; Gillan, E.G.; Ross, J.L.; Rogers, M.; Rogers, R.D.; Barron, A.R. *Organomet.* **1996**, *15*, 4880. (b) Jones, A.C.; O'Brien, P. "CVD of Compound Semiconductors: Precursors Synthesis, Development & Application," VCH Press, **1997**. (c) Kodas, T.T.; Hampden-Smith, M.J.; Eds.; "The Chemistry Of Metal CVD," Weinheim VCH, NY, **1994**. (c) Rees, W.S.; Ed.; "CVD of Nonmetals," Weinheim VCH, NY, **1996**. (d) Krunks, M.; Mikli, V.; Bijakina, O.; Rebane, H.; Mere, A.; Varema, T.; Mellikov, E.; *Thin Solid Films* **2000**, *1*, 61.
- (a) Banger, K.K.; Cowen, J.; Harris, J.; MaClaron, R.; Riga, A.; Duraj, S.; Hepp, A.F. *Book of Abstracts; 222nd ACS National Meeting*, Chicago, Illinois **2001**. (b) Hollingsworth, J.A.; Hepp, A.F.; Buhro, W.E. *Chem. Vap. Deposition* **1999**, *5*, 105.
- Banger, K.K.; Harris, J.; Cowen, J.; Hepp, A.F. *E-MRS Spring Meeting, Symposium P: Thin Film Materials for Photovoltaics*, Strasbourg, France **2001**.
- Cowen, J.; Riga, A.; Hepp, A.F.; Duraj, S.; Banger, K.K.; MaClaron, R. *NATAS Conference Session: Thermal Application of Materials; NATAS Conference* St. Louis, MO, **2001**.
- Hirpo, W.; Dhingra, S; Sutorik, A.C.; Kanatzidis, M.G. *J. Am. Chem. Soc.* **1993**, *115*, 1597.
- For **1**: <sup>1</sup>H NMR: 300 MHz; CDCl<sub>3</sub>; δ 2.75 ppm (q, CH<sub>3</sub>CH<sub>2</sub>S-); δ 1.57 ppm (br m, P(CH<sub>2</sub>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>); δ 1.42 ppm (br m, P(CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub>); δ 1.32 ppm (t,

-SCH<sub>2</sub>CH<sub>3</sub>);  $\delta$  0.94 ppm (t, P(CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 75 MHz; CDCl<sub>3</sub>;  $\delta$  26.66 ppm, (P(CH<sub>2</sub>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>);  $\delta$  24.88 ppm (P(CH<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>);  $\delta$  24.83 ppm (P(C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>);  $\delta$  23.22 ppm (-SCH<sub>2</sub>CH<sub>3</sub>);  $\delta$  20.87 ppm (-SCH<sub>2</sub>CH<sub>3</sub>);  $\delta$  13.89 ppm, (P(C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); <sup>31</sup>P NMR: 121 MHz; CDCl<sub>3</sub>;  $\delta$  -21.42 ppm, (br s, -Cu{P(Bu<sub>3</sub>)<sub>2</sub>}). Complex 2 was prepared in a similar manner to 1: <sup>1</sup>H NMR: 300 MHz; CDCl<sub>3</sub>;  $\delta$  2.69 ppm (t, C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>S-);  $\delta$  1.56 ppm (br m, P(CH<sub>2</sub>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> overlapping with CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>S-);  $\delta$  1.41 ppm (br m, P(CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>3</sub>);  $\delta$  0.94 ppm (m, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>S- overlapping with P(C<sub>3</sub>H<sub>6</sub>CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR 75 MHz; CDCl<sub>3</sub>;  $\delta$  30.92 ppm, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>S-);  $\delta$  28.73 ppm (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>S-);  $\delta$  26.66 ppm (P(CH<sub>2</sub>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>);  $\delta$  24.96 ppm (P(CH<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>);  $\delta$  24.85 ppm (P(C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>);  $\delta$  13.91 ppm, (P(C<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>);  $\delta$  13.71 ppm (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>S-); <sup>31</sup>P NMR: 121 MHz; CDCl<sub>3</sub>;  $\delta$  -21.38 ppm, (br s, -Cu{P(Bu<sub>3</sub>)<sub>2</sub>}).

9. Brisdon, A.K. "Inorganic Spectroscopic Methods," Oxford University Press, UK, 1998.
10. (a) Welch, J.T.; Banger, K.K.; Ngo, S.C.; Claessen, R.U.; Toscano, P.J.; Eisenbraun, E.T.; Kaloyeros, A.E. *Book Of Abstracts ACS Spring 2000 National Meeting*, San Francisco, USA, March 2000. (b) Kaloyeros, A.K.; Welch, J.T.; Toscano, P.J.; Claessen, R.U.; Kornilov, A.; Banger, K.K. U.S. Patent 6099903, 2000. (c) Welch, J.T.; Toscano, P.J.; Claessen, R.U.; Kornilov, A.; Banger, K.K., International Patent WO 00/69863, 2000.
11. Reading, M. (to TA Instruments) U.S. Patents B1 5224775; 5248199; 5335993, 5346306.
12. Samples were characterized by transmission spectroscopy (Perkin Elmer, Lambda-19), scanning electron microscopy (SEM) (Hitachi S-3000N), Energy dispersive Spectroscopy (SEM-EDS) (EDAX), (accurate to  $\pm 3$  percent). XRD, Philips PW3710, (Cu K $\alpha$ , 1.541 Å). TA Instruments Hi-Res-TGA, 2950, TA Instruments DSC 910, and MDSC 2920.

Figure 1. Low temperature DSC Studies.

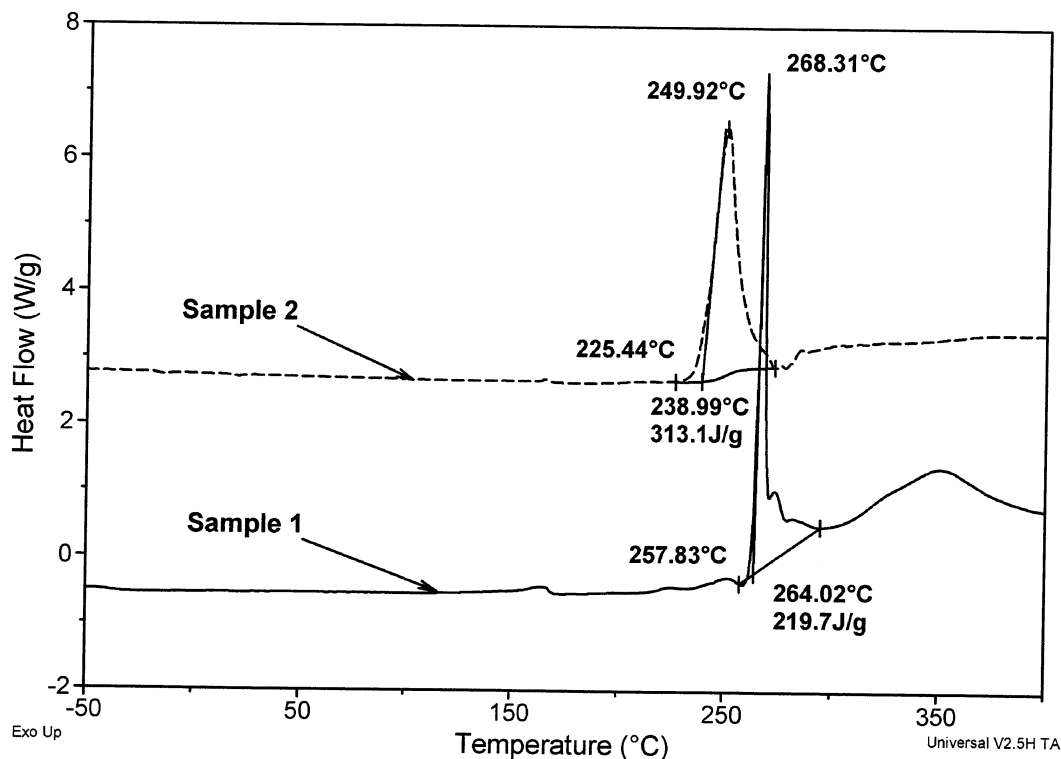


Figure 2. TGA profile for  $[\{P(n-Bu)_3\}_2Cu(S(n-Pr))_2In(S(n-Pr))_2]$ , **2**.

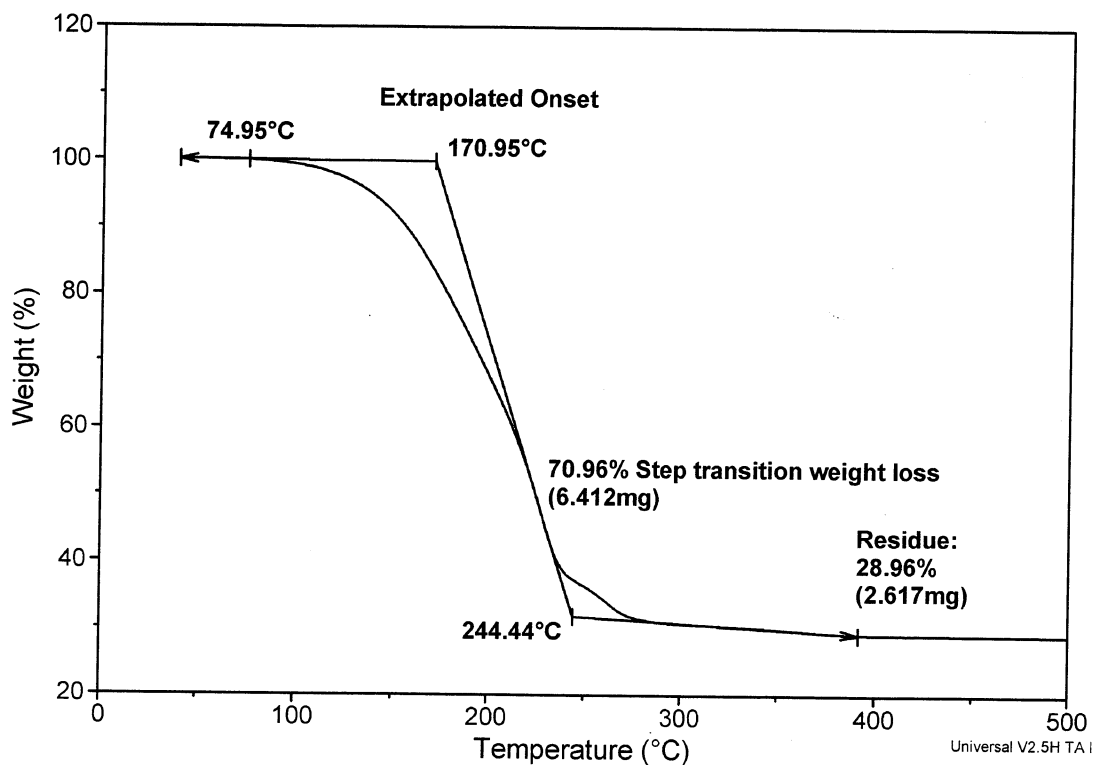


Figure 3. Low temperature MDSC for  $[\{P(n-Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$  **1** and  $[\{P(n-Bu)_3\}_2Cu(S(n-Pr))_2In(S(n-Pr))_2]$  **2**.

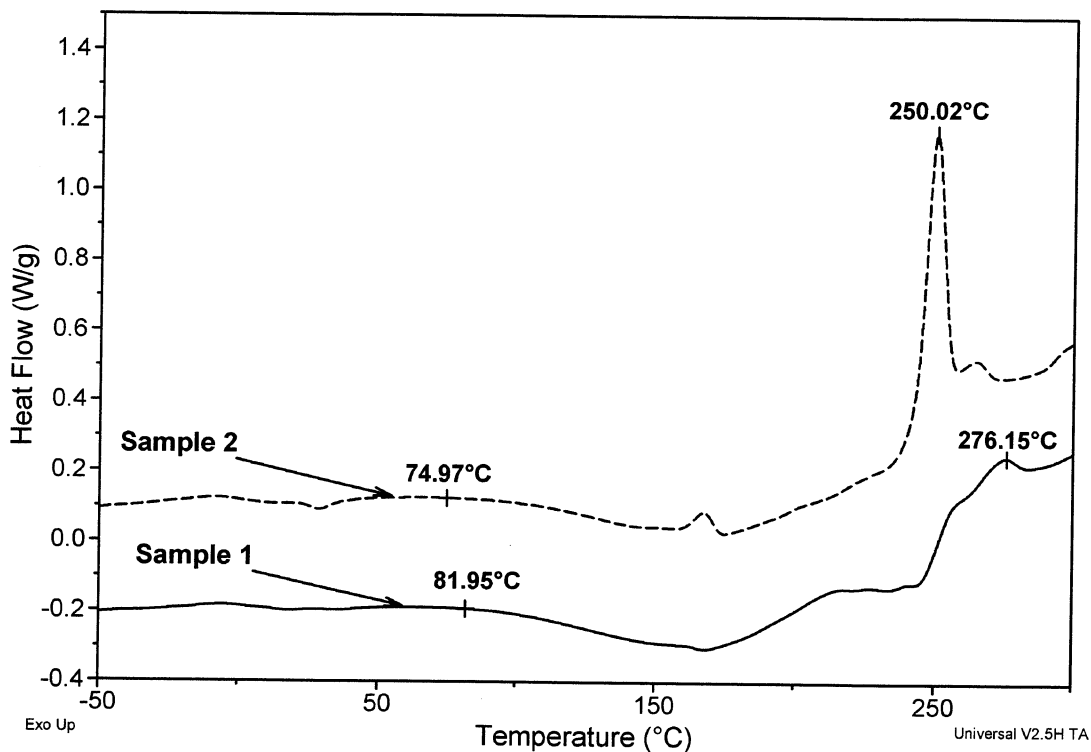




Figure 4. EGA-FTIR spectra for  $[\{P(n-Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$  1.

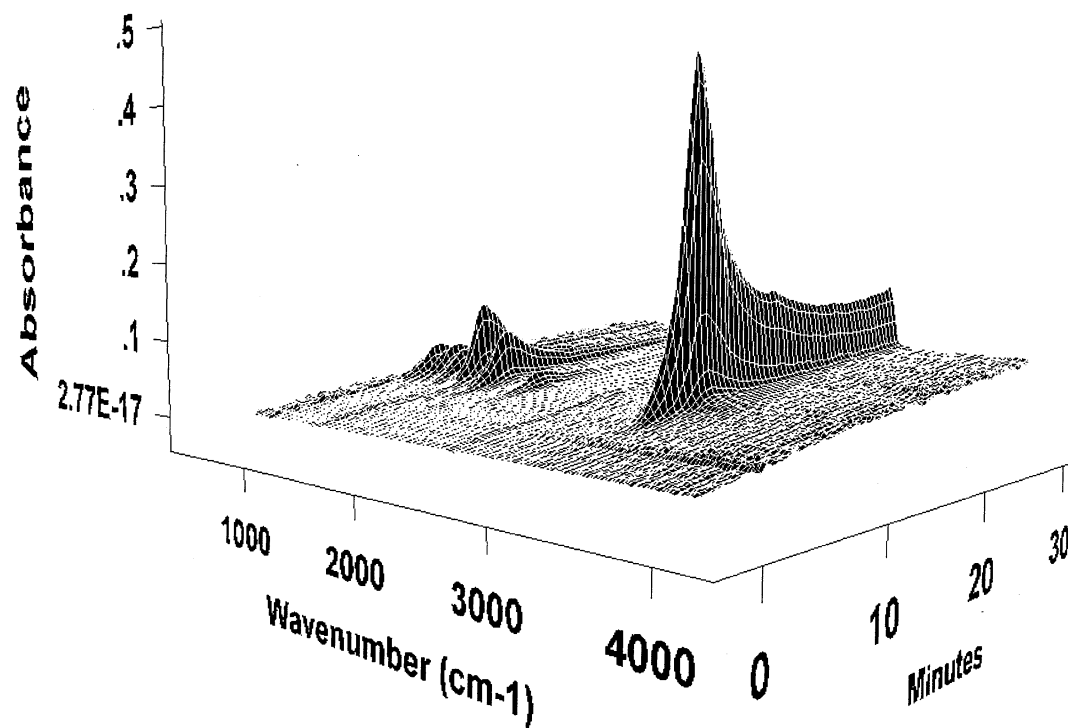
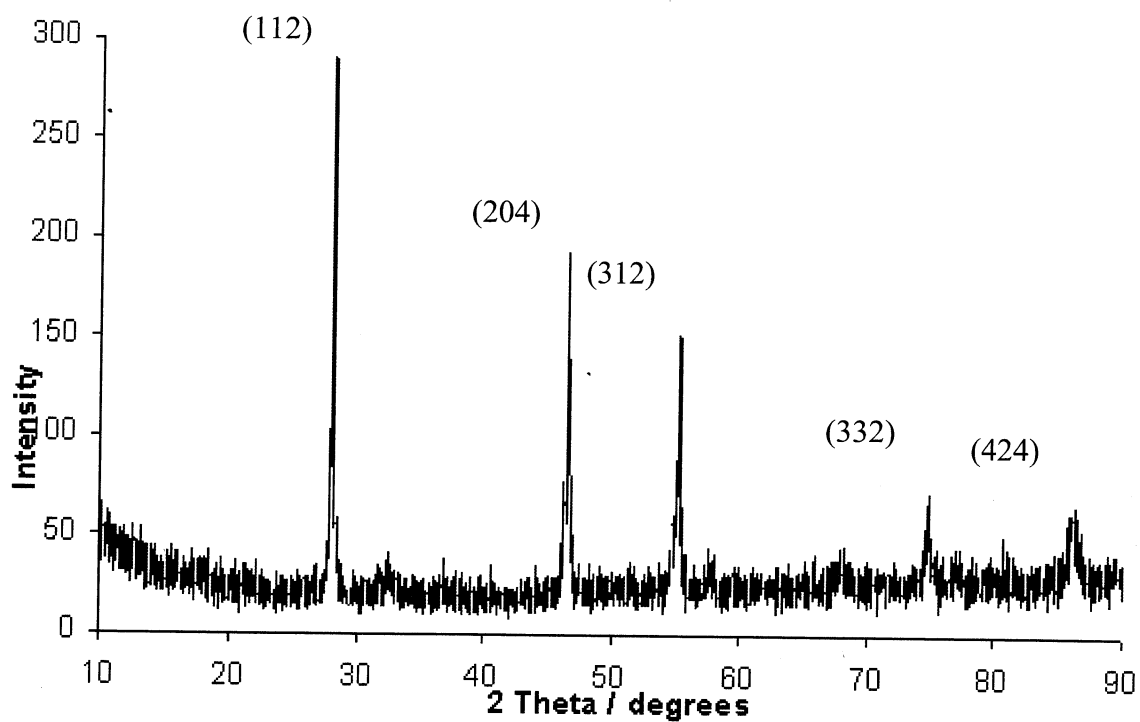


Figure 5. XRD Powder Diffraction for non-volatile residue from pyrolysis of  $[\{P(n-Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$ , (Cu  $K\alpha$ , 1.541 Å).

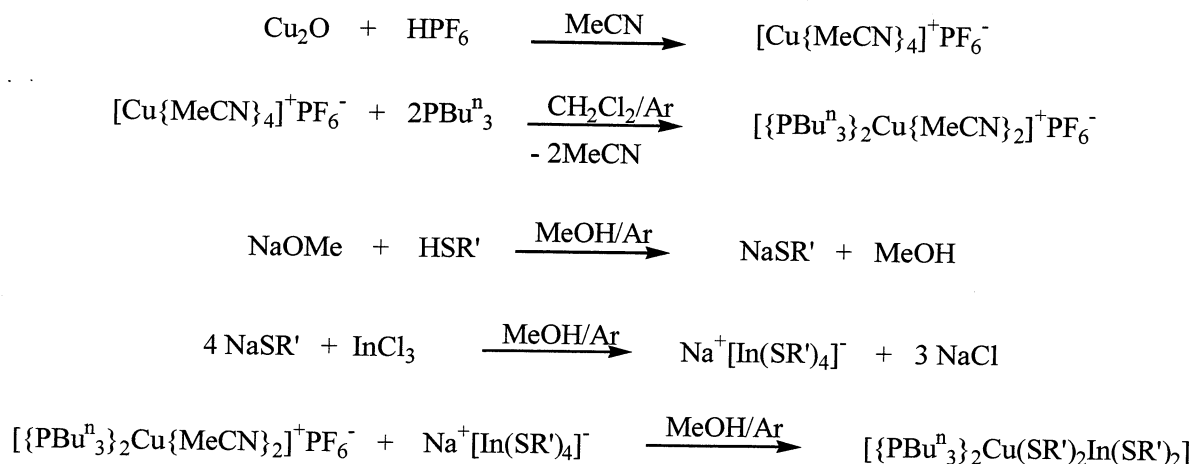




## Appendix A

### Supporting Information

Scheme 1: Preparation of single source CuInS<sub>2</sub> precursors.



**Synthesis of 1:** All manipulations were carried out under anaerobic condition. NaSEt was prepared *in situ* by reaction of NaOEt (1.31 g, 24.25 mmol) with EtSH (1.43 g, 23.01 mmol) in anhydrous methanol. After 30 min InCl<sub>3</sub> (1.27 g, 5.75 mmol) was added. The mixture was stirred for 1hr. [Cu(CH<sub>3</sub>CN)<sub>2</sub>(PBU<sub>3</sub>)<sub>2</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (4.0 g, 5.75 mmol), dissolved in anhydrous methanol (20 mL) was added dropwise to the reaction flask. The mixture was stirred (~3 d) resulting in the precipitation of a white solid. The reaction solution was then concentrated and the product extracted with anhydrous CH<sub>2</sub>Cl<sub>2</sub> (50 mL,) and filtered through celite to remove the inorganic salts. The collected filtrate was concentrated via rotary evaporation, which afforded the clear liquid precursor (69 %). Complex 2 was prepared in an analogous manner, (71 %).

Figure 1. EGA-FTIR spectra for  $[\{P(n-Bu)_3\}_2Cu(SPr^n)_2In(SPr^n)_2]$ , 2

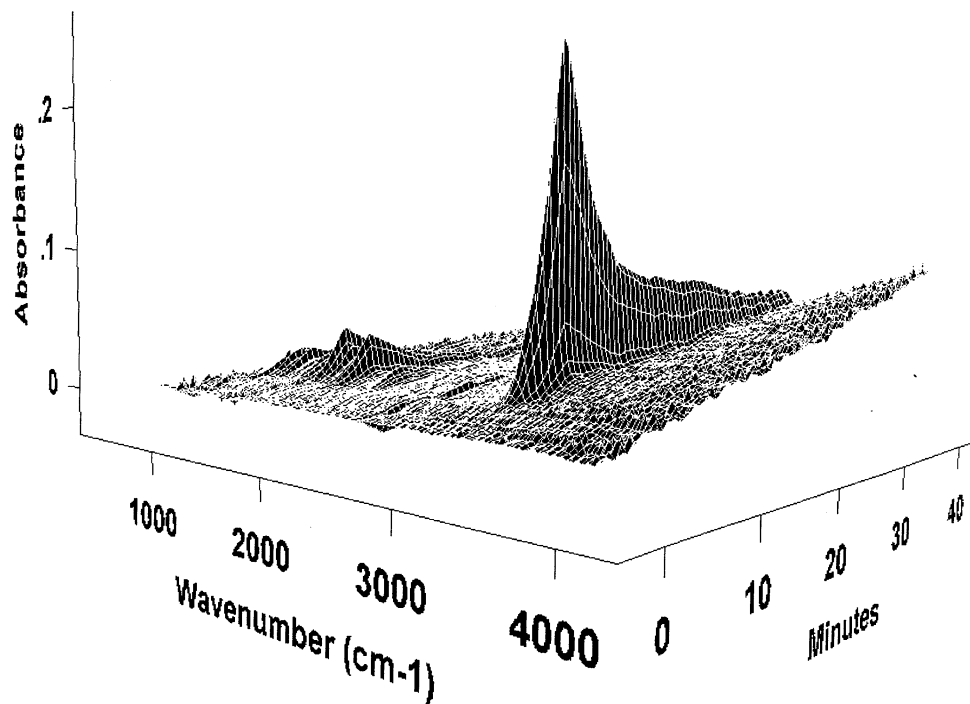


Figure 2. TGA Profile for  $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2]$ , 1 .

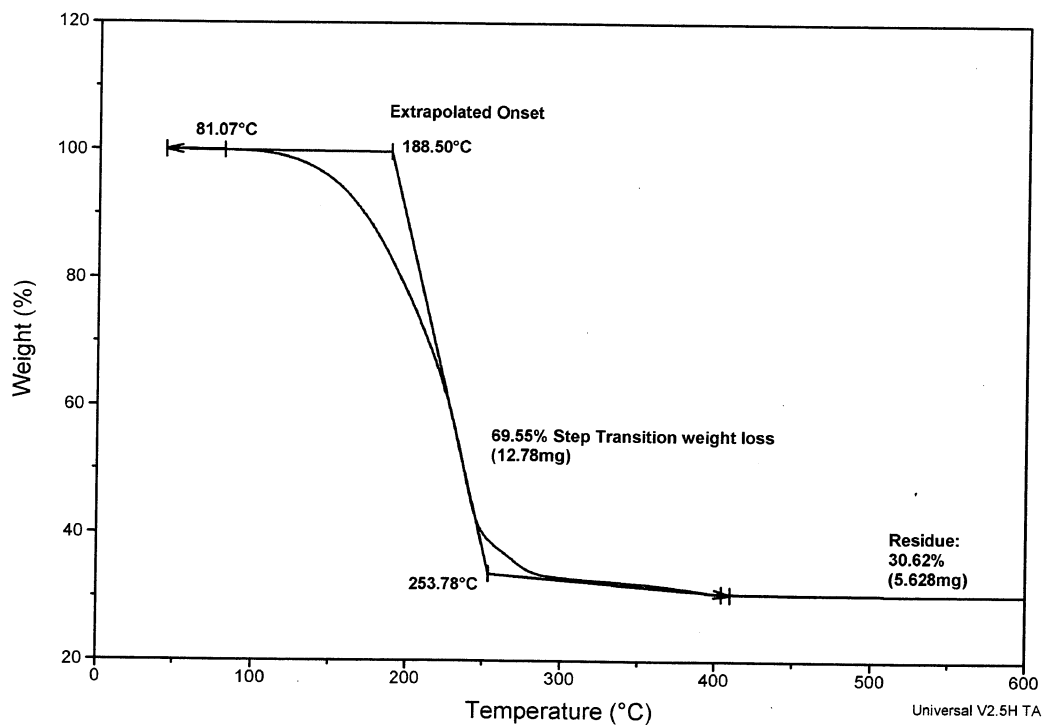


Figure 3. Vacuum TGA for  $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2]$ , 1 .

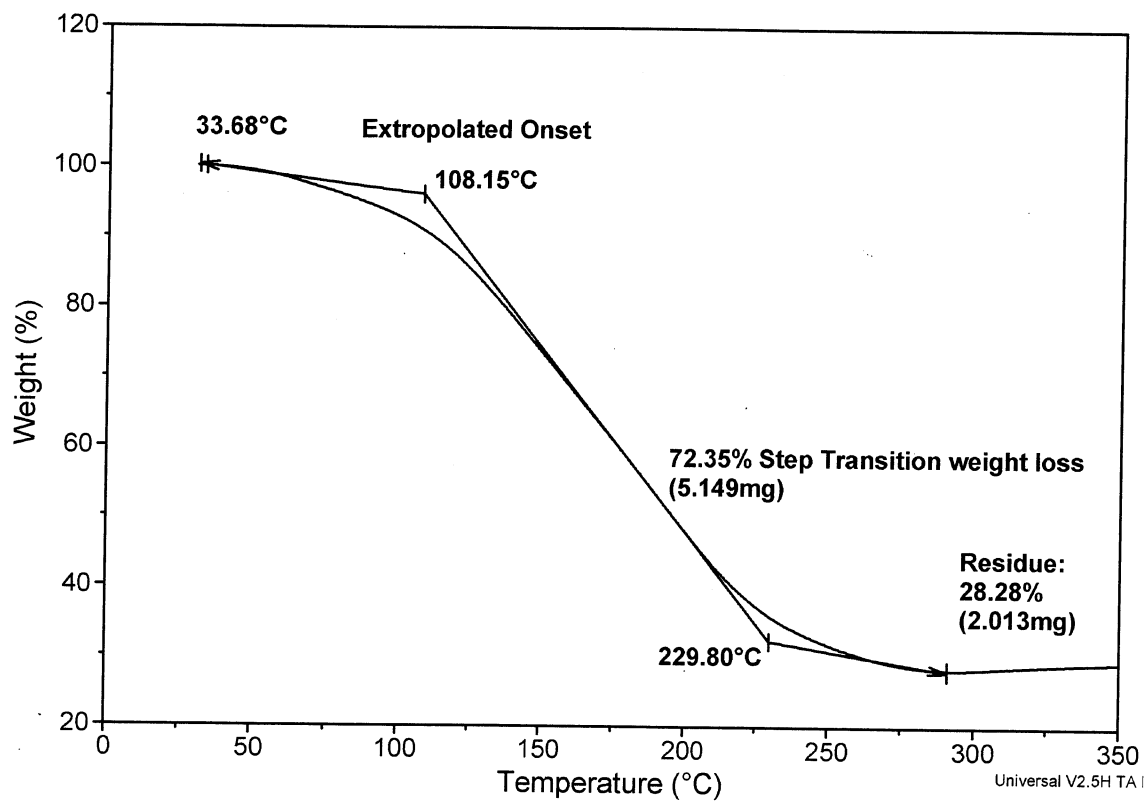
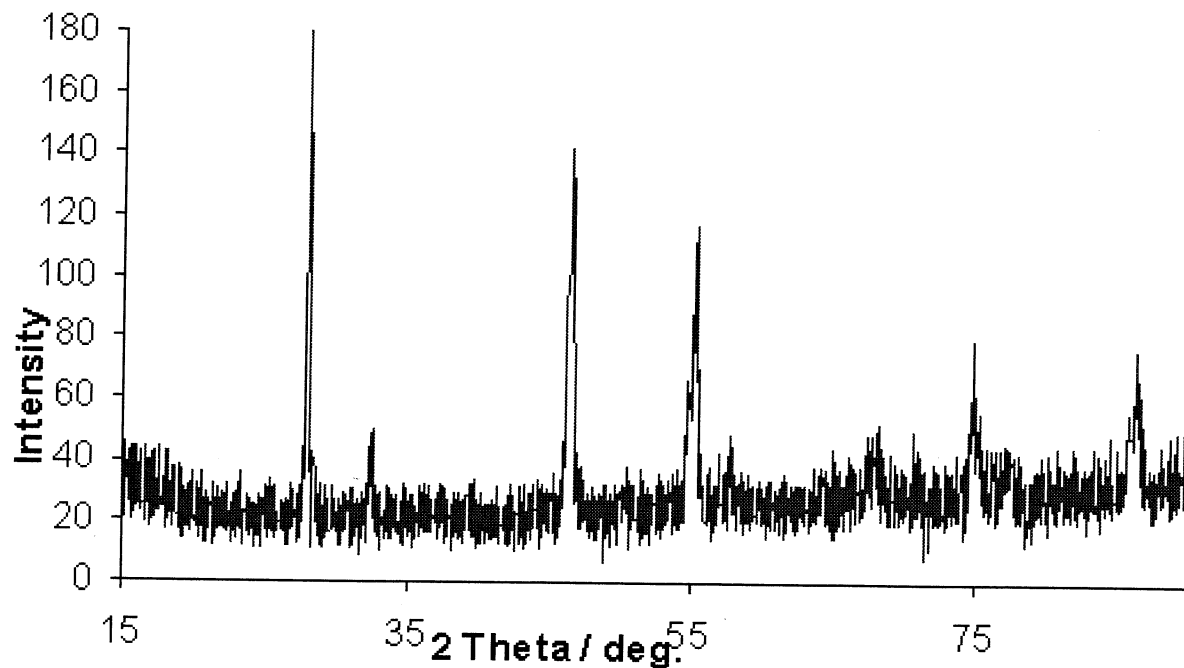


Figure 4. X-ray Powder Diffraction spectra for  $[\{P(n-Bu)_3\}_2Cu(SPr^n)_2In(SPr^n)_2]$ , **2**, (Cu  $K\alpha$ , 1.541 Å).



Diffractometer type: PW3710

Diffractometer number: 1

Anode: Cu

Wavelength Alpha1: 1.54060

Intensity ratio (alpha2/alpha1): 0.50000

Monochromator used: YES

Generator voltage [kV]: 45

Start angle [X2]: 10.0100

Type of scan: CONTINUOUS

ConvertedTo, FIXED, /

Wavelength Alpha2: 1.54439

Divergence slit: 1 Receiving slit: 0.2

Generator current [mA]: 40

End angle [X2]: 89.9900 Step size [X2]: 0.020

Time per step [s]: 1.00

**Peaks, /**

27.9550	100
28.0750	95
32.4850	14
46.3600	77
50.3800	4
55.2500	66
57.7400	11
68.0100	8
74.7900	28
77.2700	11
86.1100	30

Table 1: Acquisition Data for Powder XRD :  $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2], 1$

Diffractometer type: PW3710	Anode: Cu
Diffractometer number: 1	Wavelength Alpha2: 1.54439
Wavelength Alpha1: 1.54060	Receiving slit: 0.2
Intensity ratio (alpha2/alpha1): 0.50000	Generator current [mA]: 40
Divergence slit: 1	End angle [X2]: 89.9900
Monochromator used: YES	Type of scan: CONTINUOUS
Generator voltage [kV]: 45	ConvertedTo,FIXED,/
Start angle [X2]: 10.0100	
Step size [X2]: 0.020	
Time per step [s]: 1.00	

**Peaks,/**

28.1350	100
32.5450	10
46.5350	81
46.7200	83
55.2650	62
57.7650	9
67.7800	8
74.9950	26
77.0950	9
86.2650	29

Figure 5a: EDS spectra for  $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2], 1$ .

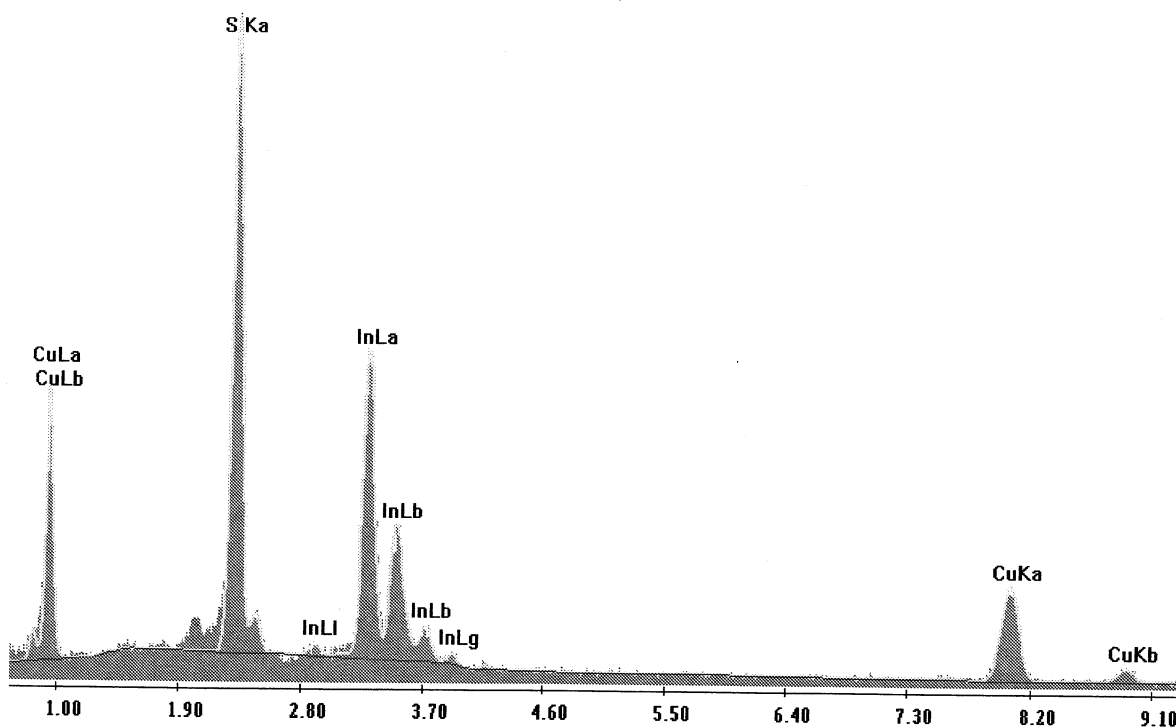
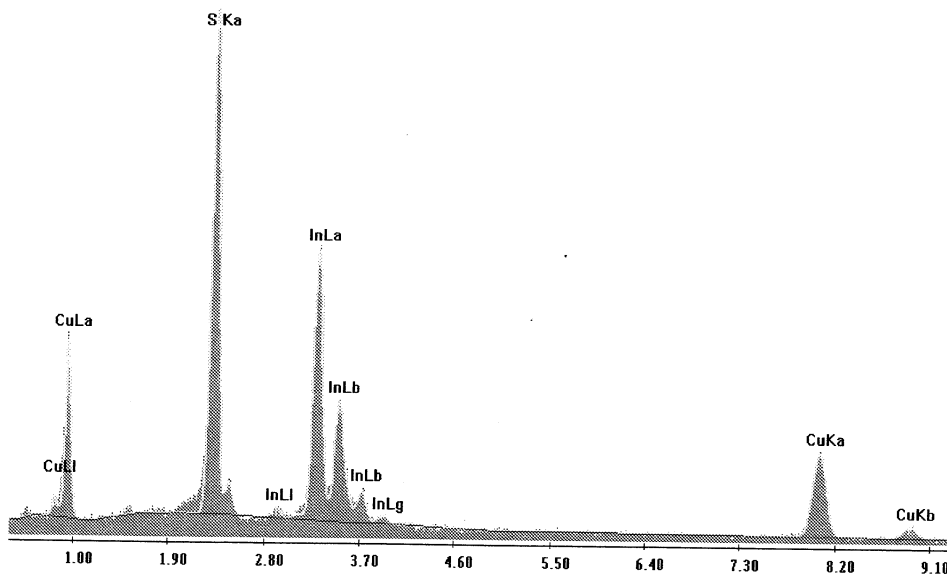


Figure 5b. EDS spectra for  $[\{P(n-Bu)_3\}_2Cu(SPr^i)_2In(SPr^i)_2]$ , **2**.



Elem	Wt %	At %	K-Ratio	Z	A	F
S K	25.94	<b>48.70</b>	0.2037	1.1569	0.6715	1.0109
InL	44.62	<b>23.40</b>	0.3629	0.9051	0.8987	1.0000
CuK	29.44	<b>27.90</b>	0.2826	1.0016	0.9584	1.0000
Total	100.00	<b>100.00</b>				

Element Net Inte. Backgrd Inte. Error P/B

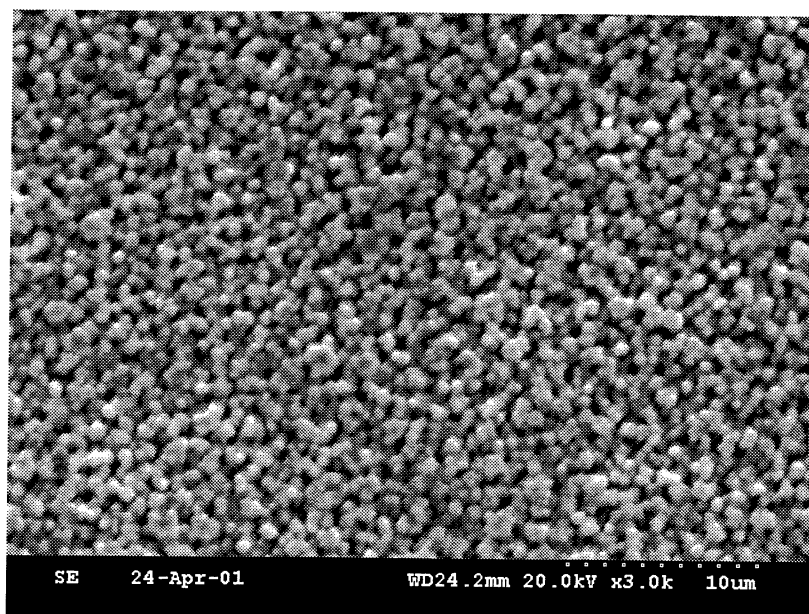
S K	155.55	8.43	0.84	18.45
InL	87.25	6.45	1.15	13.53
CuK	42.70	2.88	1.63	14.83

kV: 20.00 Tilt: 0.00 Take-off: 29.88 Tc: 50.0

Det Type: SUTW, Sapphire Res: 128.39 Lsec: 100



Figure 6. SEM of non-volatile residue from TGA for  $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2]$ , **1**.



Grain size  $\sim 1\mu m$

Figure 7. SEM of non-volatile residue from TGA for  $[\{P(n-Bu)_3\}_2Cu(SPr^m)_2In(SPr^m)_2]$ , **2**.

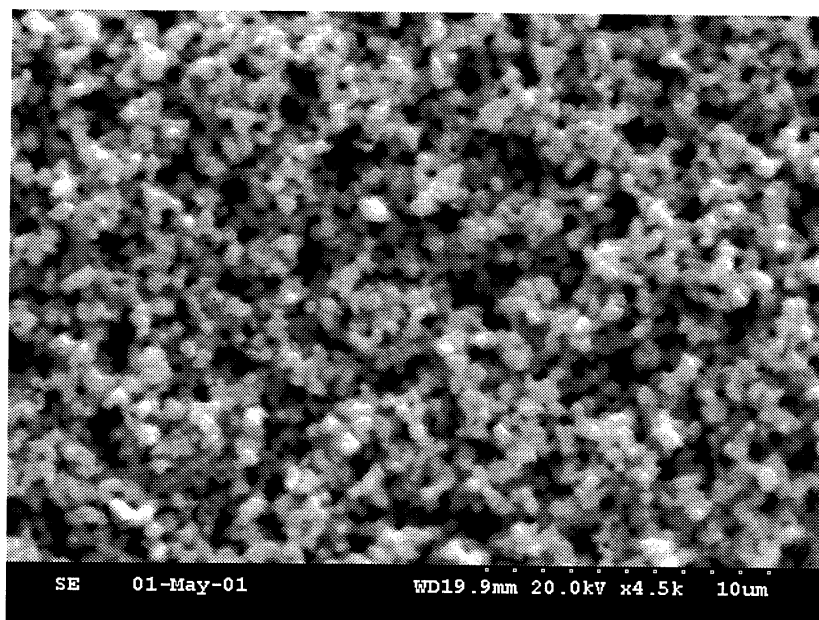
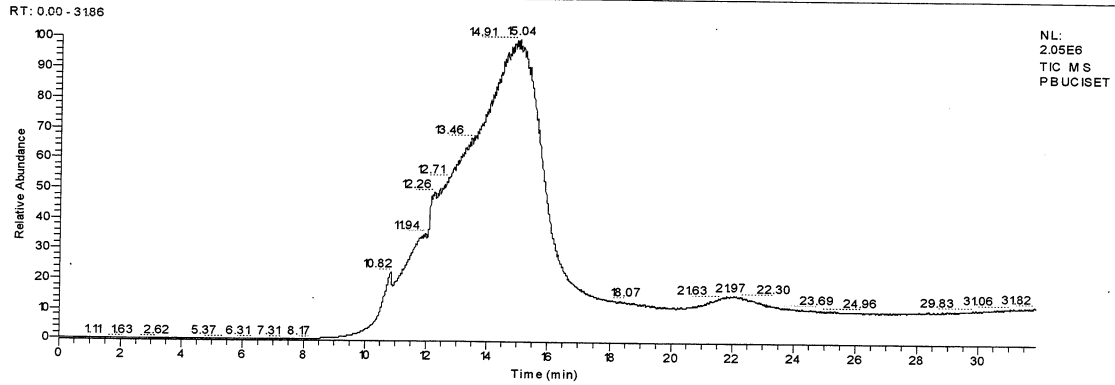


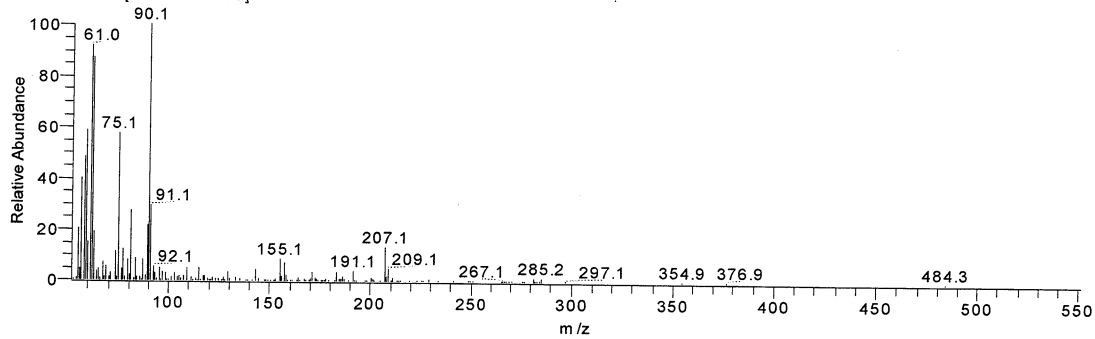
Figure 8: EGA: Mass Spec data from TGA for  $[\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2]$ , 1.

D:\cis-thermal anal\mass-spec\PBUCISET

04/30/2001 11:23:29 AM

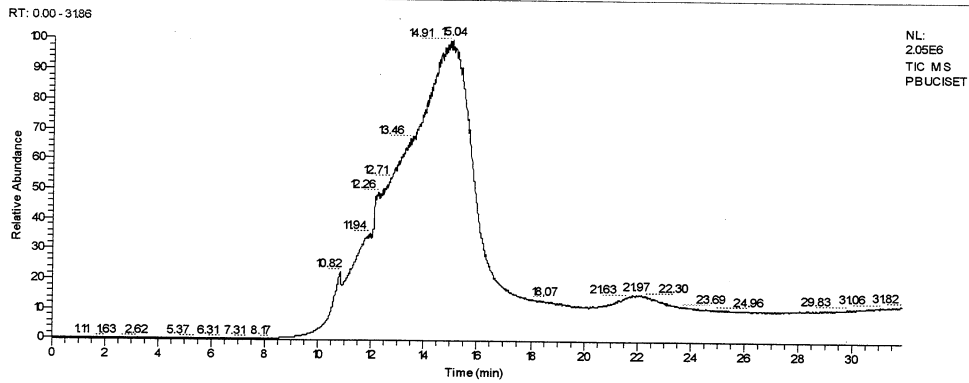


PBUCISET #888 RT: 8.82 AV: 1 NL: 1.36E3  
T: + c Full ms [ 50.00-650.00]

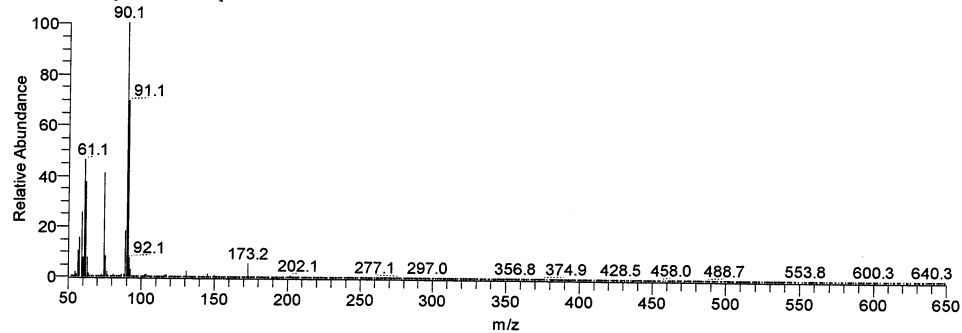


D:\cis-thermal anal\mass-spec\PBUCISET

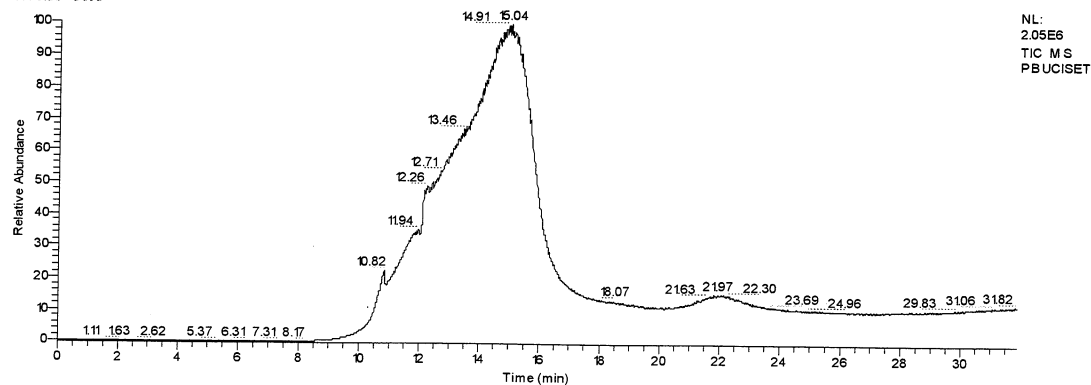
04/30/2001 11:23:28 AM



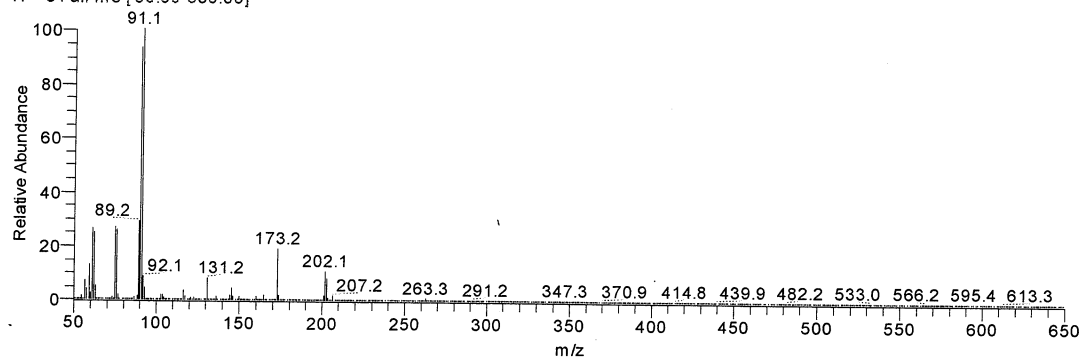
PBUCISET #924-1085 RT: 9.17-10.67 AV: 162 NL: 2.22E4  
T: + c Full ms [ 50.00-650.00]



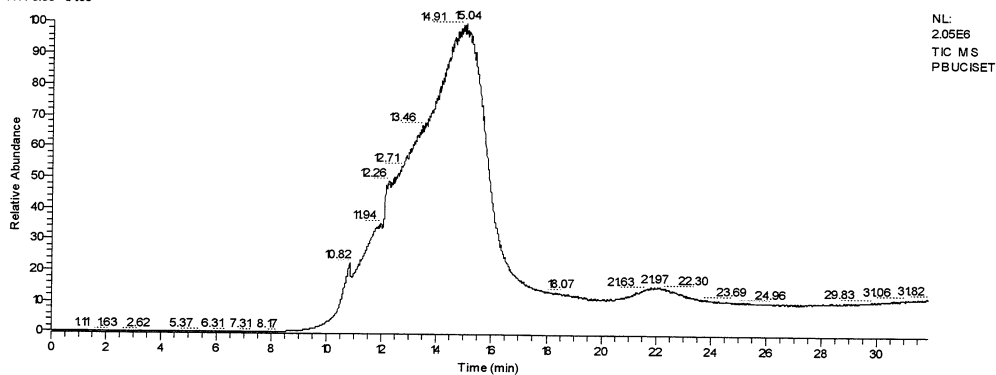
RT: 0.00 - 3186



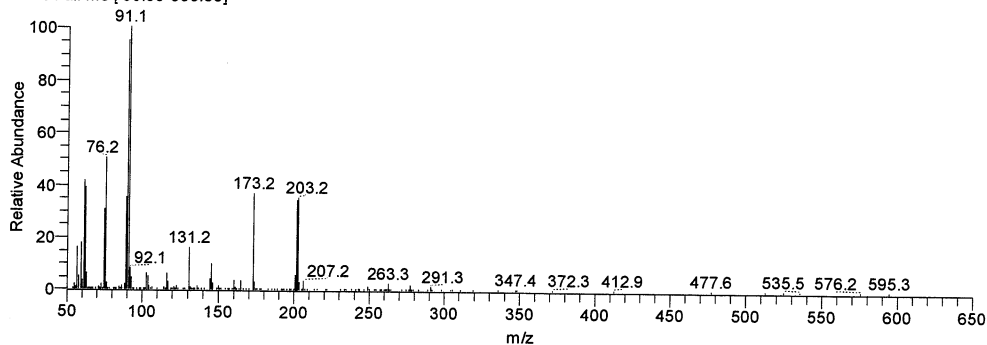
PBUCISET #1102-1262 RT: 10.82-12.21 AV: 161 NL: 1.30E5  
T: + c Full ms [ 50.00-650.00]



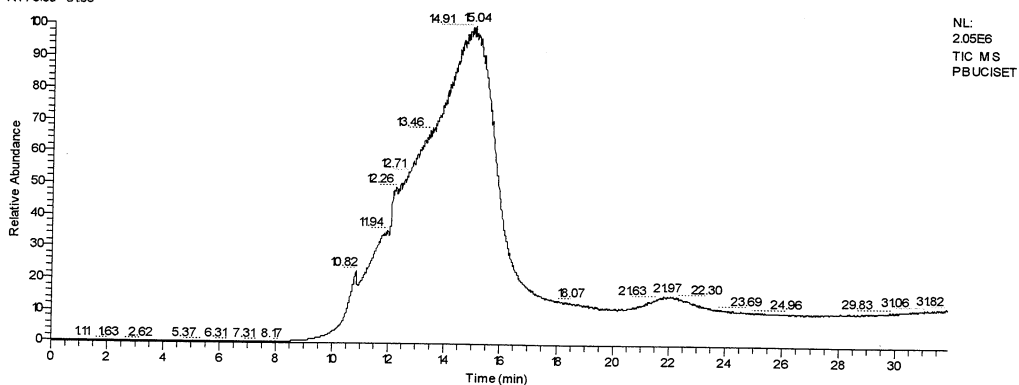
RT: 0.00 - 3186



PBUCISET #1274 RT: 12.32 AV: 1 NL: 1.46E5  
T: + c Full ms [ 50.00-650.00]

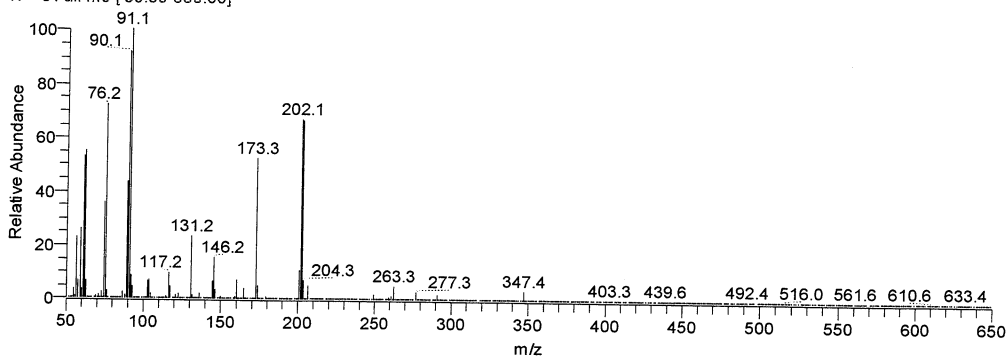


RT: 0.00 - 31.86

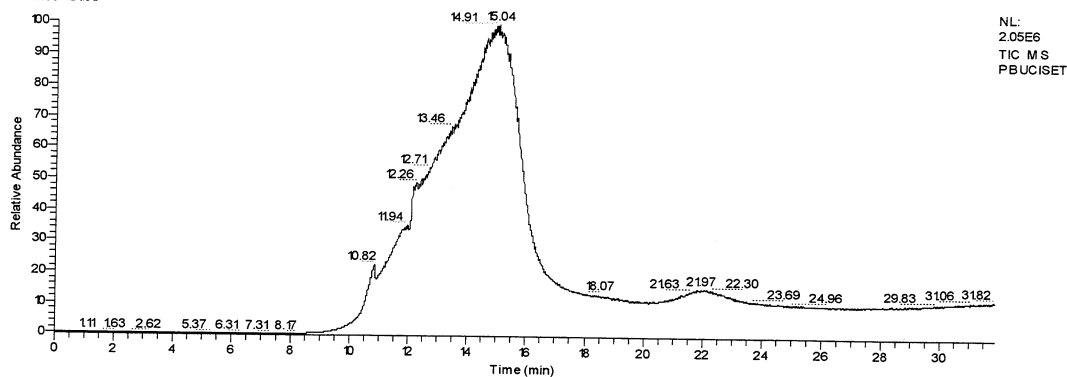


PBUCISET #1257-1371 RT: 12.17-13.16 AV: 115 NL: 1.23E5

T: + c Full ms [ 50.00-650.00]

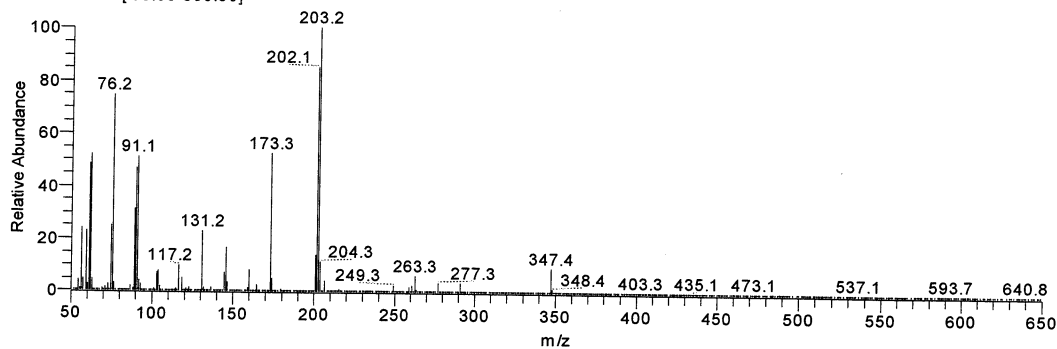


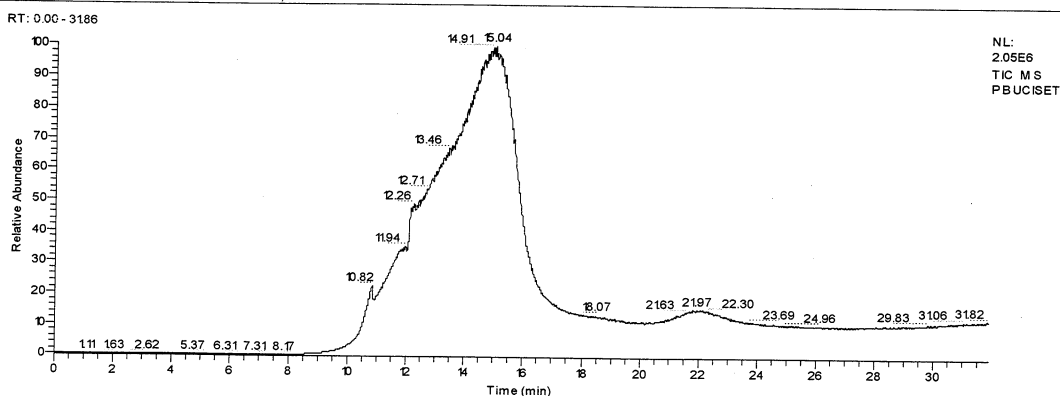
RT: 0.00 - 31.86



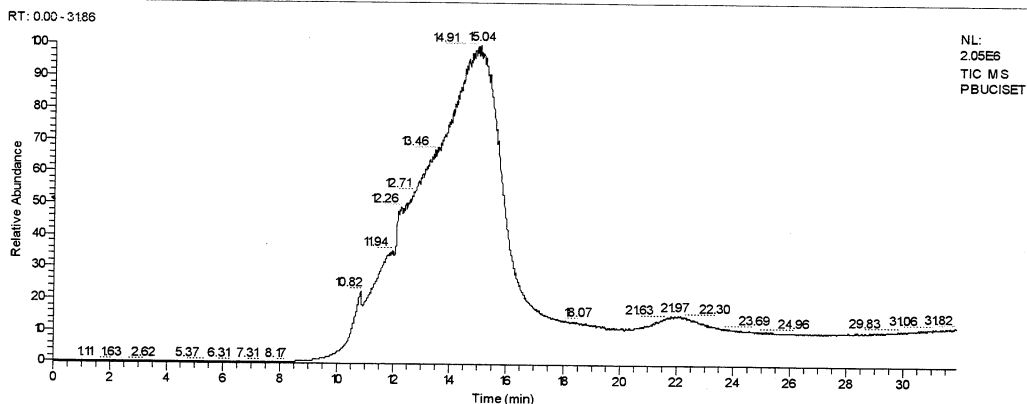
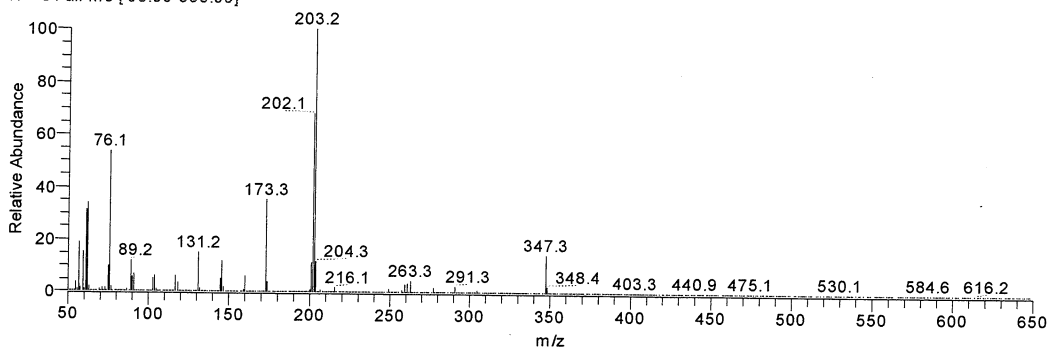
PBUCISET #1348-1434 RT: 12.96-13.71 AV: 87 NL: 1.59E5

T: + c Full ms [ 50.00-650.00]

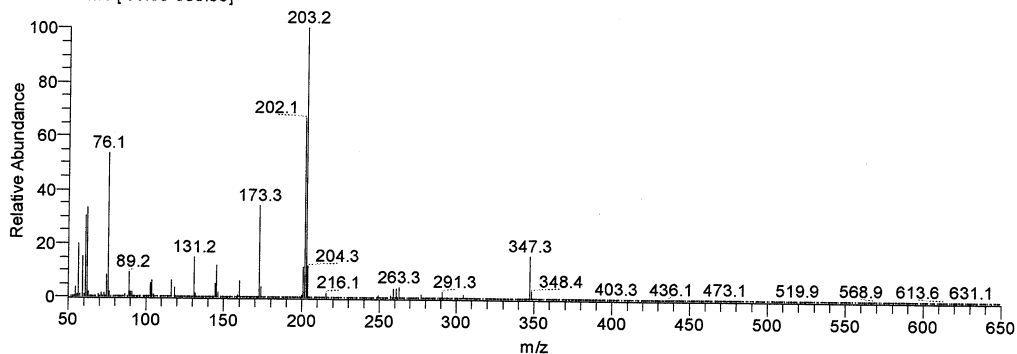




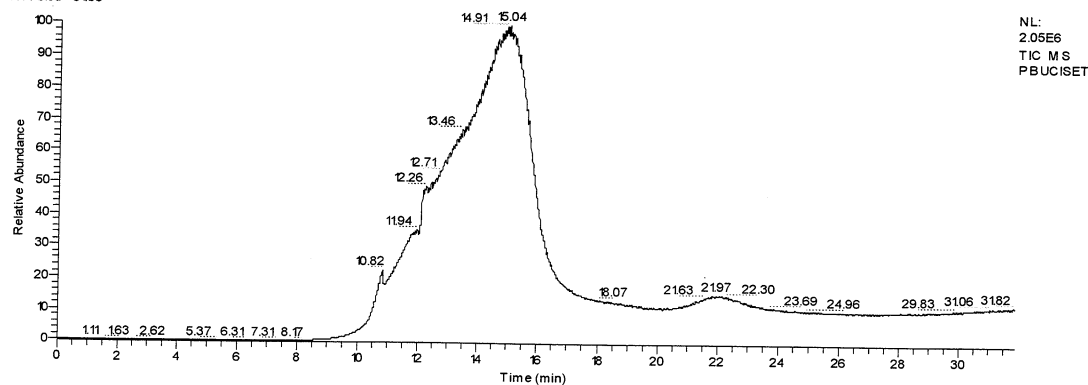
PBUCISET #1462-1531 RT: 13.96-14.56 AV: 70 NL: 3.17E5  
T: + c Full ms [ 50.00-650.00]



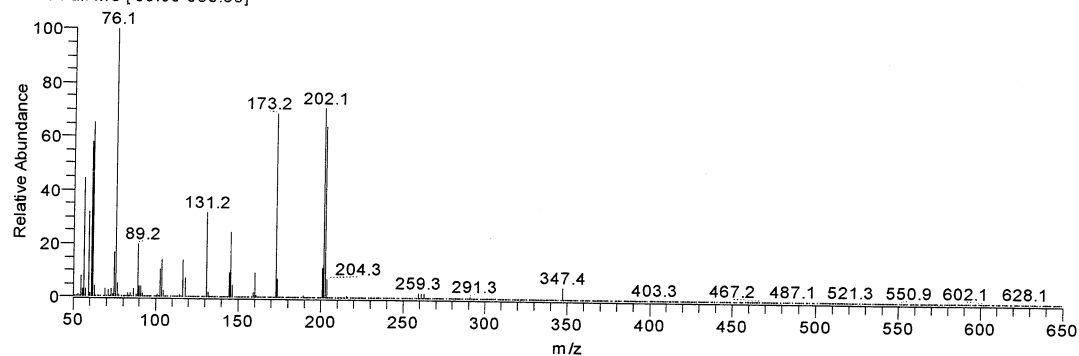
PBUCISET #1570-1707 RT: 14.90-16.10 AV: 138 NL: 2.94E5  
T: + c Full ms [ 50.00-650.00]



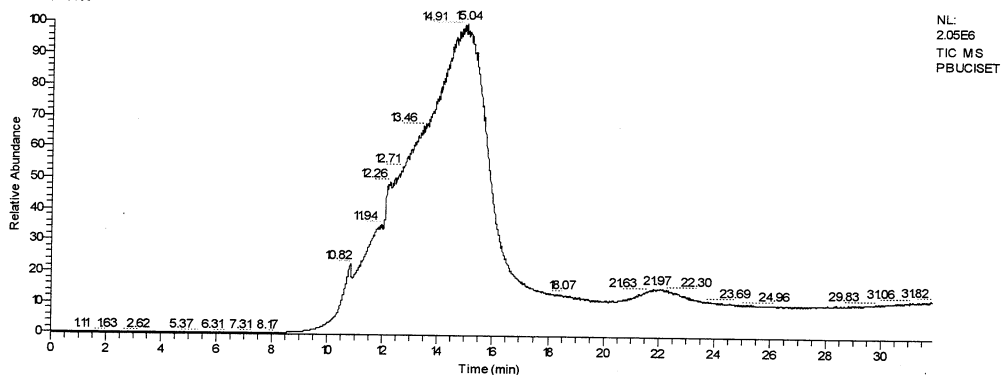
RT: 0.00 - 31.86



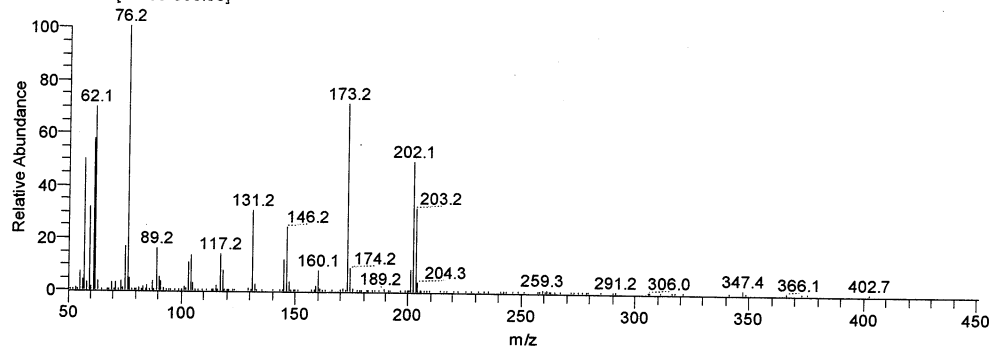
PBUCISET #1725-1856 RT: 16.26-17.40 AV: 132 NL: 5.35E4  
T: + c Full ms [ 50.00-650.00]

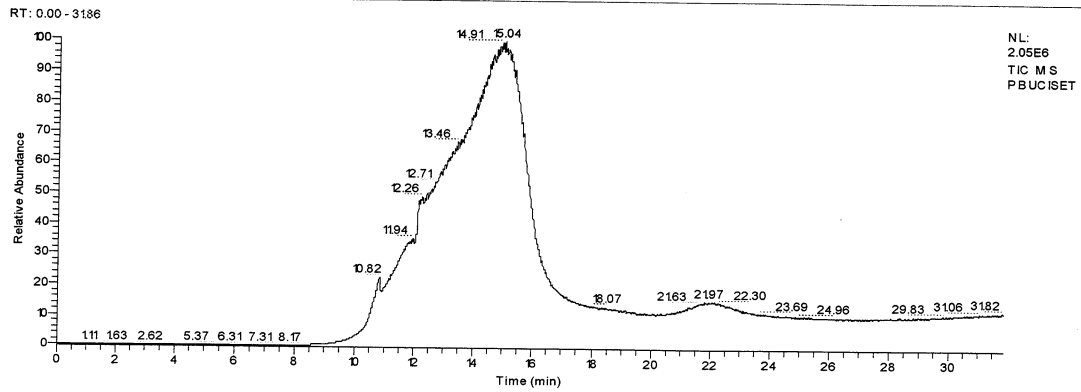


RT: 0.00 - 31.86

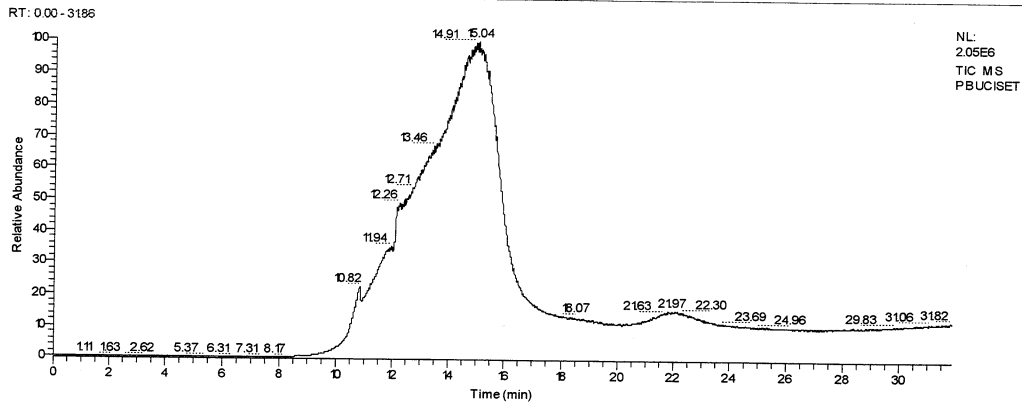
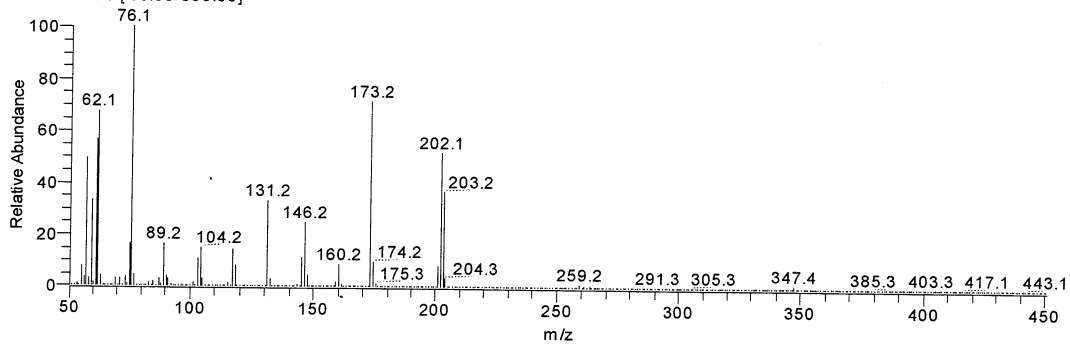


PBUCISET #2168 RT: 20.14 AV: 1 NL: 3.23E4  
T: + c Full ms [ 50.00-650.00]

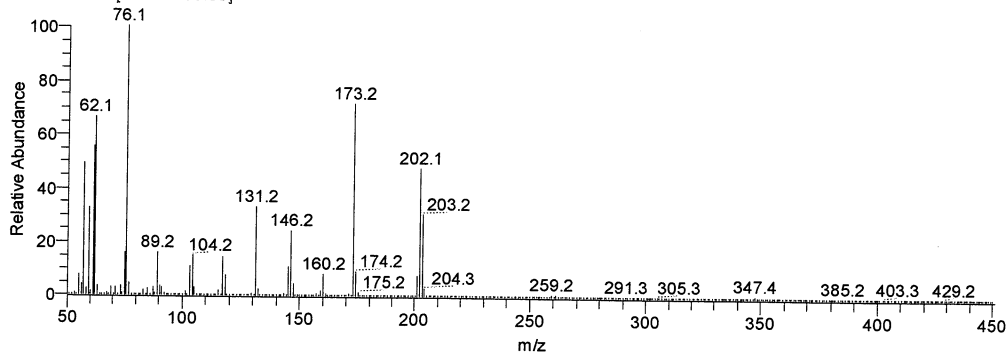


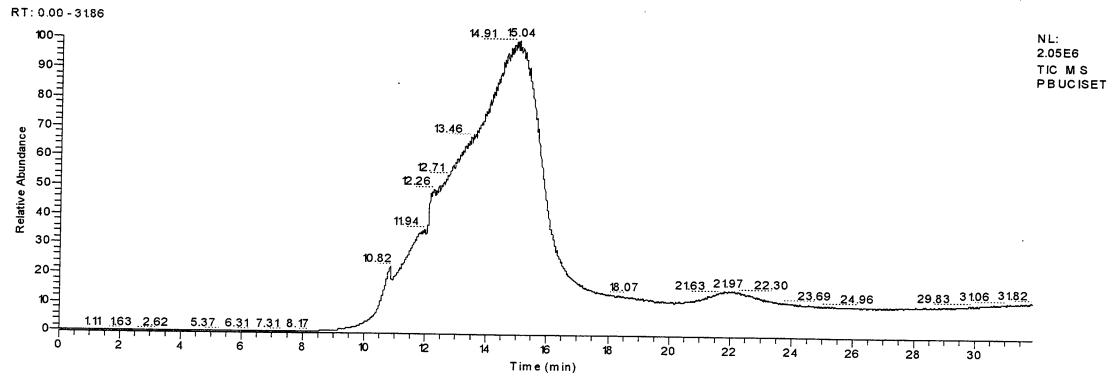


PBUCISET #2236-2532 RT: 20.74-23.34 AV: 297 NL: 3.88E4  
T: + c Full ms [ 50.00-650.00]



PBUCISET #2549-3500 RT: 23.49-31.86 AV: 952 NL: 3.12E4  
T: + c Full ms [ 50.00-650.00]





PBUCISET #2549-3500 RT: 23.49-31.86 AV: 952 NL: 3.12E4  
T: + c Full m s [ 50.00-650.00]

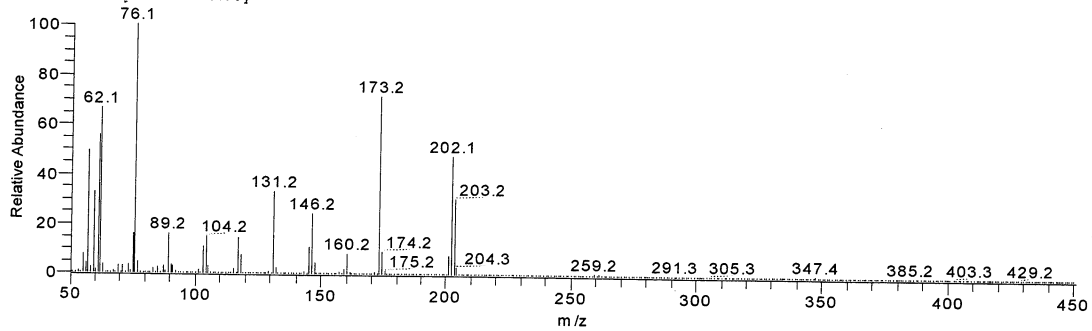
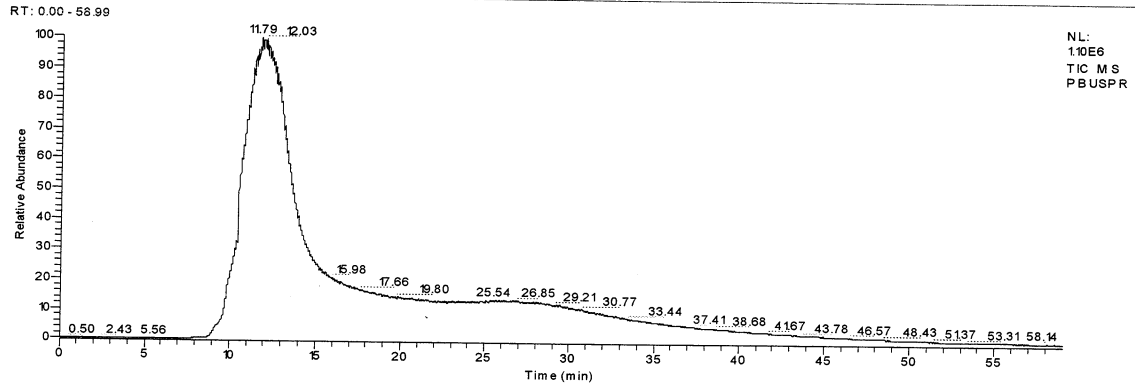




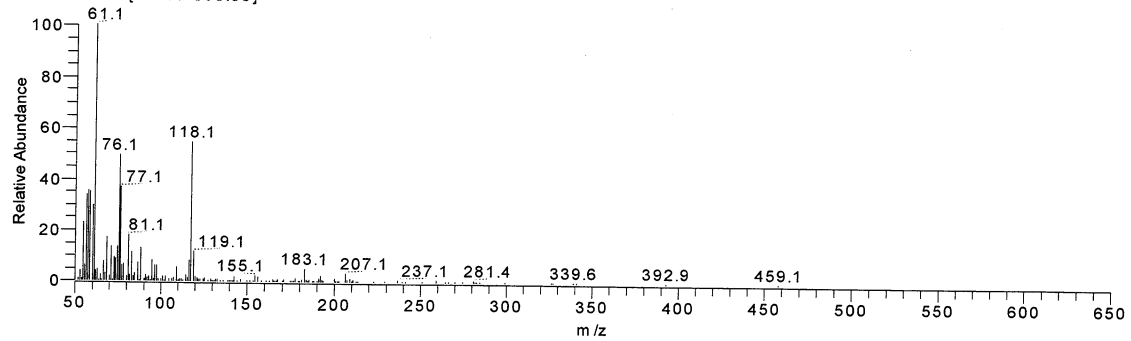
Figure 9. EGA: Mass Spec data from TGA for  $[\{P(n-Bu)_3\}_2Cu(SPr^n)_2In(SPr^n)_2]$ , 1.

D:\cis-thermal anal\mass-spec\PBUSPR

05/01/2001 10:53:13 AM

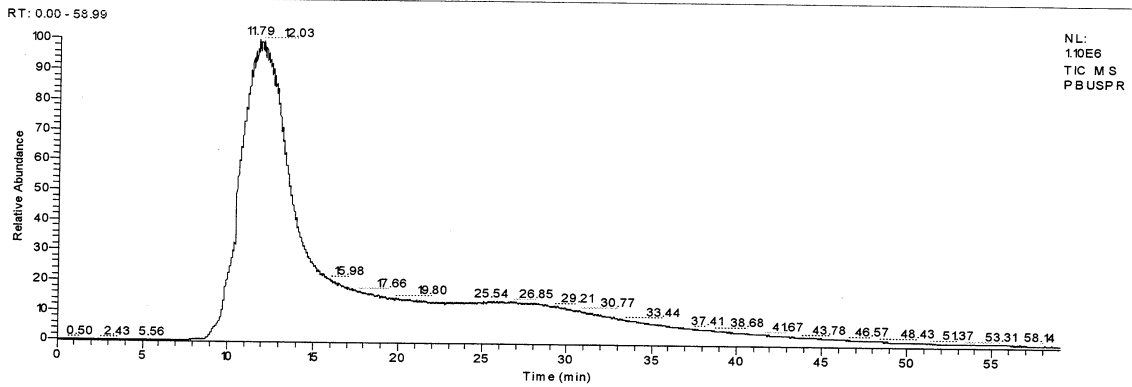


PBUSPR #865 RT: 8.59 AV: 1 NL: 1.10E3  
T: + c Full ms [50.00-650.00]

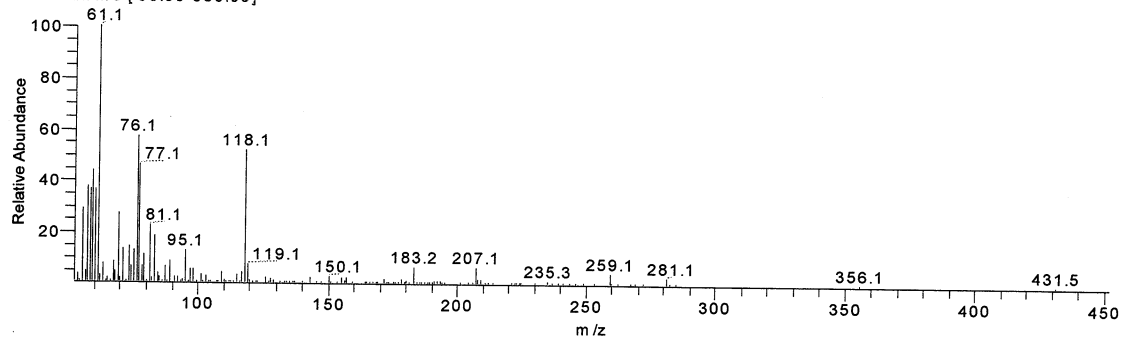


D:\cis-thermal anal\mass-spec\PBUSPR

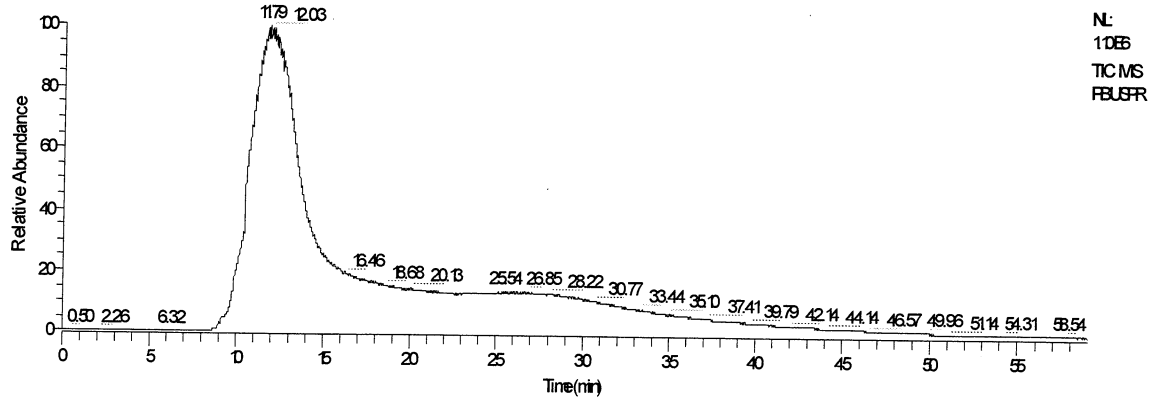
05/01/2001 10:53:13 AM



PBUSPR #846 RT: 8.40 AV: 1 NL: 8.02E2  
T: + c Full ms [50.00-650.00]

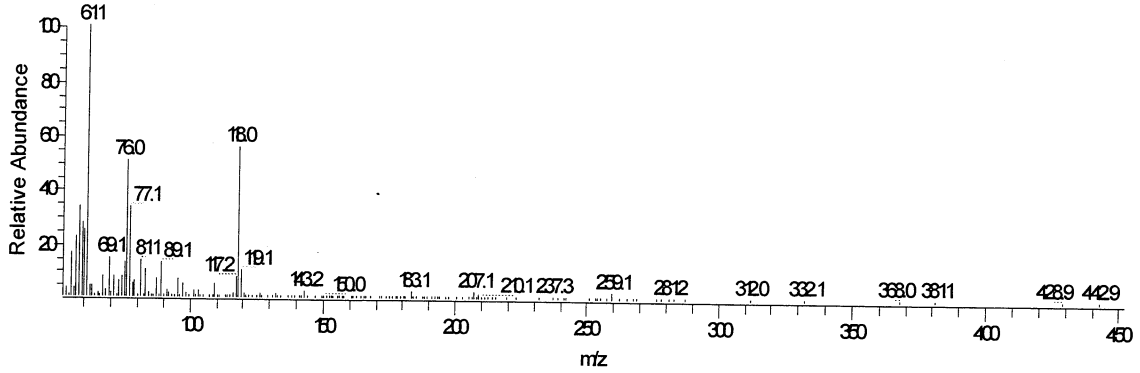


RT: 0.00 - 58.99

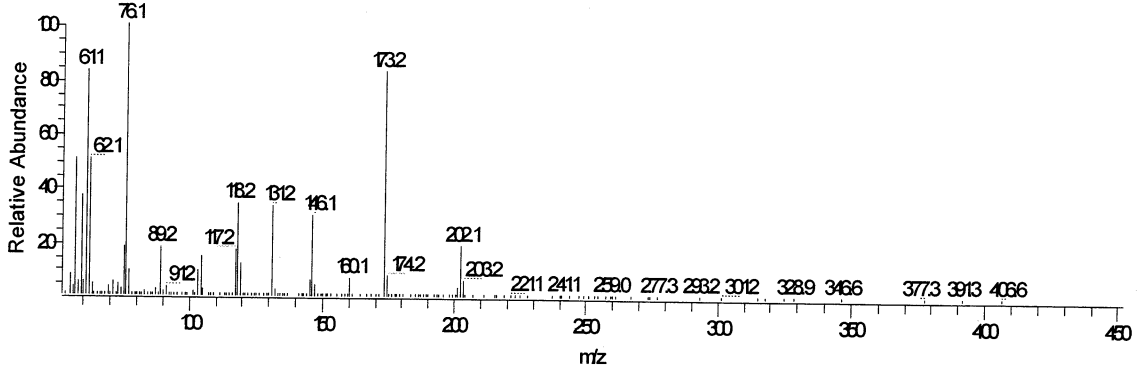


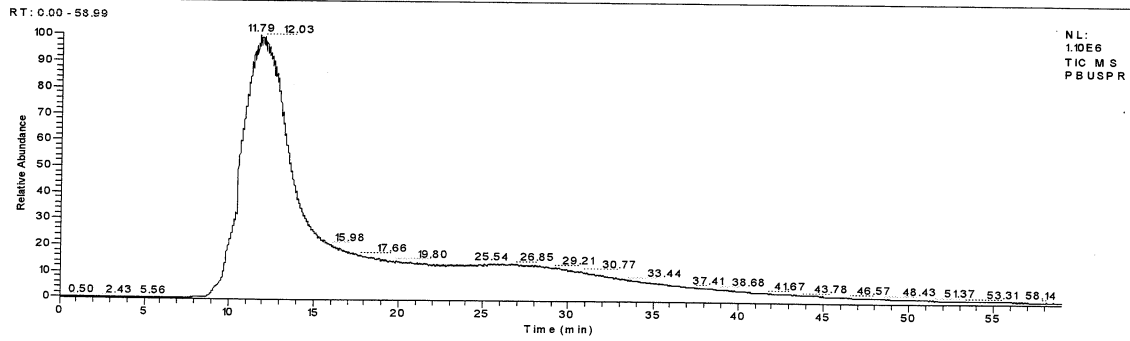
NL  
10E6  
TIC:MS  
FBUSPR

FBUSPR#374 RT: 8.68 AV: 1 NL: 138E3  
T: +cFull.ms[500065000]

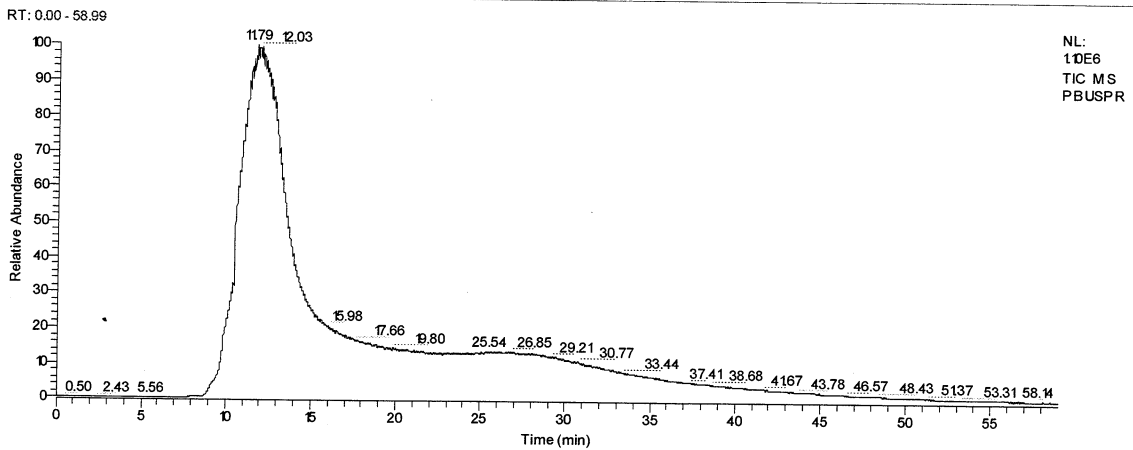
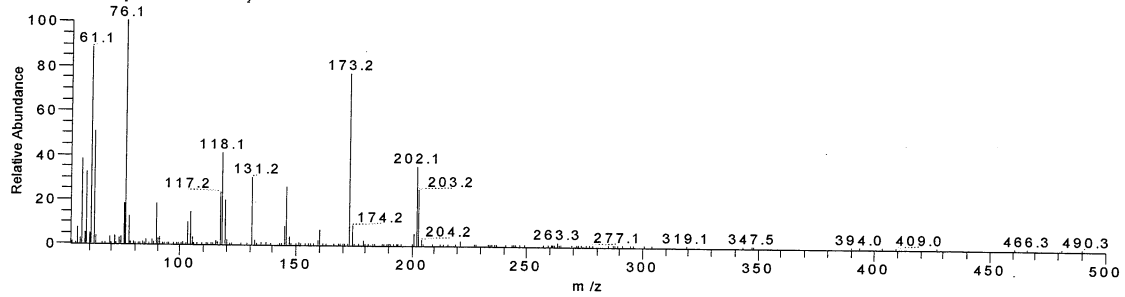


FBUSPR#370 RT: 9.60 AV: 1 NL: 16E4  
T: +cFull.ms[500065000]

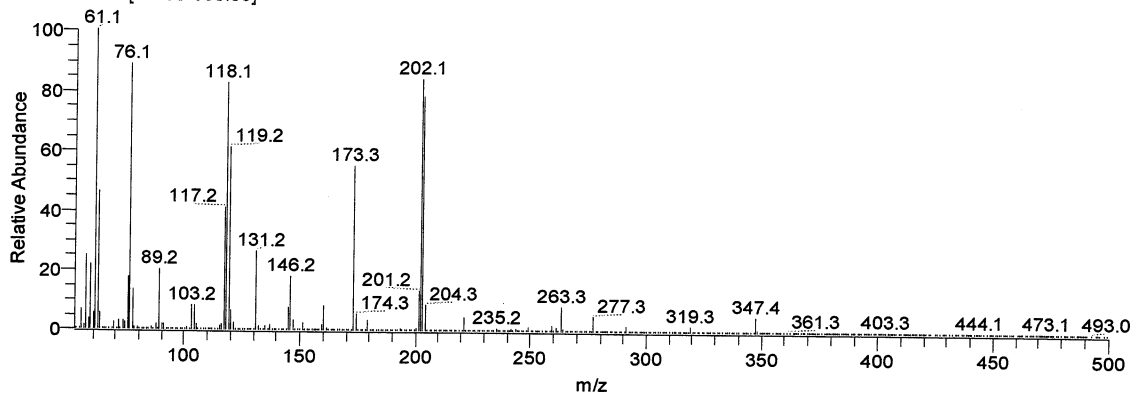


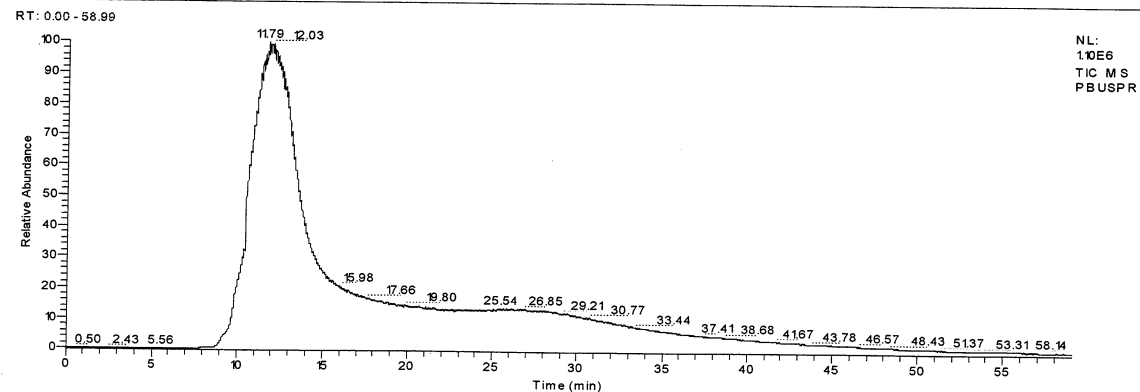


PBUSPR #1033 RT: 10.16 AV: 1 NL: 3.61E4  
T: + c Full ms [50.00-650.00]

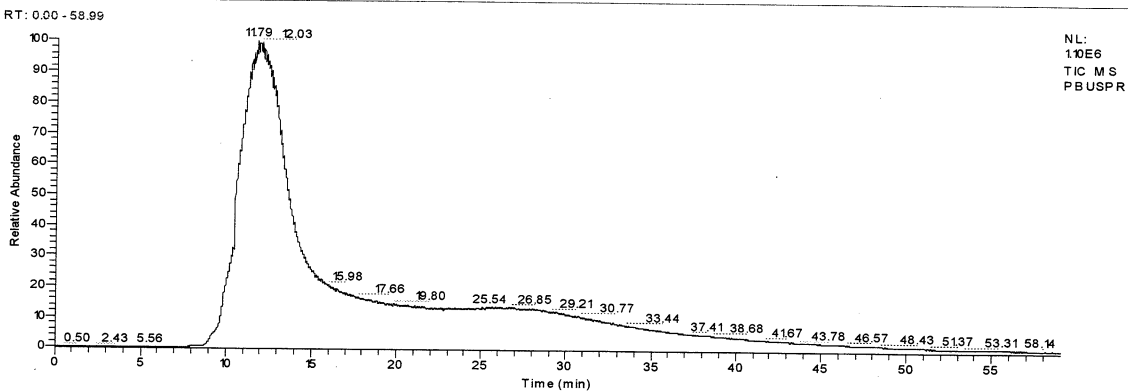
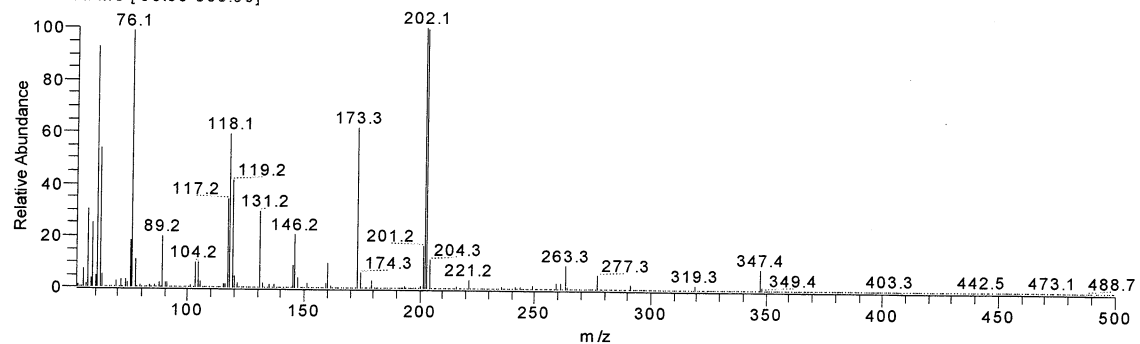


PBUSPR #1128-1192 RT: 10.98-11.54 AV: 65 NL: 9.72E4  
T: + c Full ms [50.00-650.00]

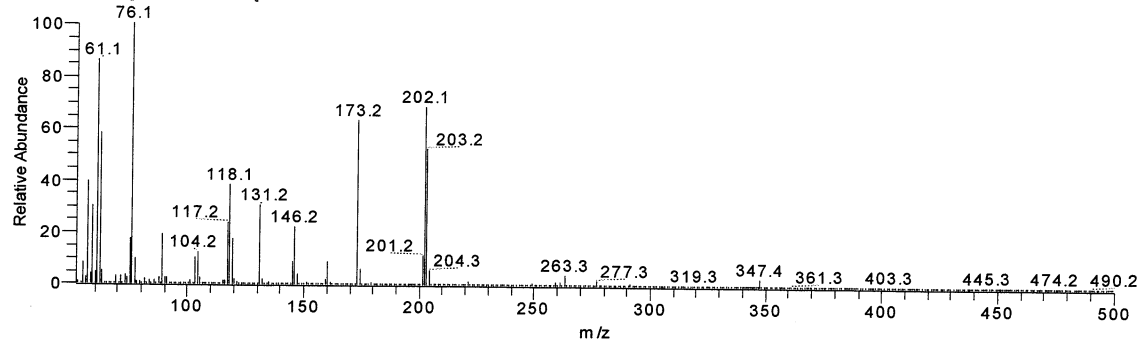


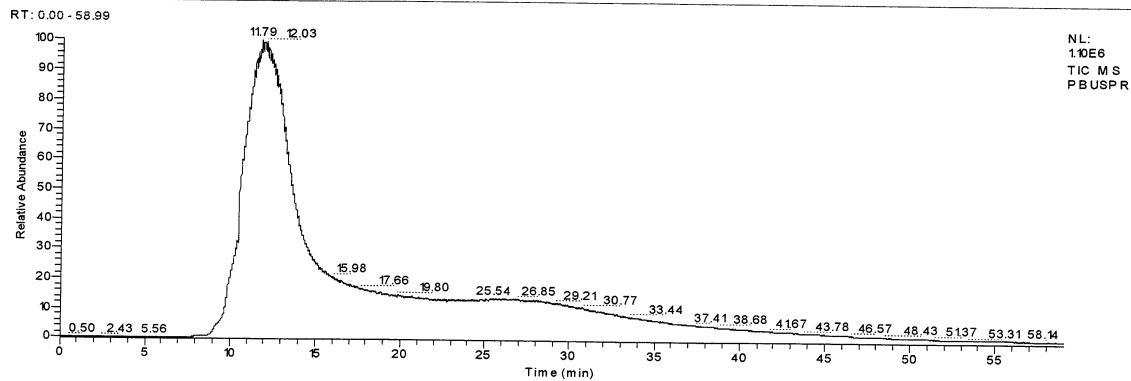


PBUSPR #1266-1361 RT: 12.19-13.02 AV: 96 NL: 9.73E4  
T: + c Full ms [ 50.00-650.00]

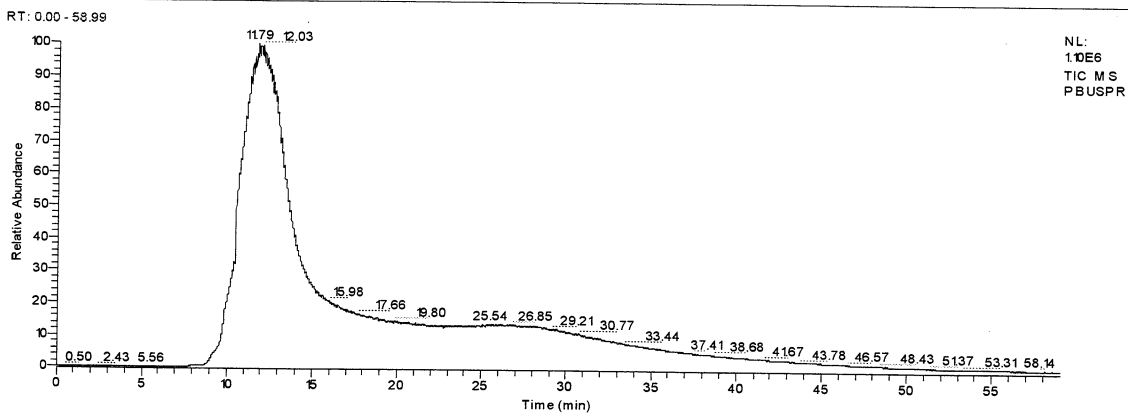
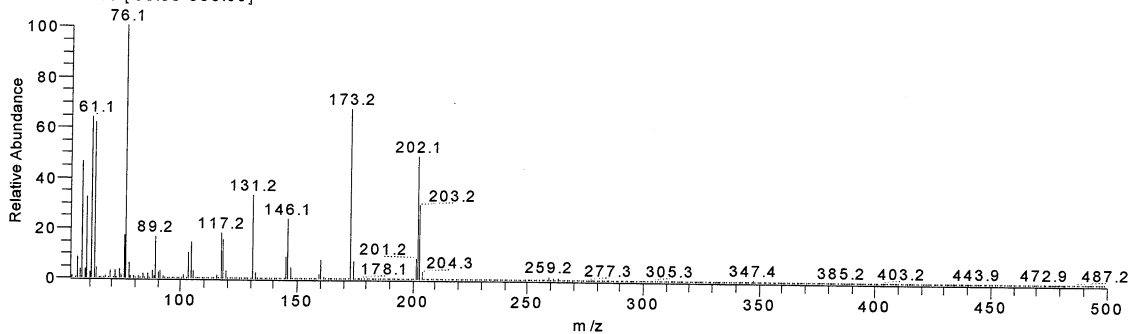


PBUSPR #1414-1583 RT: 13.48-14.96 AV: 170 NL: 4.82E4  
T: + c Full ms [ 50.00-650.00]

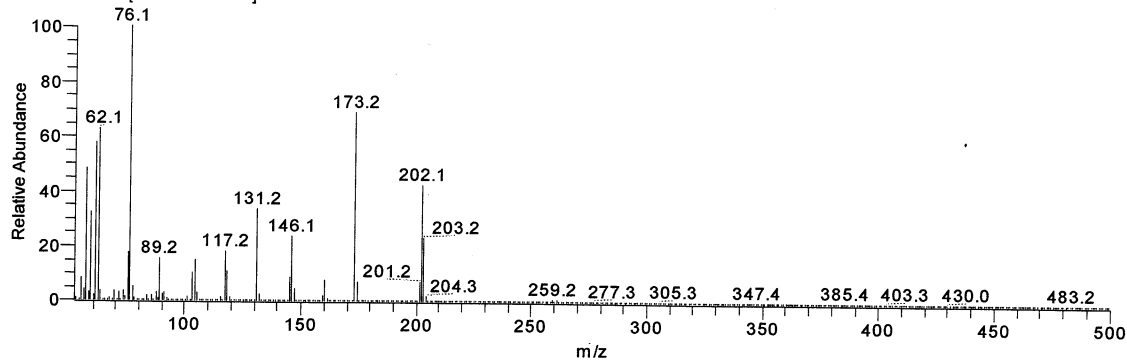


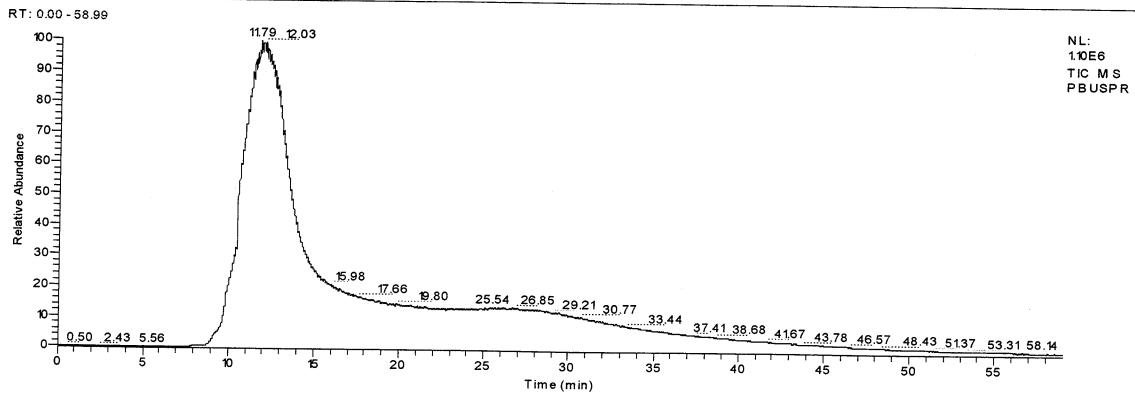


PBUSPR #1646-1876 RT: 15.51-17.54 AV: 231 NL: 2.93E4  
T: + c Full ms [ 50.00-650.00]

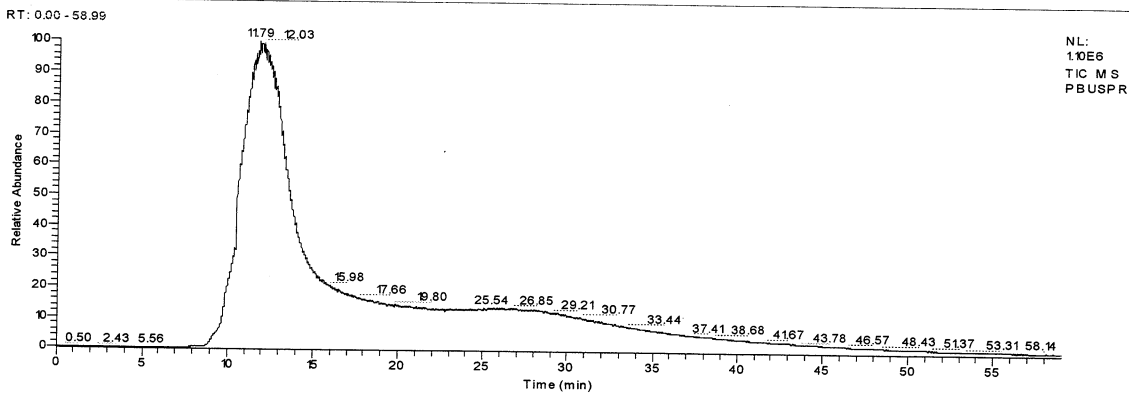
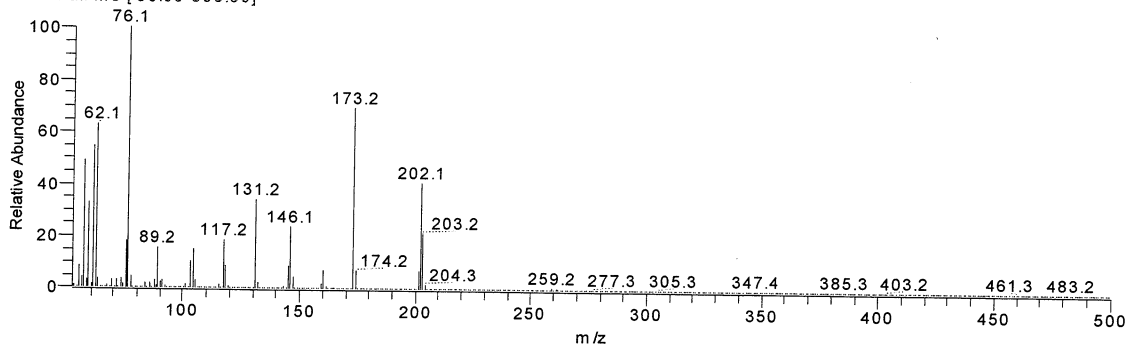


PBUSPR #1928-2542 RT: 18.00-23.45 AV: 615 NL: 2.24E4  
T: + c Full ms [ 50.00-650.00]





PBUSPR #2604-3320 RT: 24.00-30.37 AV: 717 NL: 2.09E4  
T: + c Full ms [ 50.00-650.00]



PBUSPR #3382-4092 RT: 30.93-37.39 AV: 711 NL: 1.24E4  
T: + c Full ms [ 50.00-650.00]

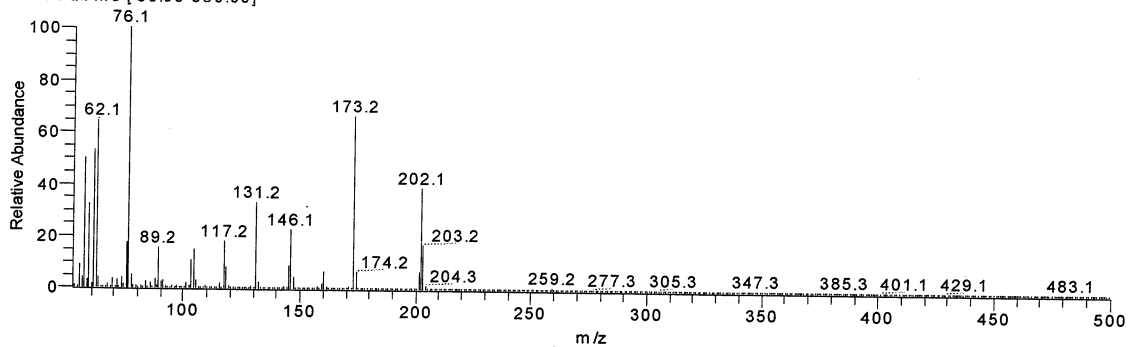


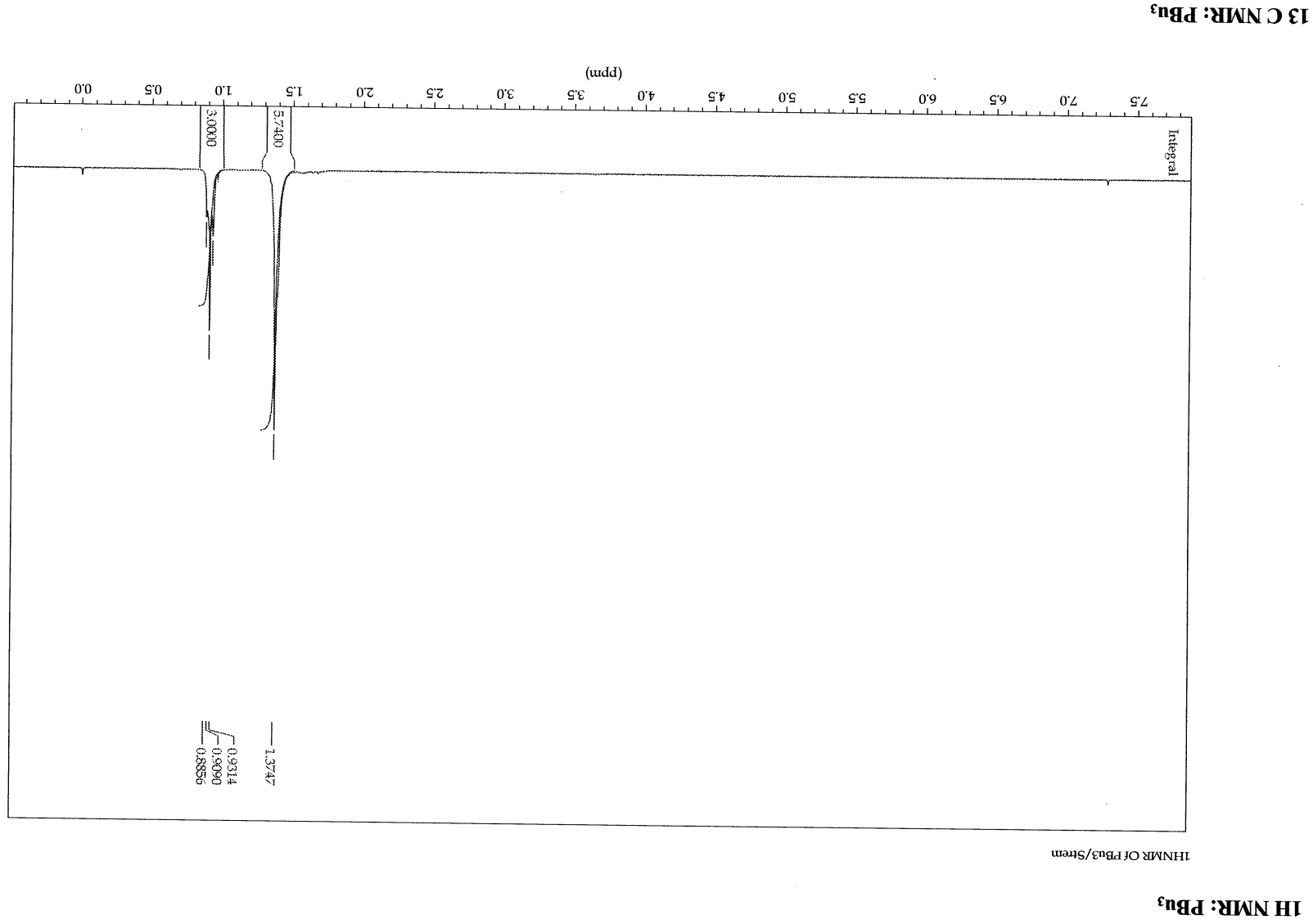
Figure 10.  $^1\text{H}$ ,  $^{13}\text{C}$  &  $^{31}\text{P}$  NMR data for **1**, **2**, and  $[\{\text{P}(n\text{Bu}_3)_3\}\text{Cu}\{\text{MeCN}\}_2]\text{PF}_6$ .

NOTE

To confirm the liquid properties of **1** and **2** were not as a result of impurities due to un-reacted starting materials, a series of test were conducted.  $^{31}\text{P}$  NMR spectra of a mixture of  $\text{PBu}_3$  and either **1**, or **2** gave a single broad peak around -28 ppm, which can be attributed to the mean chemical shift as a result of exchange between the free, and the ligated phosphine group, thereby further supporting the absence of “free”  $\text{PBu}_3$  in both precursors.  $^1\text{H}$ ,  $^{13}\text{C}$ , NMR spectra for both precursors show the absence of a signal associated with a nitrile group, thus confirming that the intermediate  $[\{\text{PBu}_3\}_2\text{Cu}\{\text{MeCN}\}_2]^+\text{PF}_6^-$  (which is a liquid), was not present in either sample. In addition, DSC thermal “finger-printing” also confirmed products **1** and **2**, where free from any starting reagents.

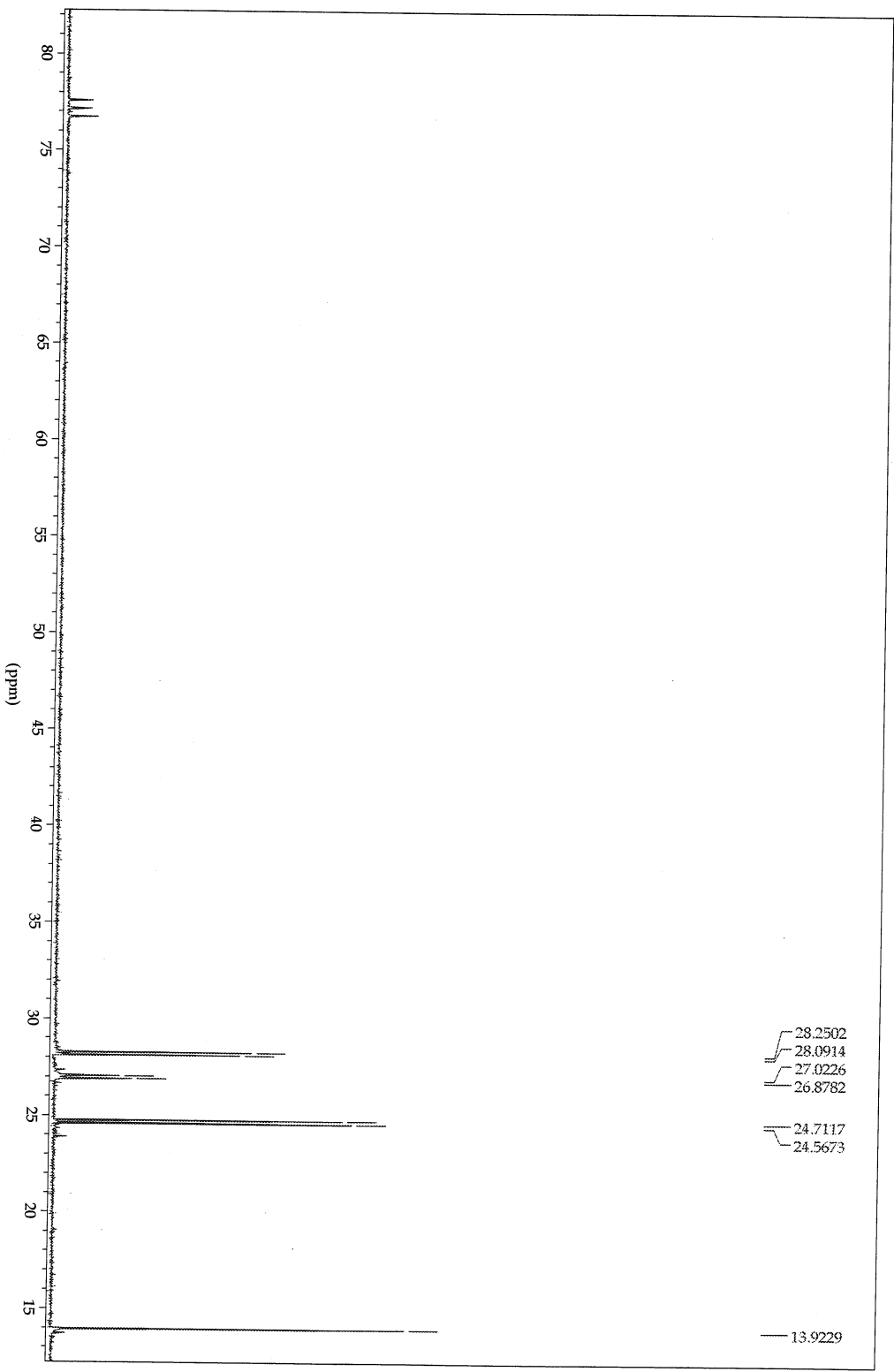
For  $[\{\text{P}(n\text{Bu}_3)_3\}\text{Cu}\{\text{MeCN}\}_2]\text{PF}_6$ :  $^1\text{H}$  NMR: 300 MHz;  $\text{CDCl}_3$ ;  $\delta$  2.25 ppm (s,  $\text{CH}_3\text{CN}$ );  $\delta$  1.62 ppm (br,  $\text{P}(\text{CH}_2\text{C}_3\text{H}_7)_3$ );  $\delta$  1.42 ppm (br,  $\text{P}(\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3)_3$ );  $\delta$  0.94 ppm (t,  $\text{P}(\text{C}_3\text{H}_6\text{CH}_3)_3$ );  $^{13}\text{C}$  NMR 75 MHz;  $\text{CDCl}_3$ ;  $\delta$  119.68 ppm ( $\text{CH}_3\text{CN}$ );  $\delta$  27.15 ppm ( $\text{P}(\text{CH}_2\text{C}_3\text{H}_7)_3$ );  $\delta$  24.55 ppm ( $\text{P}(\text{CH}_2\text{CH}_2\text{C}_2\text{H}_5)_3$ );  $\delta$  24.12 ppm ( $\text{P}(\text{C}_2\text{H}_4\text{CH}_2\text{CH}_3)_3$ );  $\delta$  13.85 ppm, ( $\text{P}(\text{C}_2\text{H}_4\text{CH}_2\text{CH}_3)_3$ );  $^{31}\text{P}$  NMR: 121 MHz;  $\text{CDCl}_3$ ;  $\delta$  -19.26 ppm, (br s,  $-\text{Cu}\{\text{P}(\text{Bu}_3)\}_2$ );  $\delta$  -145.92 ppm, (sep,  $^-\text{PF}_6$ ).

Figure 10.  $^1\text{H}$ ,  $^{13}\text{C}$  &  $^{31}\text{P}$  NMR data for 1, 2, and starting reagents.



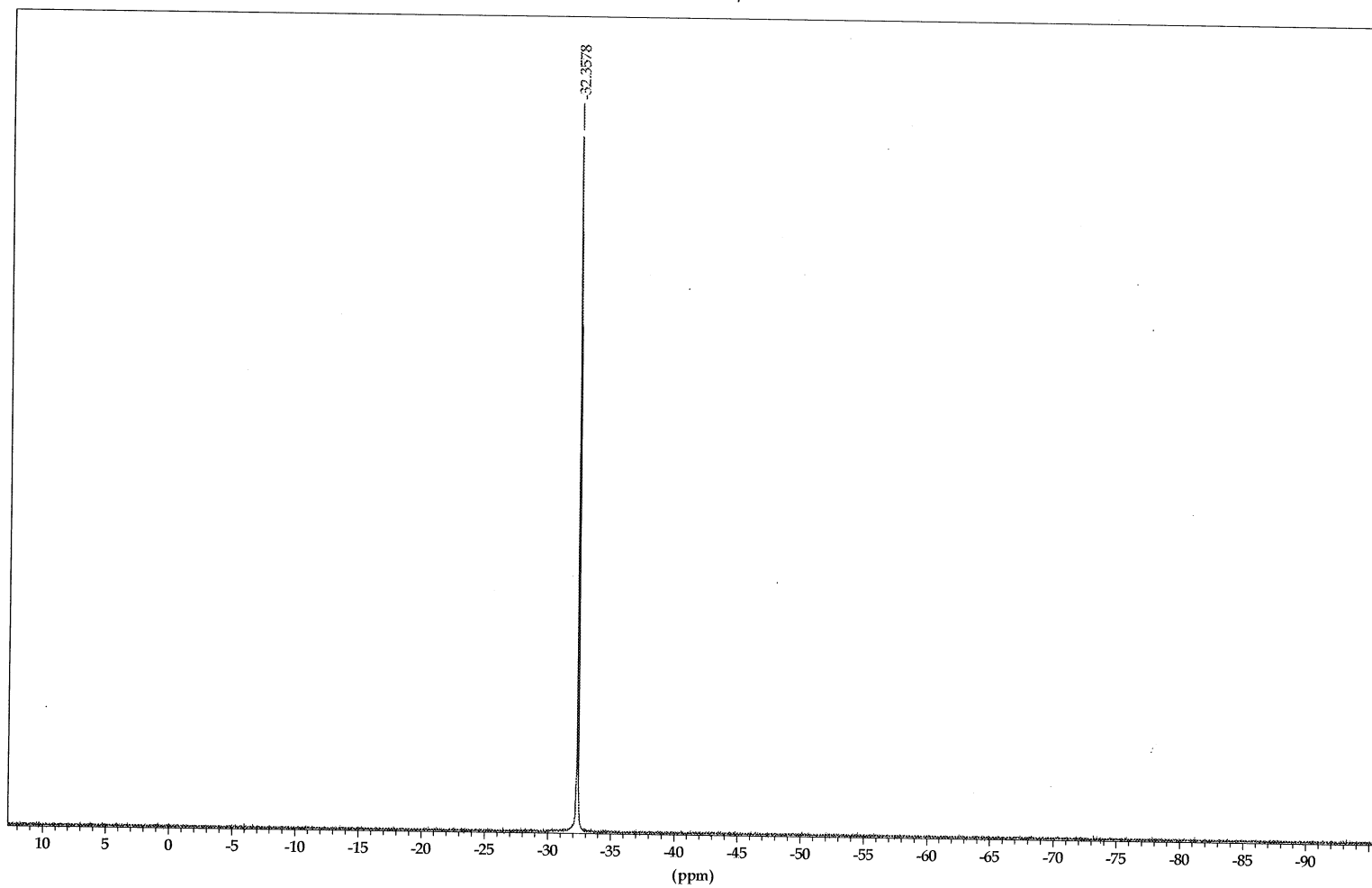


<sup>13</sup>C NMR PBUN-STREAM/CDCL<sub>3</sub> PBUS



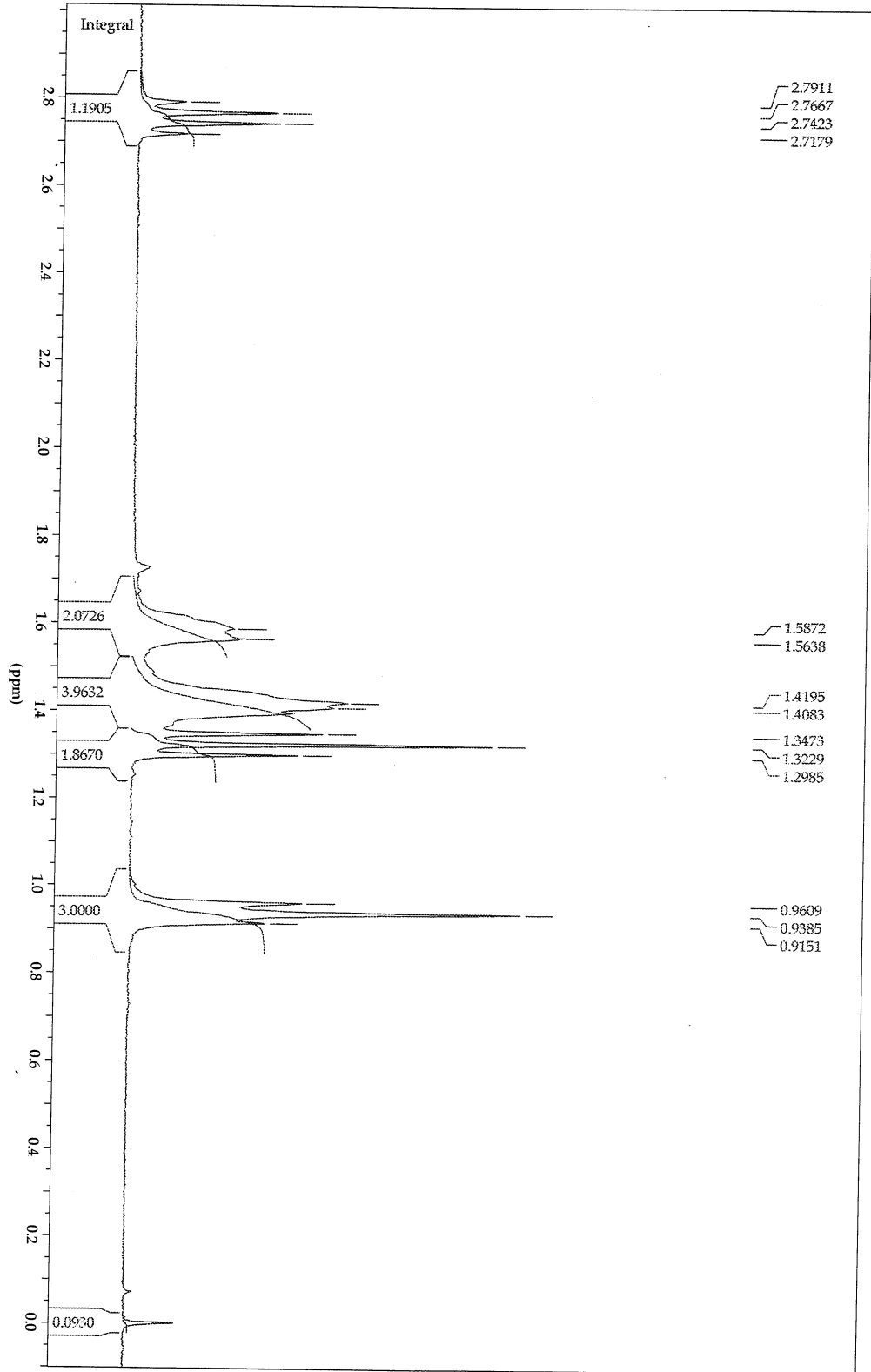
**31P NMR: PBu<sub>3</sub>**

31P NMR PBu3/Strem



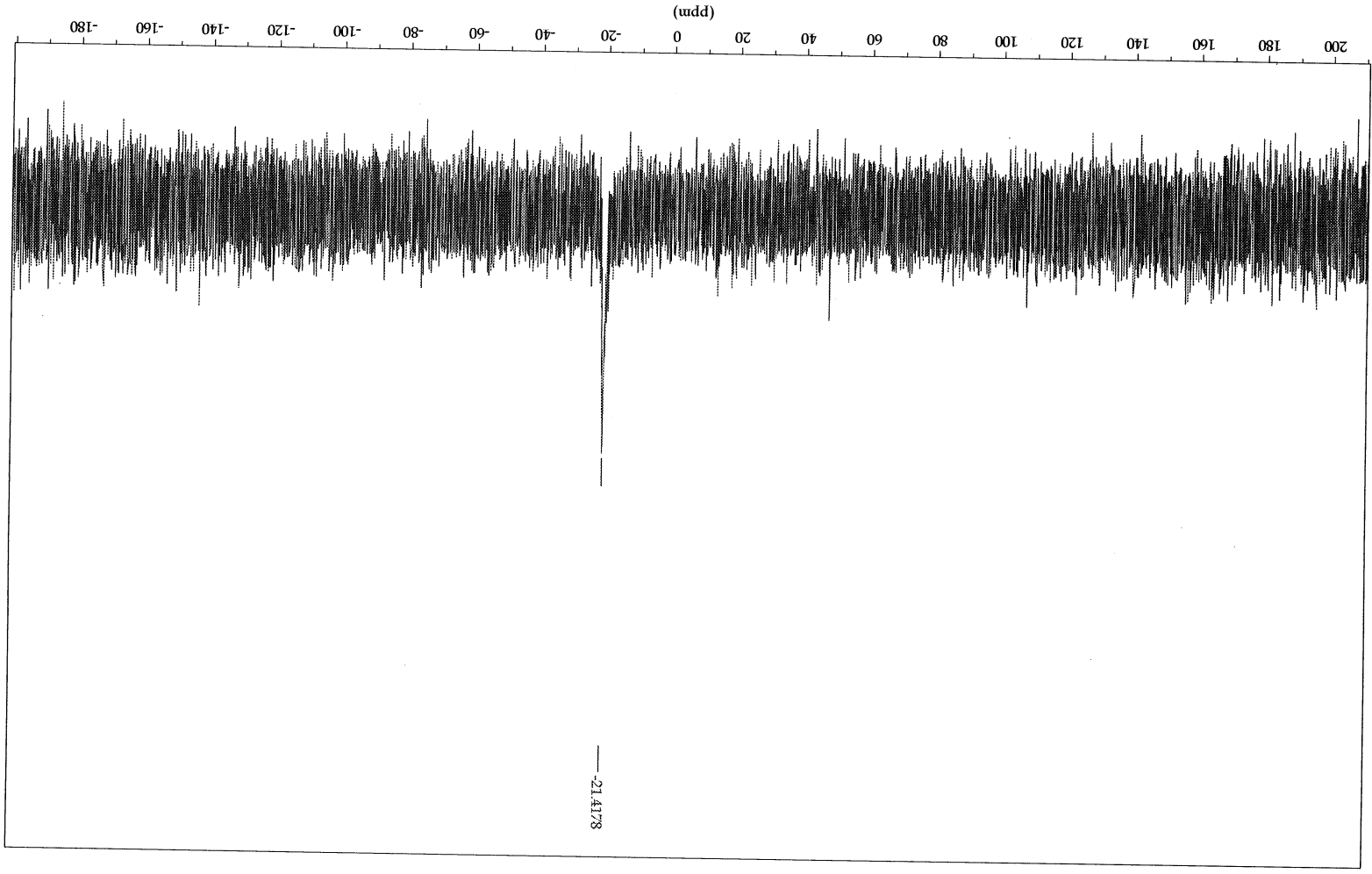
**1H NMR: [{P(*n*-Bu)<sub>3</sub>]<sub>2</sub>Cu(SEt)<sub>2</sub>In(SEt)<sub>2</sub>] 1**

1H NMR OF CON [PBU3]2CU(SRT)2 MATCH P31BUSERT.001/28/4



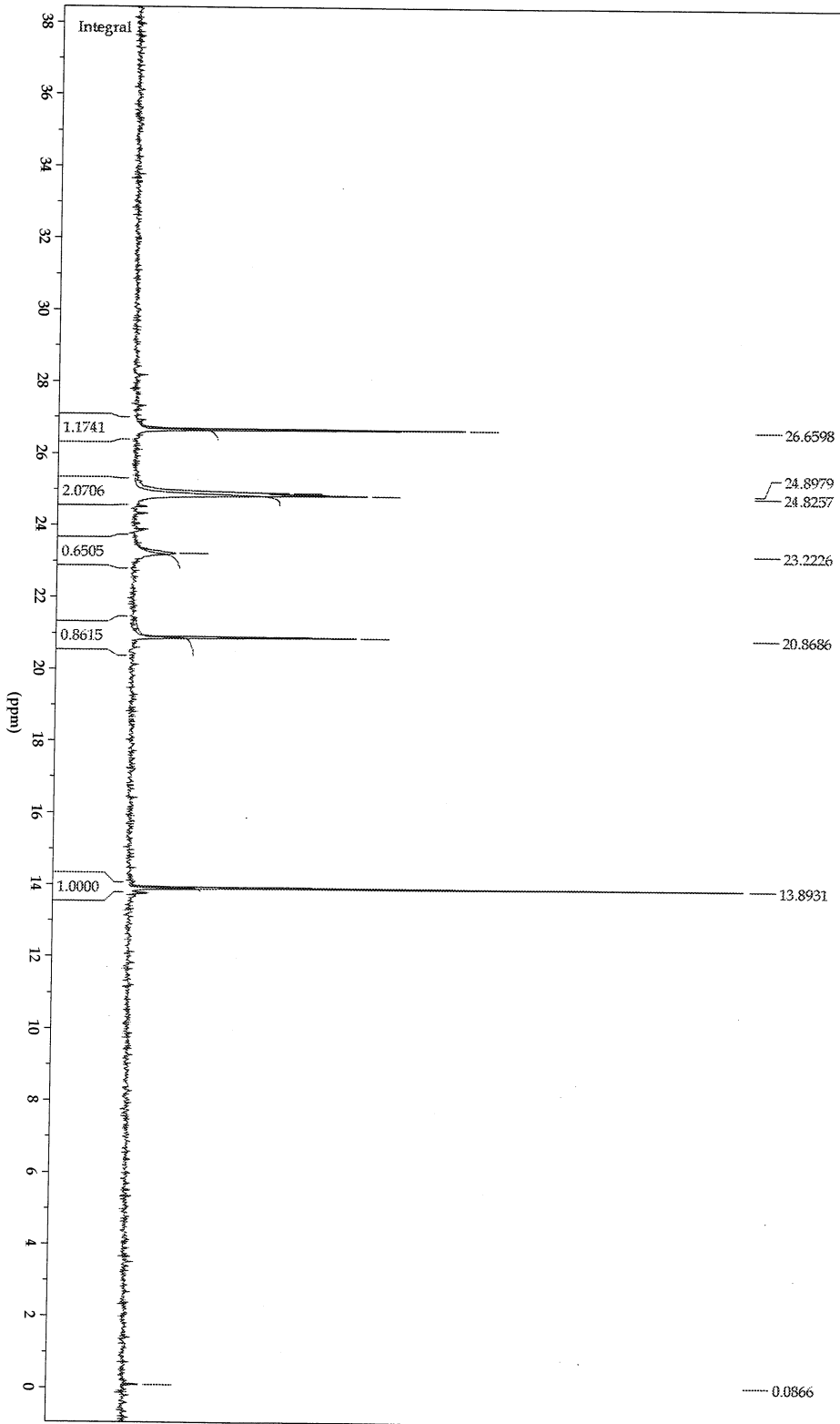
**${}^{31}\text{P}$  NMR:  $[\{\text{P}(n\text{-Bu})_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2]$  (I)**

${}^{31}\text{P}$  NMR PBU-CISEPT DILUTE/CDCl<sub>3</sub> (-22PPM) 26/ APR/01



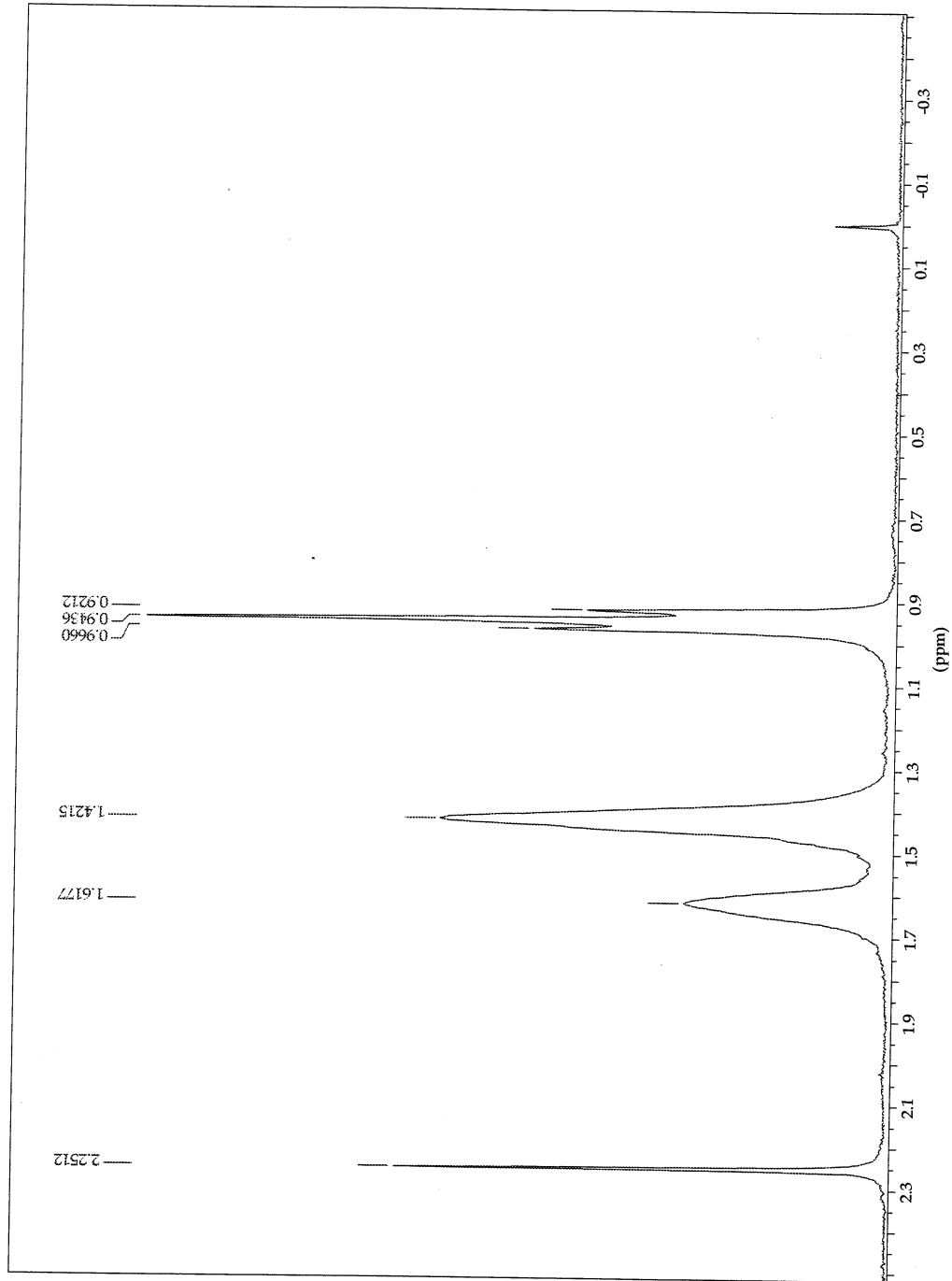
**$^{13}\text{C}$  NMR:  $\{\text{P}(n\text{-Bu})_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2\}$**

$^{13}\text{C}$ NMR: [PBU3]2[CUS(SET)2]IN(SET)2] CONC MATCH P31BUSER.001/28/4/01



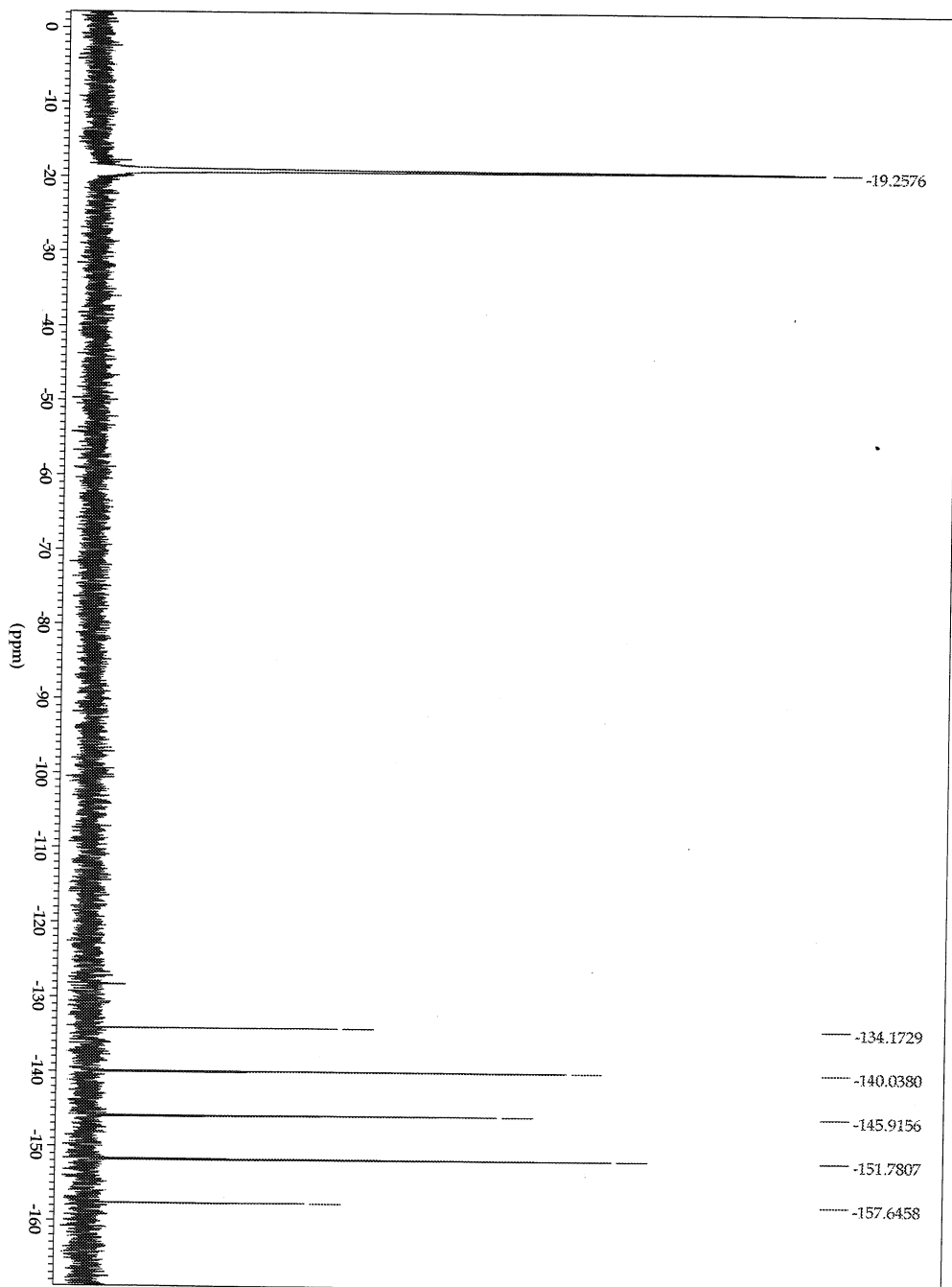
**${}^1\text{H NMR}$ :  $\{[\text{PBu}_3]_2\text{Cu}\{\text{MeCN}\}_2\}_2[\text{PF}_6]_6$**

${}^1\text{H NMR}$  OF CON  $[\text{PBu}_3]_2\text{Cu}\{\text{MeCN}\}_2[\text{PF}_6]$  MATCH H1BUBCN.001 29/4/01



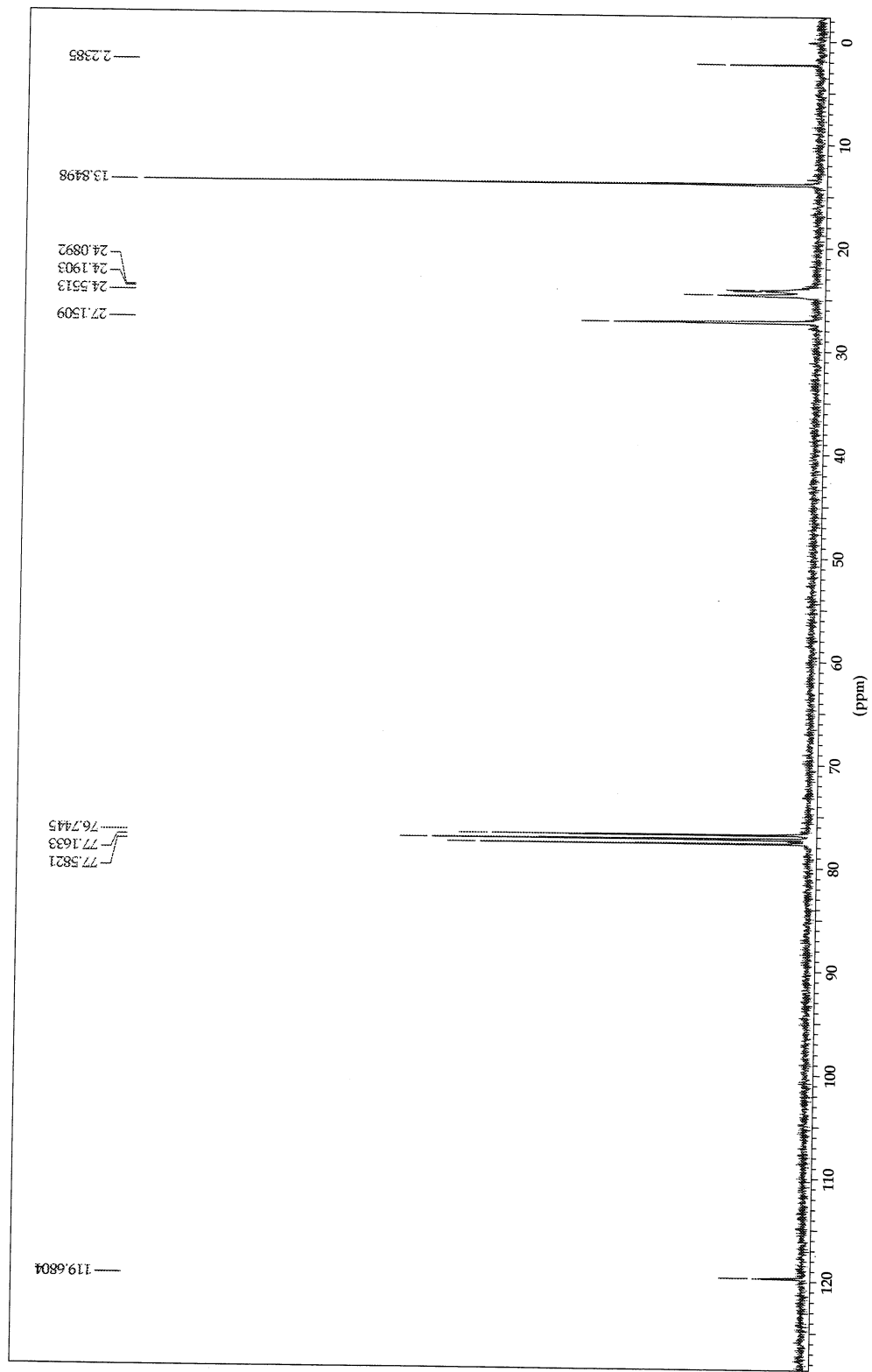
**${}^{31}\text{P NMR}$ :  $\{[\text{PBu}_3]_2\text{Cu}\{\text{MeCN}\}_2\}_2[\text{PF}_6]_6$**

31P NMR OF [PPBU<sub>3</sub>PCU(MECN)<sub>2</sub>]PF<sub>6</sub> / CDCl<sub>3</sub> DILUTE 26/4/01



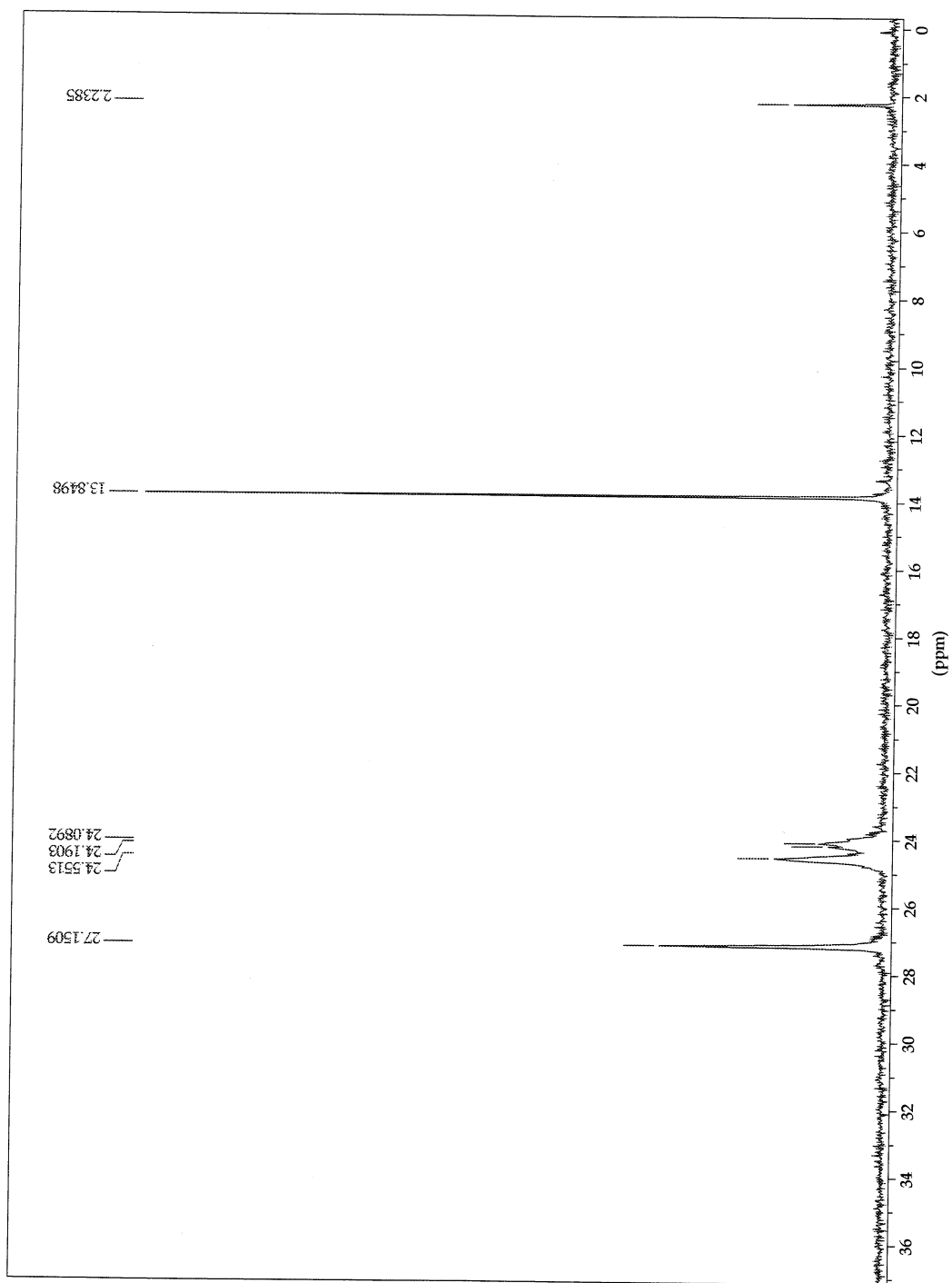
<sup>13</sup>C NMR: [PPBU<sub>3</sub>]<sub>2</sub>Cu[MeCN]<sub>2</sub>]PF<sub>6</sub>

<sup>13</sup>C NMR [(PBu<sub>3</sub>)<sub>2</sub>Cu][MBCN]<sub>2</sub>PF<sub>6</sub> CONC. MATCH P31BUBCN.001/CDCl<sub>3</sub>/28/4/01



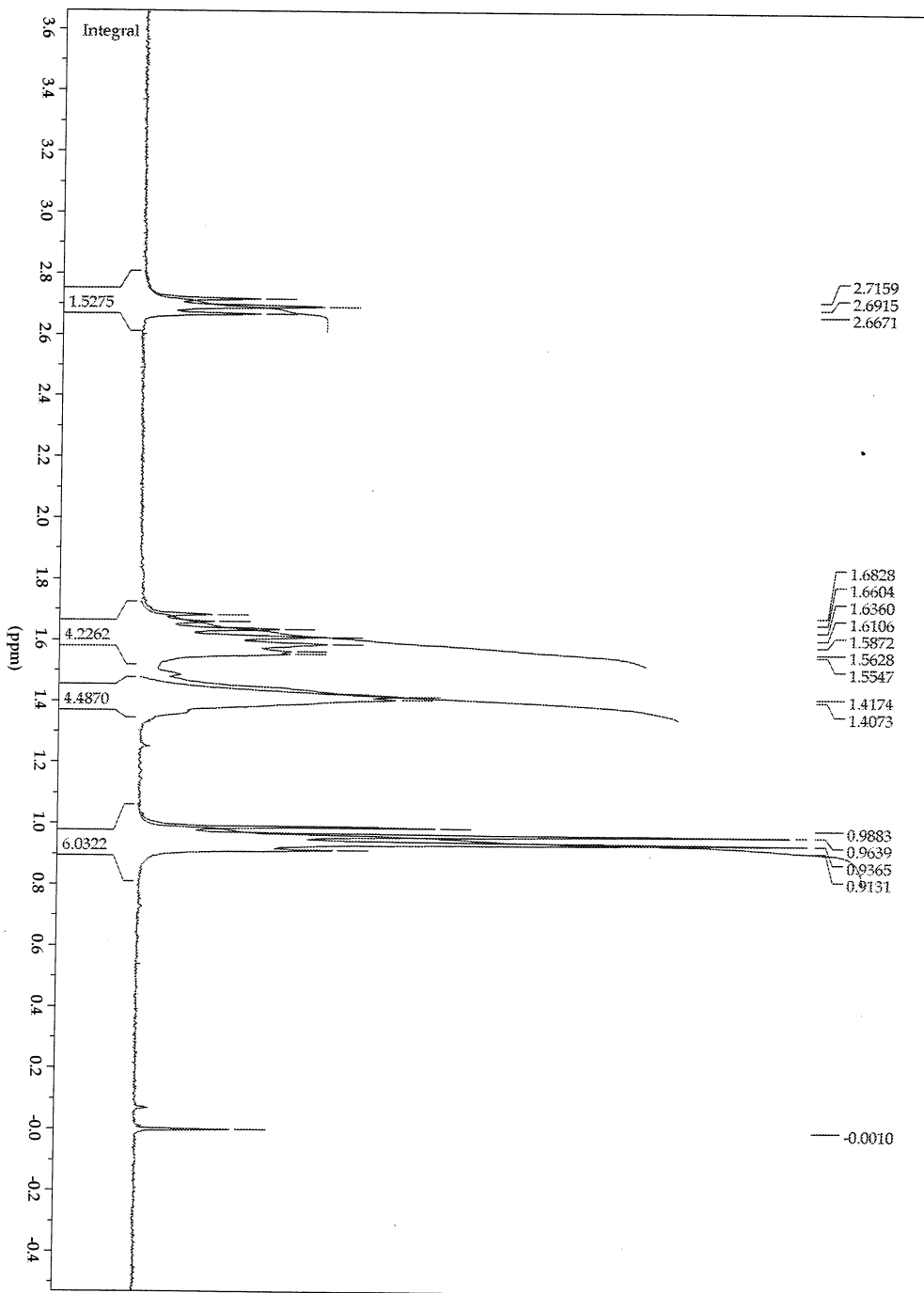


<sup>13</sup>C NMR [PPBU<sub>3</sub>PCU]MBCN[2]PF6 CONC MATCH P31BUBCN.001 / CDCl<sub>3</sub> / 28 / 4 / 01



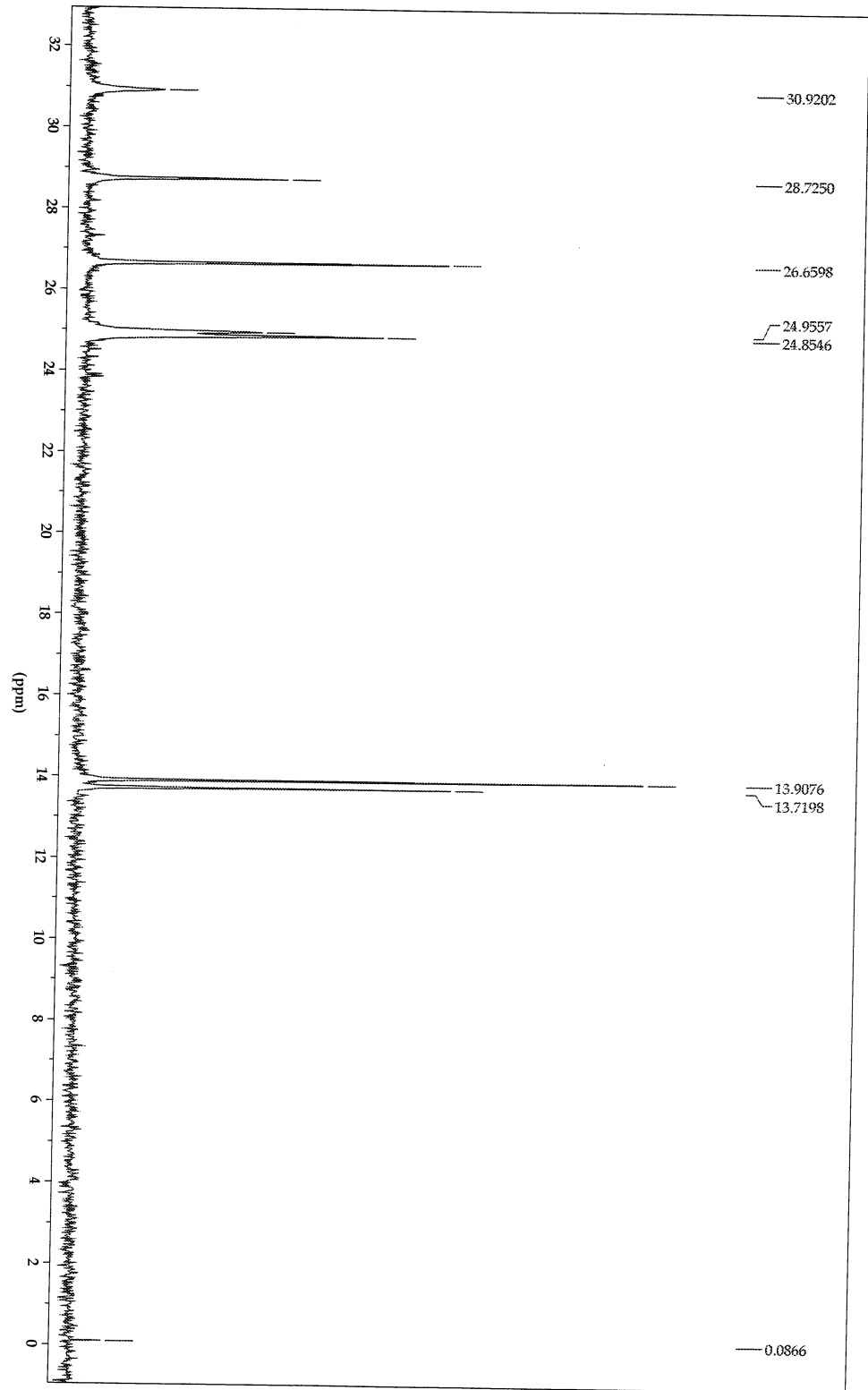
**<sup>1</sup>H NMR: [P(*n*-Bu)<sub>3</sub>]<sub>2</sub>Cu(SPr)<sub>2</sub>In(SPr)<sub>2</sub>]**

1H NMR OF CONC [IPBU]3ZCU(SPR2N)2(SPR2) MATCH P31BUSPR001/28/4/01



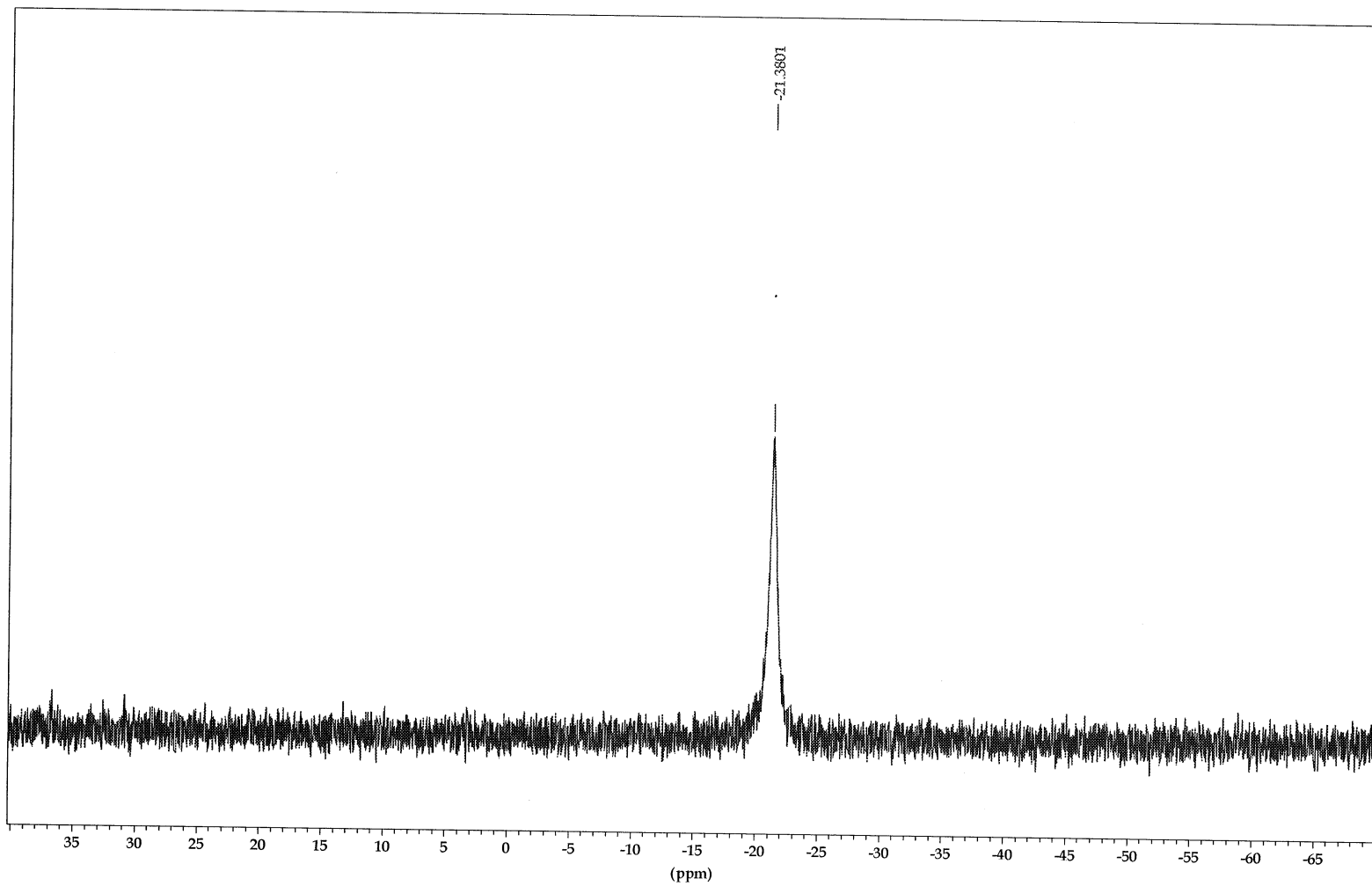
**$^{13}\text{C}$  NMR: [ $\{\text{P}(n\text{-Bu})_3\}_2\text{Cu}(\text{SP}^n)_2\text{In}(\text{SP}^n)_2$ ]**

$^{13}\text{C}$  NMR: [PBU3]2CU[SPR]2IN[SPR] CONG. MATCH P31BDSPR.001



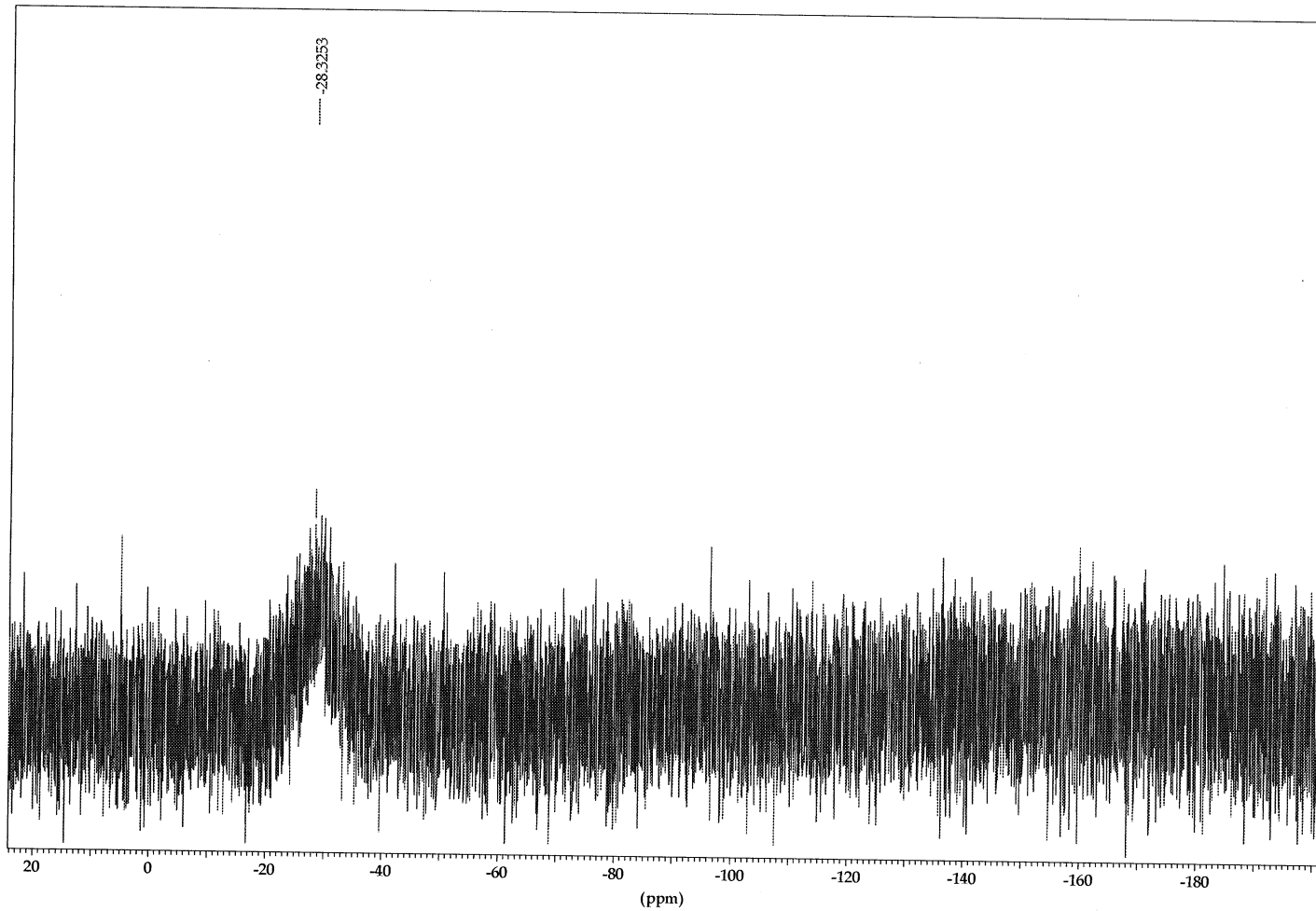
**31 P NMR: [ $\{P(n-Bu)_3\}_2Cu(SPr)_2In(SPr)_2$ ]**

31PNMR OF [IPBU3]2CU(SPR)2IN(SPR)2] DILUTE IN CDCL3 26/ APR/01



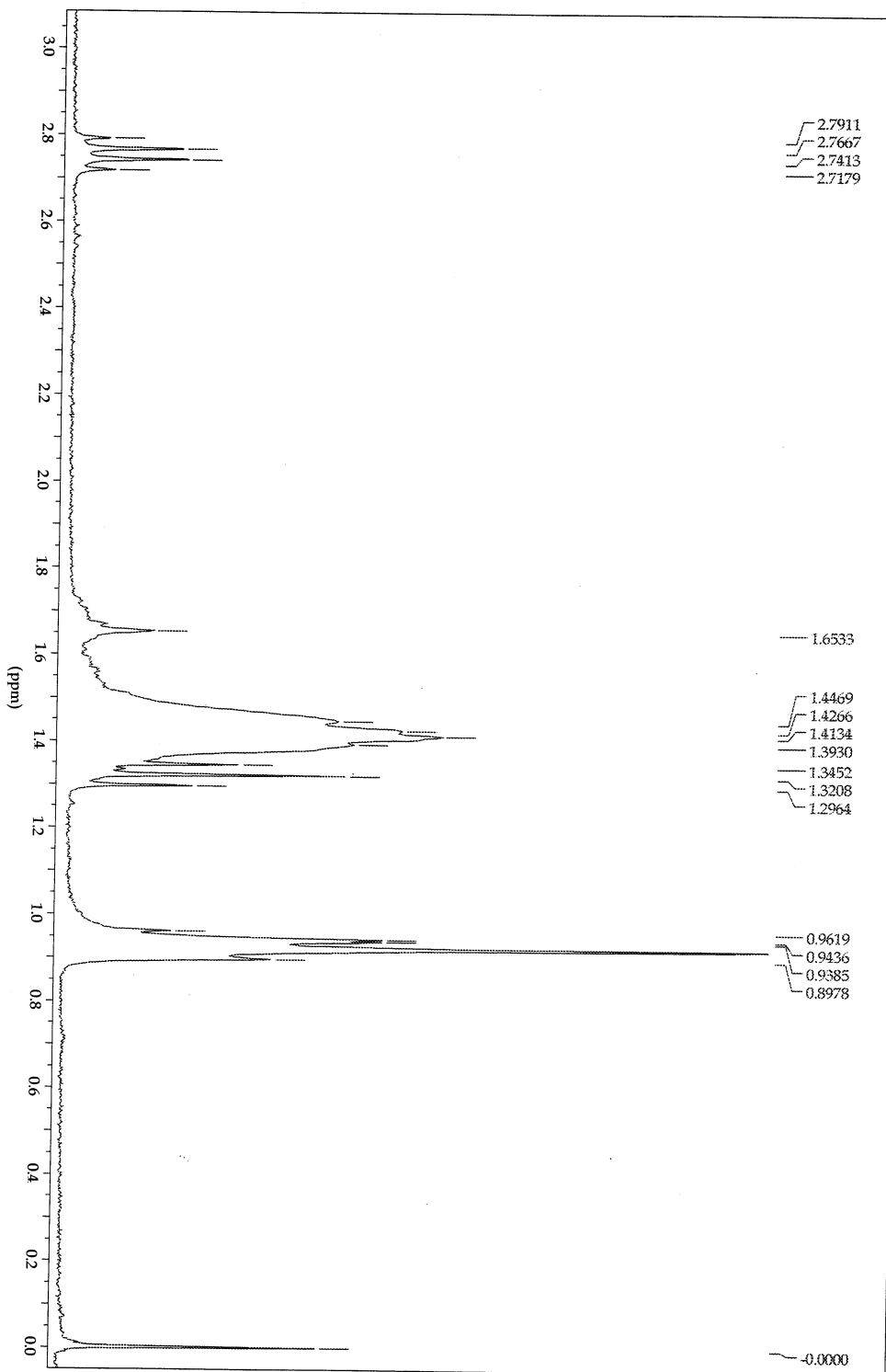
31P NMR:  $\{P(n-Bu)_3\}_2Cu(SET)_2In(SET)_2\}$  &  $PBu_3$

31P NMR OF  $\{[PBu_3]_2CuSET_2In(SET)_2\}$  DILUTE + 2 DROPS OF  $PBu_3$  26/4



**$^1\text{H NMR}$ :  $[\{\text{P}(i\text{-Bu})_3\}_2\text{Cu}(\text{SEt})_2\text{In}(\text{SEt})_2] \& \text{PBU}_3$**

$^1\text{H NMR}$  OF PRODUCT PBU<sub>3</sub>-CIS-FT DILUTE + 2DROPS PBU<sub>3</sub> MATCH P31CISL1.001





# REPORT DOCUMENTATION PAGE

*Form Approved*  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

<b>1. AGENCY USE ONLY</b> ( <i>Leave blank</i> )		<b>2. REPORT DATE</b> February 2002	<b>3. REPORT TYPE AND DATES COVERED</b> Technical Memorandum	
<b>4. TITLE AND SUBTITLE</b> Synthesis and Characterization of the First Liquid Single Source Precursors for the Deposition of Ternary Chalcopyrite (CuInS <sub>2</sub> ) Thin Film Materials			<b>5. FUNDING NUMBERS</b>  WU-755-1A-01-00	
<b>6. AUTHOR(S)</b>  Kulbinder K. Banger, Jonathan Cowen, and Aloysius F. Hepp				
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  E-12977	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> National Aeronautics and Space Administration Washington, DC 20546-0001			<b>10. SPONSORING/MONITORING AGENCY REPORT NUMBER</b>  NASA TM-2002-211128	
<b>11. SUPPLEMENTARY NOTES</b>  Kulbinder K. Banger, Ohio Aerospace Institute, 22800 Cedar Point Road, Brook Park, Ohio 44142; Jonathan Cowen, Department of Chemistry, 1983 E. 24th Street, Cleveland State University, Cleveland, Ohio 44115; and Aloysius F. Hepp, NASA Glenn Research Center. Responsible person, Aloysius F. Hepp, organization code 5410, 216-433-3835.				
<b>12a. DISTRIBUTION/AVAILABILITY STATEMENT</b> Unclassified - Unlimited Subject Category: 34 Available electronically at <a href="http://gltrs.grc.nasa.gov/GLTRS">http://gltrs.grc.nasa.gov/GLTRS</a> This publication is available from the NASA Center for AeroSpace Information, 301-621-0390.			<b>12b. DISTRIBUTION CODE</b>	
<b>13. ABSTRACT</b> ( <i>Maximum 200 words</i> )  Molecular engineering of ternary single source precursors based on the [P <sub>3</sub> Bu <sub>3</sub> ] <sub>2</sub> Cu(SR') <sub>2</sub> In(SR') <sub>2</sub> architecture have afforded the first liquid CIS ternary single source precursors (when R = Et, n-Pr), which are suitable for low temperature deposition, (< 350 °C). Thermogravimetric analyses (TGA) and Modulated-DSC confirm their liquid phase and reduced stability. X-ray diffraction studies, EDS and SEM support the formation of the single-phase chalcopyrite CuInS <sub>2</sub> at low temperatures.				
<b>14. SUBJECT TERMS</b>  Sulfides; Thermal analysis; Copper compounds; Indium compounds			<b>15. NUMBER OF PAGES</b> 48	
			<b>16. PRICE CODE</b>	
<b>17. SECURITY CLASSIFICATION OF REPORT</b> Unclassified	<b>18. SECURITY CLASSIFICATION OF THIS PAGE</b> Unclassified	<b>19. SECURITY CLASSIFICATION OF ABSTRACT</b> Unclassified	<b>20. LIMITATION OF ABSTRACT</b>	