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Synthesis and Characterization of the First Liquid Single Source Precursors for the Deposition of Ternary Chalcopyrite ($CuInS_2$) Thin Film Materials

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February 2002

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Synthesis and Characterization of the First Liquid Single Source Precursors for the Deposition of Ternary Chalcopyrite ($CuInS_2$) Thin Film Materials

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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.[1] 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 $Cu(In,Ga)Se_2$ based thin film solar cell has been reported to display an AM1.5 conversion of 18.8 percent.[2] 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.[3] Ternary single source precursors, (type $I–III–VI_2$) 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,[4–6] we have discovered new liquid single source precursors to the ternary semiconductor $CuInS_2$, based on the $[\{PR_3\}_2 Cu(SR')_2In(SR')_2]$ architecture.[7] 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, $[\{P(n\text{-}Bu)_3\}_2Cu(SEt)_2In(SEt)_2]$ **1** and $[\{P(n\text{-}Bu)_3\}_2Cu(S(n\text{-}Pr))_2In(S(n\text{-}Pr))_2]$ **2**, respectively.

The complexes are synthesised based on a modification of the procedure reported by Kanatzidis,[7] 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.[8] One of the key features of these new precursors is their liquid phase, which is remarkable considering their high molecular mass and stoichiometery, 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 Caloriometry (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). ^{31}P NMR spectra shows a shift for PBu_3, from –32.50 to –19.2 for $[\{PBu_3\}_2Cu\{MeCN\}_2]+PF_6$-, –22.4 for **1** and –22.5 ppm for **2**, which is indicative of ligand to metal co-ordination and hence complex formation.[9] 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.[3c,10]

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 $CuInS_2$ 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 Caloriometry, (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.[11] 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.[6]

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^{-1}, 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_3, 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 $CuInS_2$ 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 $CuInS_2$ (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 $CuInS_2$, albeit slightly copper rich.[12] The stoichiometry of CIS deposition is known to be temperature dependent,[4c] 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 $CuInS_2$. Thermal analysis supports that selective adjustment of the sterically demanding groups either on the donor group, or chalcognide, 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 $CuInS_2$ quantum dots and impregnated CIS_2 polymer films.

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8. For **1**: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 2.75 ppm (q, CH_3CH_2S-); δ 1.57 ppm (br m, $P(CH_2C_3H_7)_3$); δ 1.42 ppm (br m, $P(CH_2C_2H_4CH_3)_3$); δ 1.32 ppm (t,

-SCH_2CH_3); δ 0.94 ppm (t, $P(CH_2C_2H_4CH_3)_3$); ^{13}C NMR 75 MHz; $CDCl_3$; δ 26.66 ppm, ($P(CH_2C_3H_7)_3$); δ 24.88 ppm ($P(CH_2CH_2C_2H_5)_3$); δ 24.83 ppm ($P(C_2H_4CH_2CH_3)_3$); δ 23.22 ppm (-SCH_2CH_3); δ 20.87 ppm (-SCH_2CH_3); δ 13.89 ppm, ($P(C_2H_4CH_2CH_3)_3$); ^{31}P NMR: 121 MHz; $CDCl_3$; δ –21.42 ppm, (br s, -Cu{$P(Bu_3)$}$_2$). Complex **2** was prepared in an similar manner to **1**: ^1H NMR: 300 MHz; $CDCl_3$; δ 2.69 ppm (t, $C_2H_5CH_2S$-); δ 1.56 ppm (br m, $P(CH_2C_3H_7)_3$ overlapping with $CH_3CH_2CH_2S$-); δ 1.41 ppm (br m, $P(CH_2C_2H_4CH_3)_3$); δ 0.94 ppm (m, $CH_3CH_2CH_2S$- overlapping with $P(C_3H_6CH_3)_3$); ^{13}C NMR 75 MHz; $CDCl_3$; δ 30.92 ppm, ($CH_3CH_2CH_2S$-); δ 28.73 ppm ($CH_3CH_2CH_2S$-); δ 26.66 ppm ($P(CH_2C_3H_7)_3$); δ 24.96 ppm ($P(CH_2CH_2C_2H_5)_3$); δ 24.85 ppm ($P(C_2H_4CH_2CH_3)_3$); δ 13.91 ppm, ($P(C_2H_4CH_2CH_3)_3$); δ 13.71 ppm ($CH_3CH_2CH_2S$-); ^{31}P NMR: 121 MHz; $CDCl_3$; δ –21.38 ppm, (br s, -Cu{$P(Bu_3)$}$_2$).

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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 ±3 percent). XRD, Philips PW3710, (Cu Kα, 1.541 Å). TA Instruments Hi-Res-TGA, 2950, TA Instruments DSC 910, and MDSC 2920.

Figure 1. Low temperature DSC Studies.

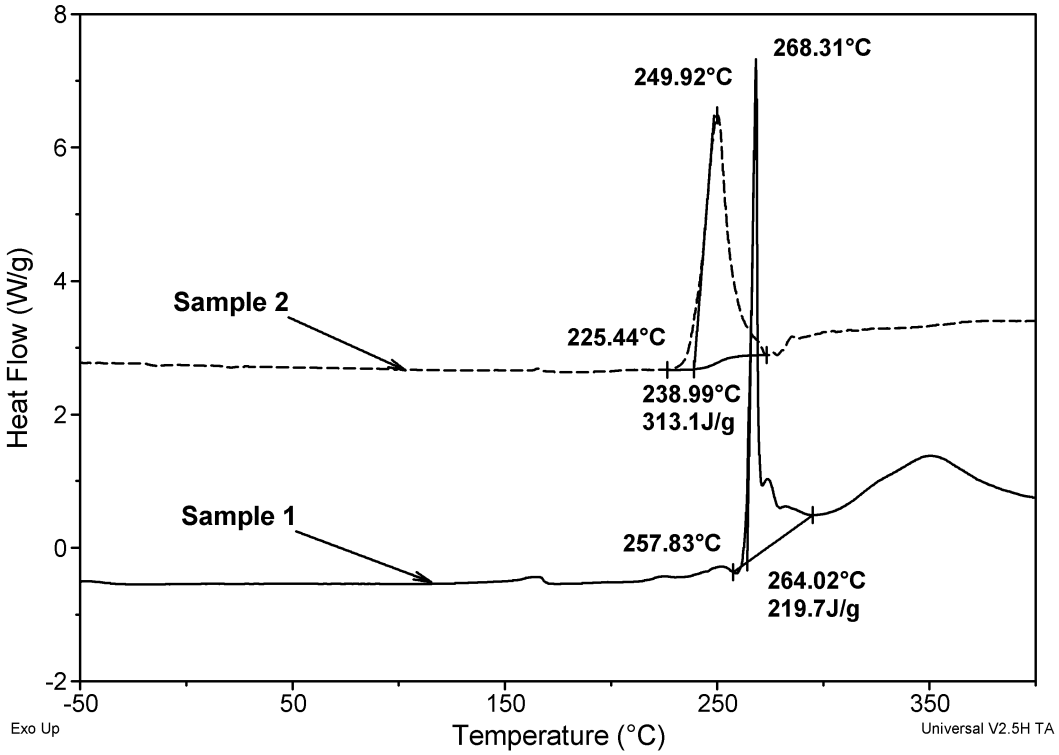


Figure 2. TGA profile for [{P(*n*-Bu)$_3$}$_2$Cu(S(*n*-Pr))$_2$In(S(*n*-Pr))$_2$], **2**.

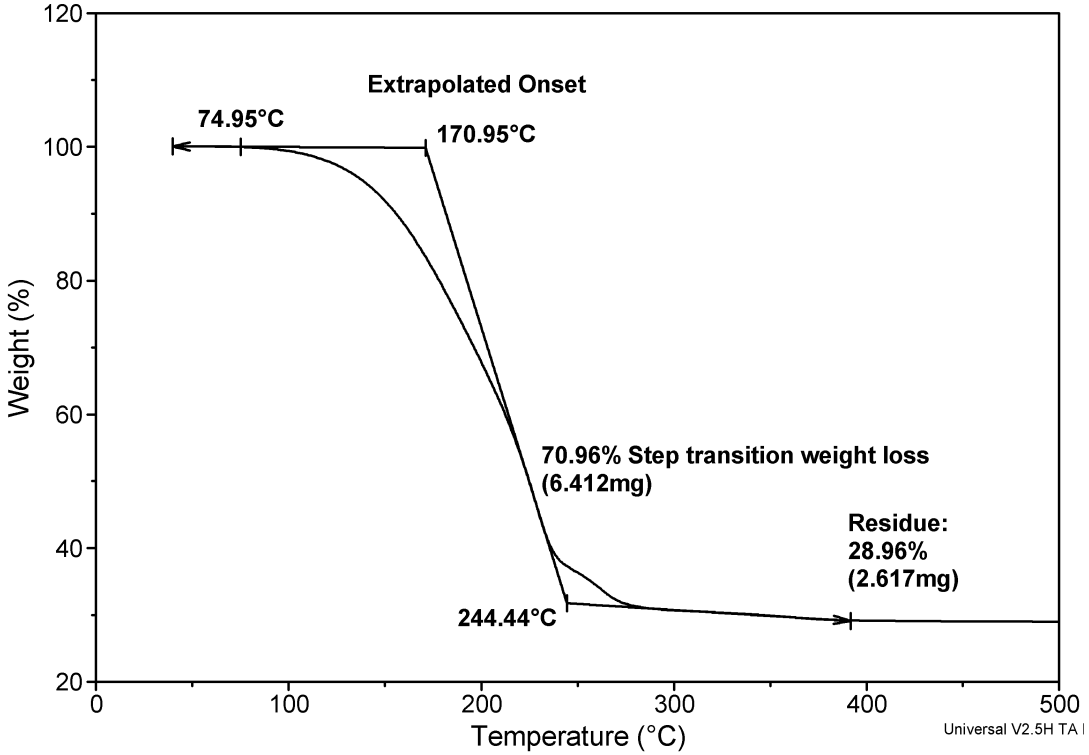


Figure 3. Low temperature MDSC for [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$] **1** and [{P(*n*-Bu)$_3$}$_2$Cu(S(*n*-Pr))$_2$In(S(*n*-Pr))$_2$] **2**.

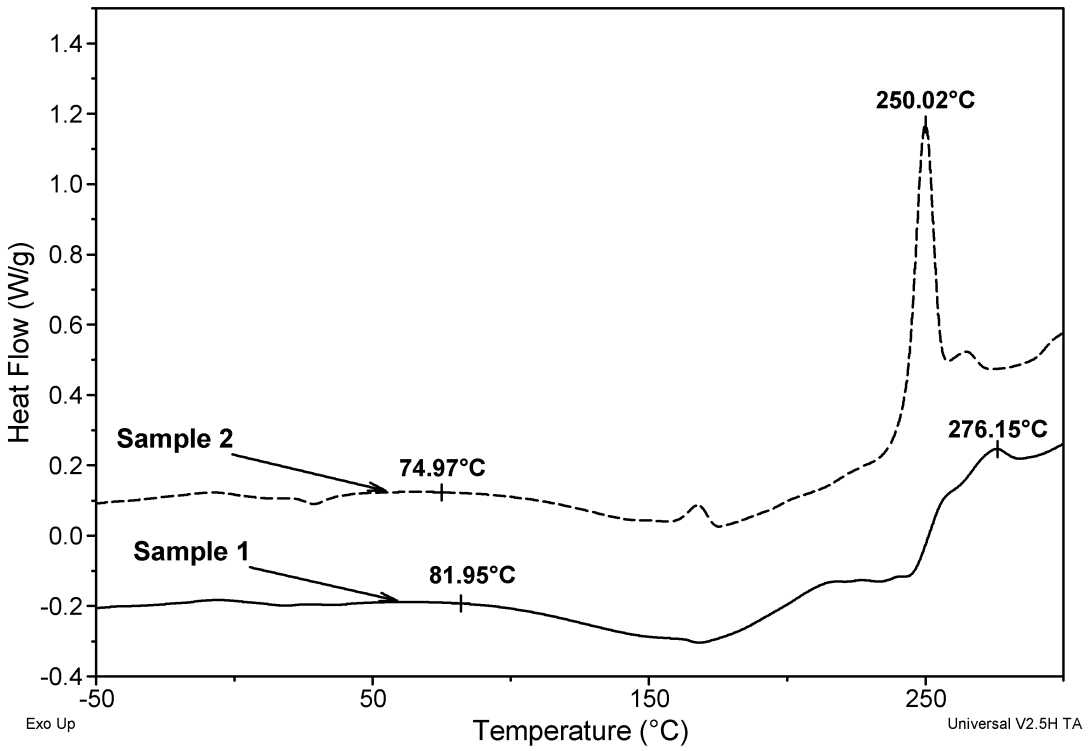


Figure 4. EGA-FTIR spectra for [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$] **1**.

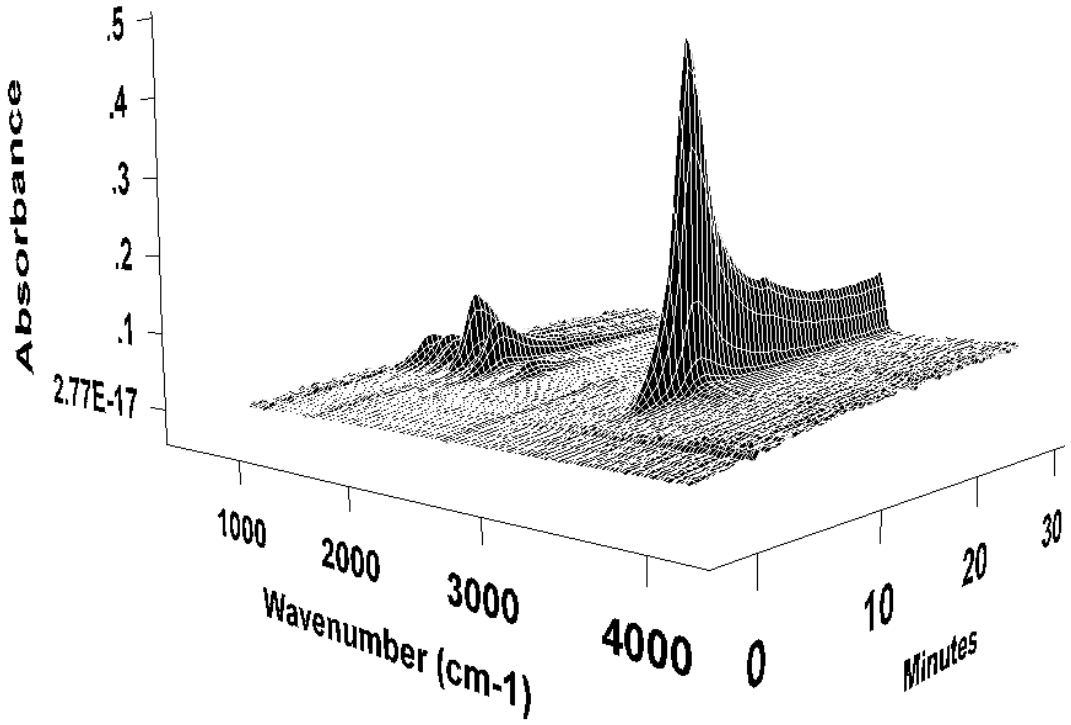
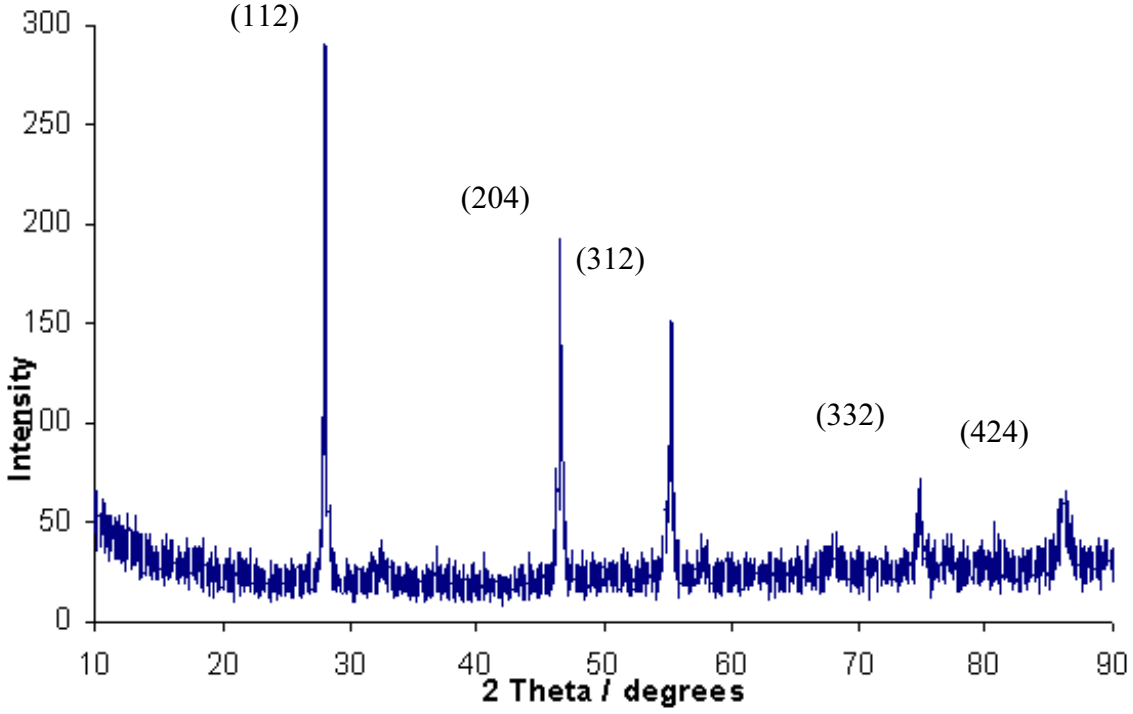


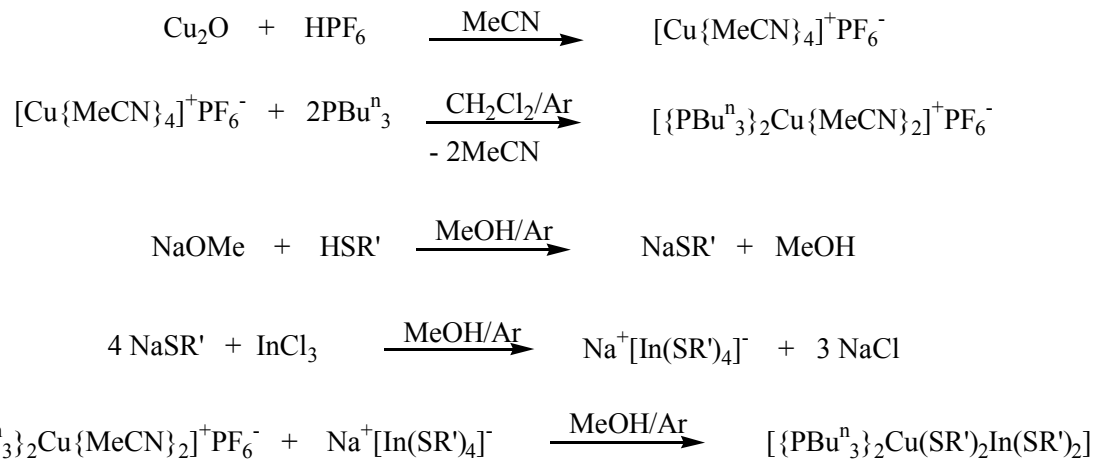
Figure 5. XRD Powder Diffraction for non-volatile residue from pyrolysis of [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], (Cu Kα, 1.541 Å).



Appendix A

Supporting Information

Scheme 1: Preparation of single source $CuInS_2$ 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 $InCl_3$ (1.27 g, 5.75 mmol) was added. The mixture was stirred for 1hr. $[Cu(CH_3CN)_2(PBu_3)_2]PF_6$ (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_2Cl_2 (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)$_3$}$_2$Cu(SPr^n)$_2$In(SPr^n)$_2$], 2

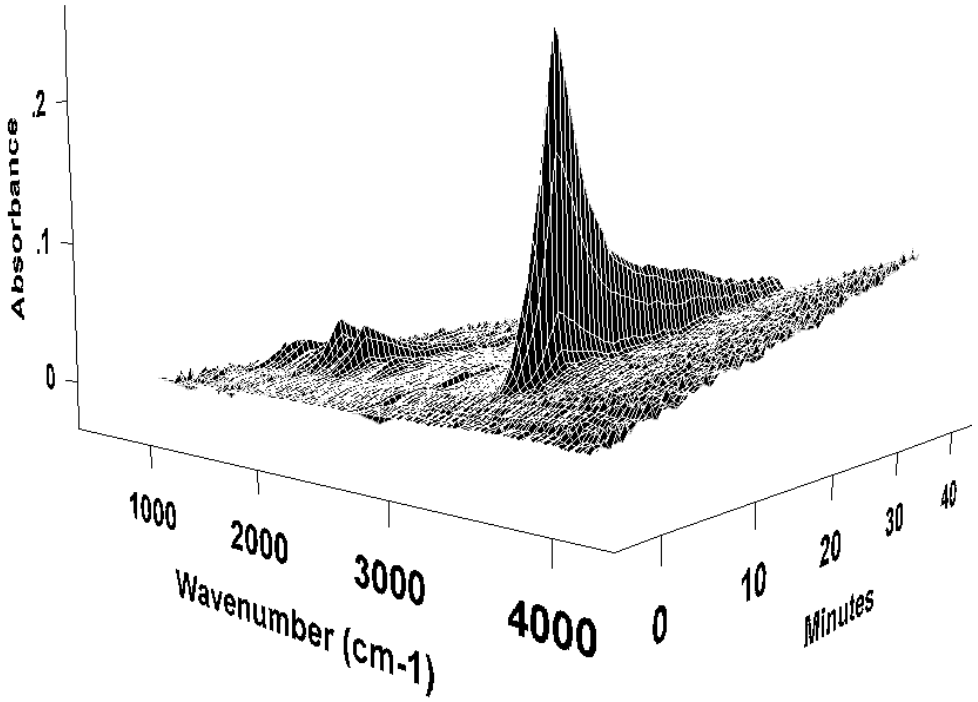


Figure 2. TGA Profile for [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **1** .

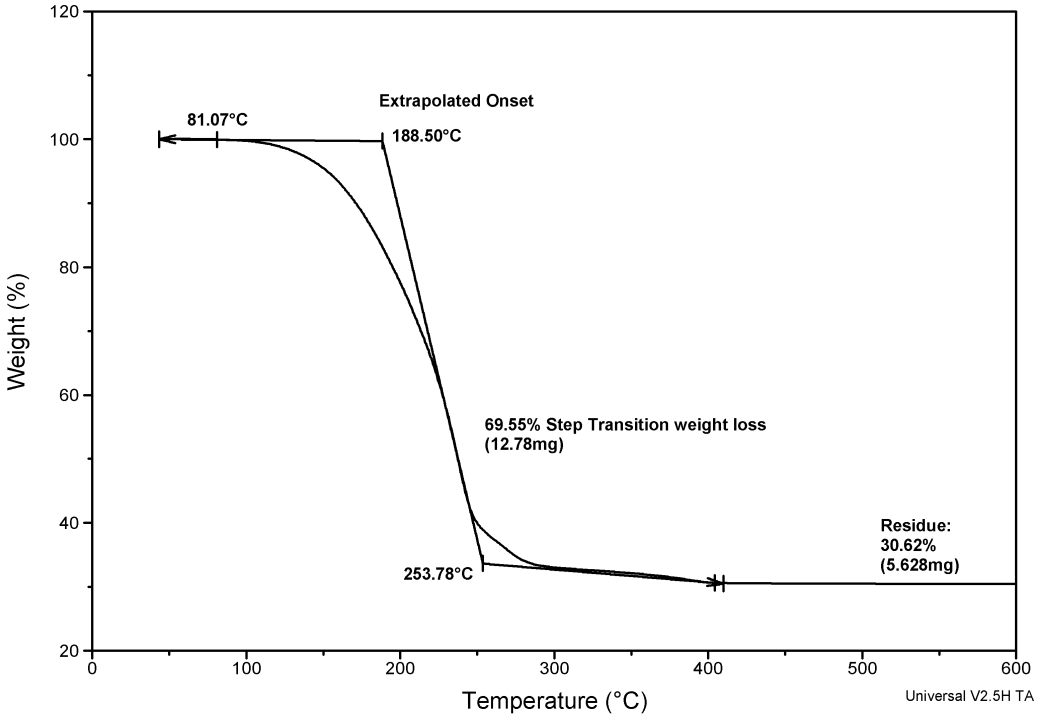


Figure 3. Vacuum TGA for [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **1** .

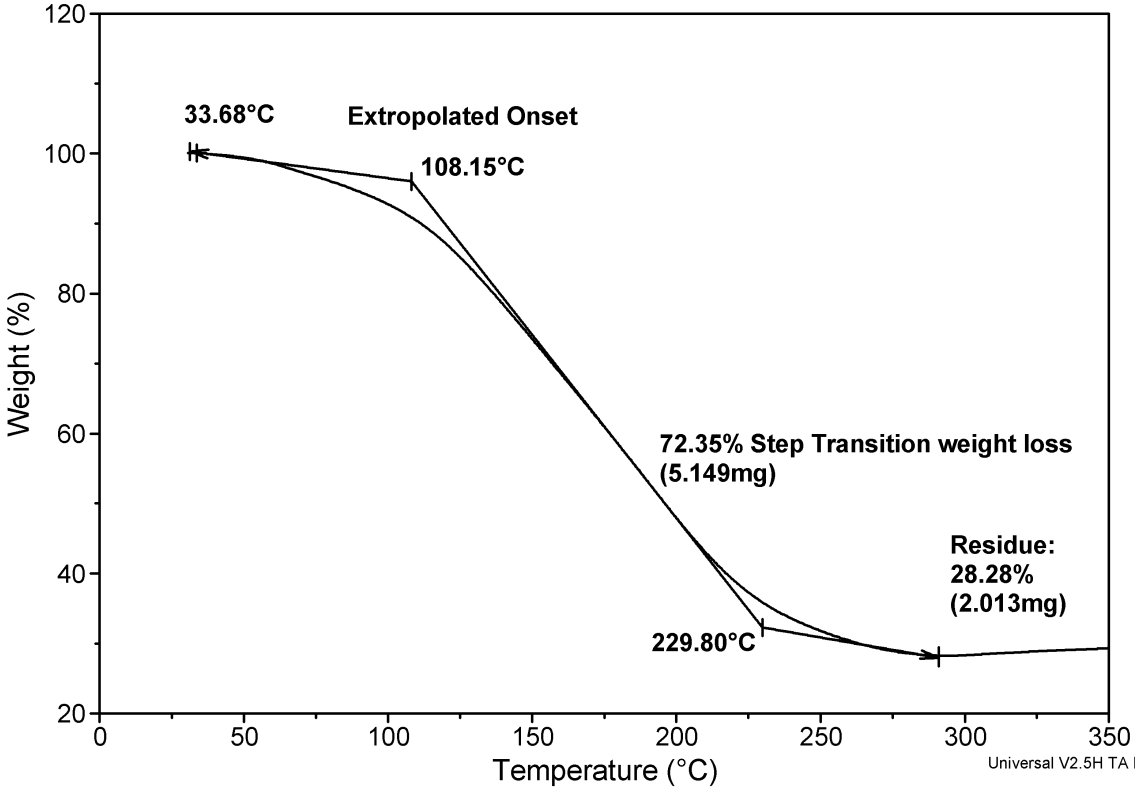
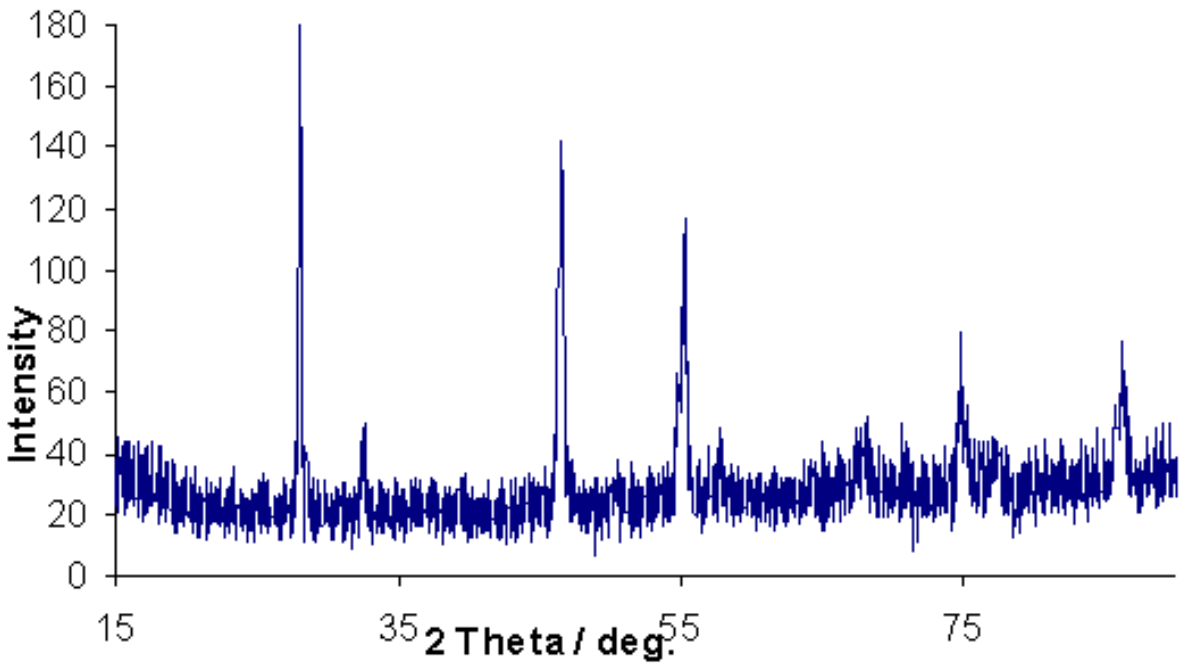


Figure 4. X-ray Powder Diffraction spectra for [{P(*n*-Bu)$_3$}$_2$Cu(SPr^n)$_2$In(SPr^n)$_2$], **2,** (Cu Kα, 1.541 Å).



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

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)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **1**

Diffractometer type: PW3710
Diffractometer number: 1 Anode: Cu
Wavelength Alpha1: 1.54060 Wavelength Alpha2: 1.54439
Intensity ratio (alpha2/alpha1): 0.50000
Divergence slit: 1 Receiving slit: 0.2
Monochromator used: YES
Generator voltage [kV]: 45 Generator current [mA]: 40
Start angle [X2]: 10.0100 End angle [X2]: 89.9900
Step size [X2]: 0.020 Type of scan: CONTINUOUS
Time per step [s]: 1.00 ConvertedTo,FIXED,/
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)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **1**.

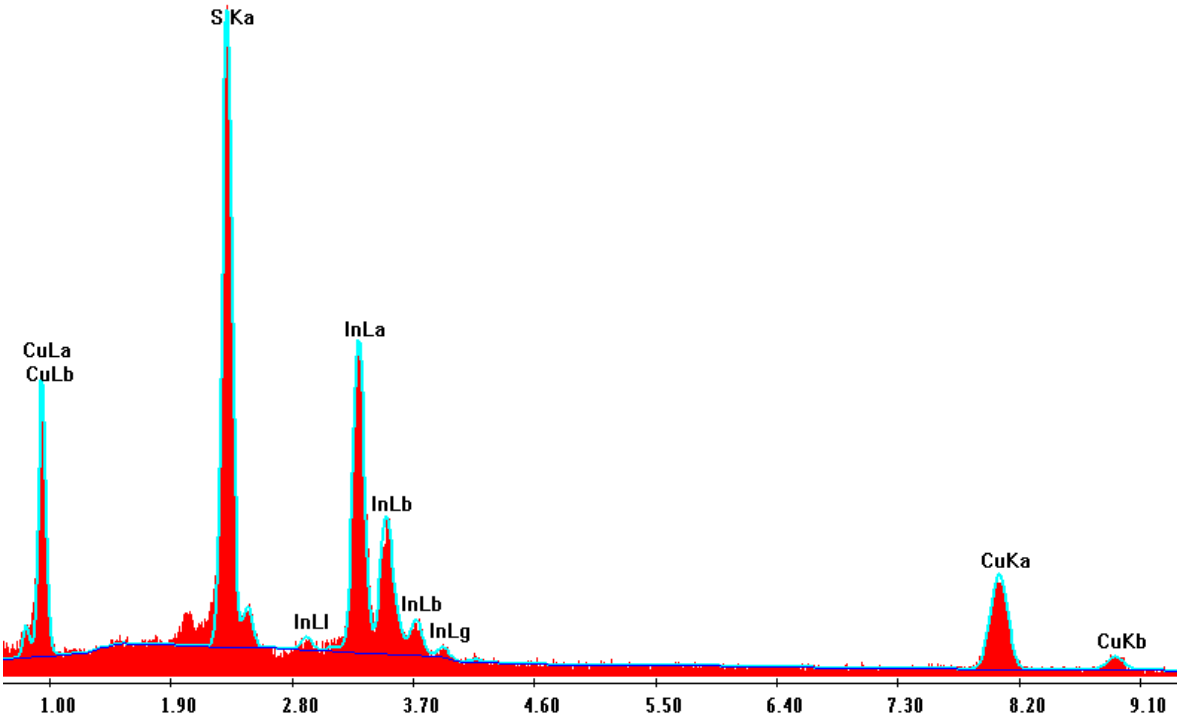
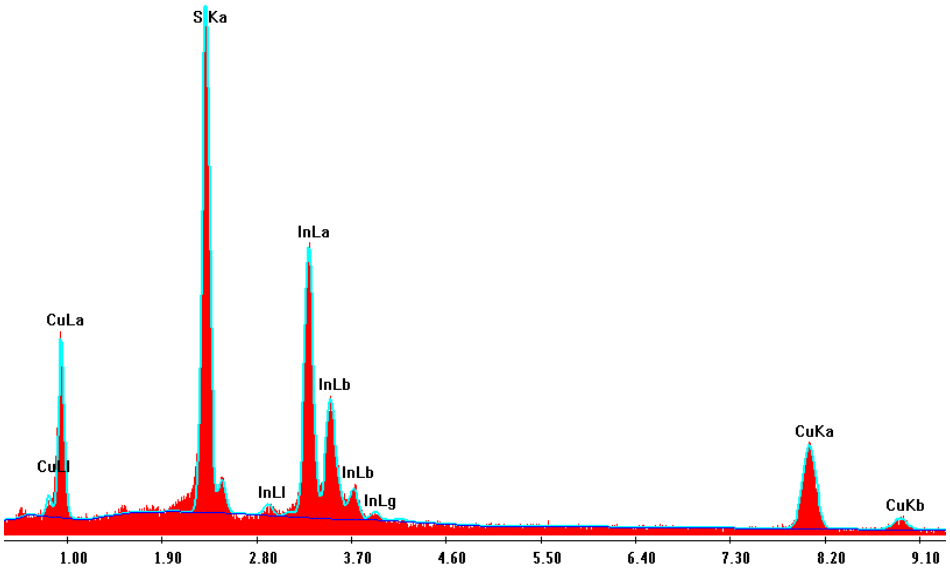


Figure 5b. EDS spectra for [{P(*n*-Bu)$_3$}$_2$Cu(SPr^n)$_2$In(SPr^n)$_2$], **2**.

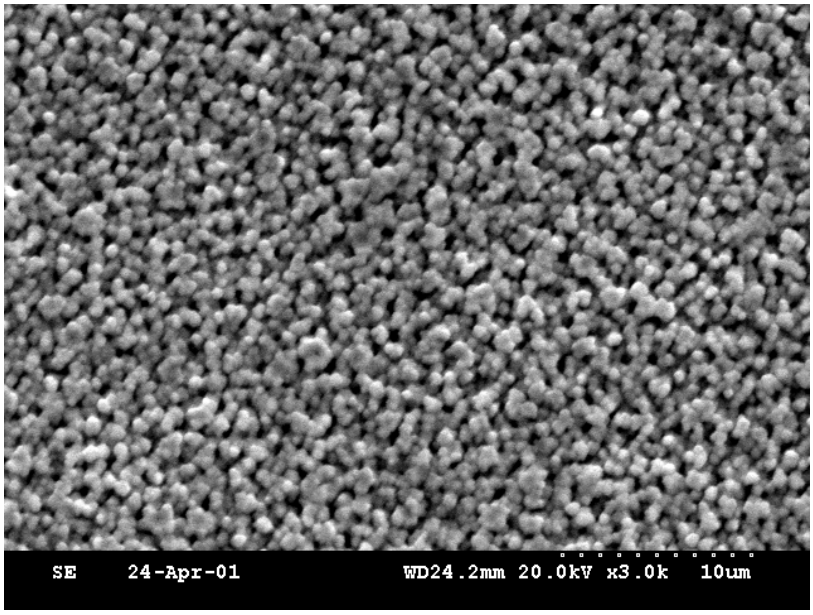


Elem	Wt %	At %	K-Ratio	Z	A	F
S K	25.94	**48.70**	0.2037	1.1569	0.6715	1.0109
InL	44.62	**23.40**	0.3629	0.9051	0.8987	1.0000
CuK	29.44	**27.90**	0.2826	1.0016	0.9584	1.0000
Total	100.00	**100.00**				

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)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **1**.



Grain size ~ 1μm

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

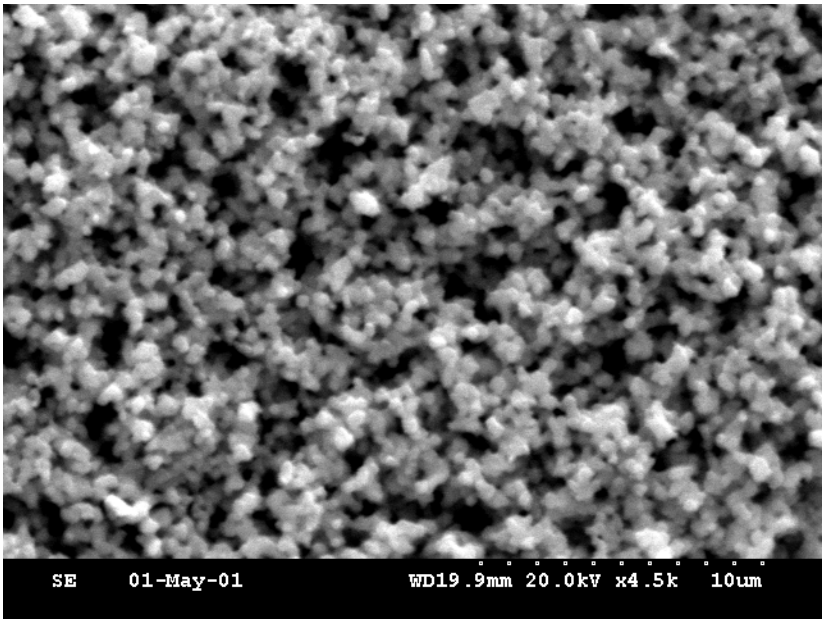
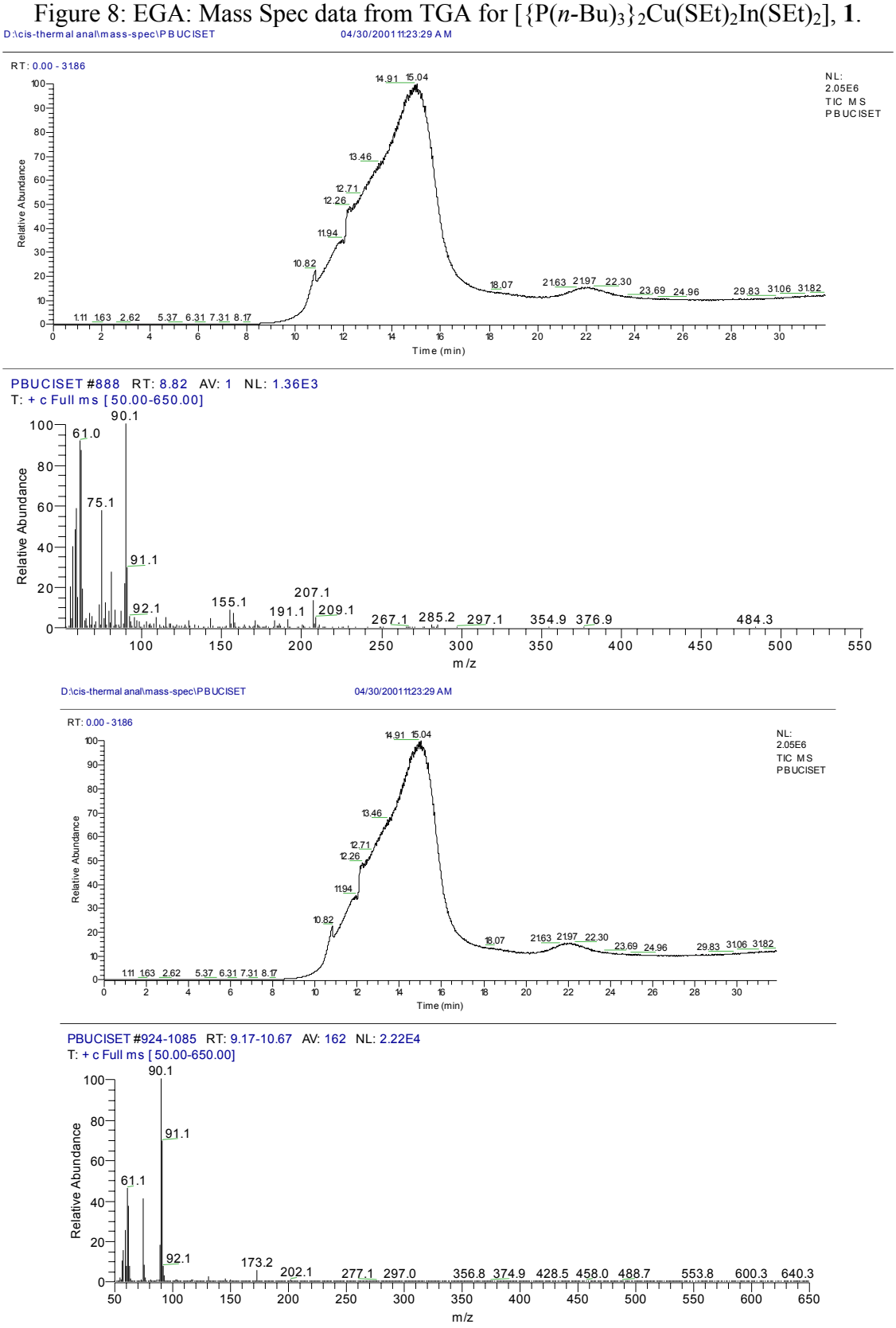
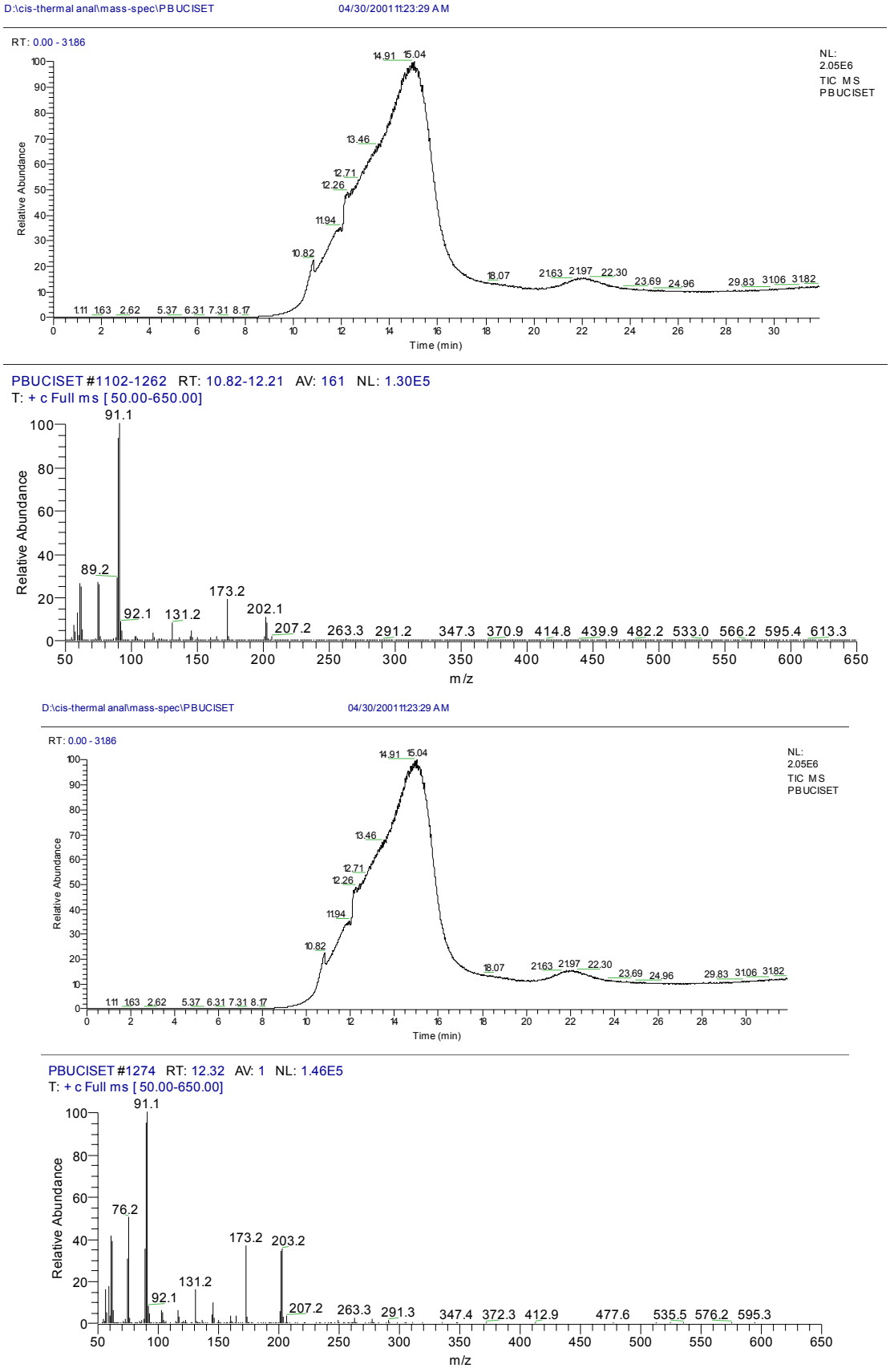
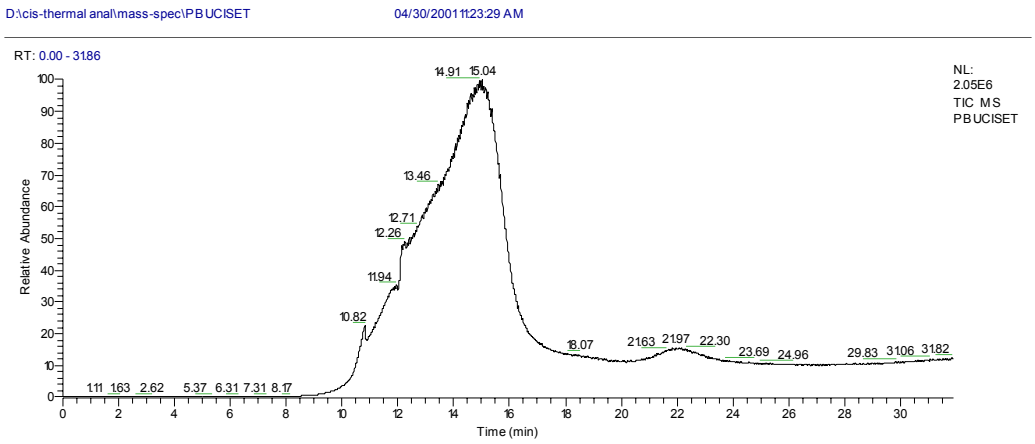
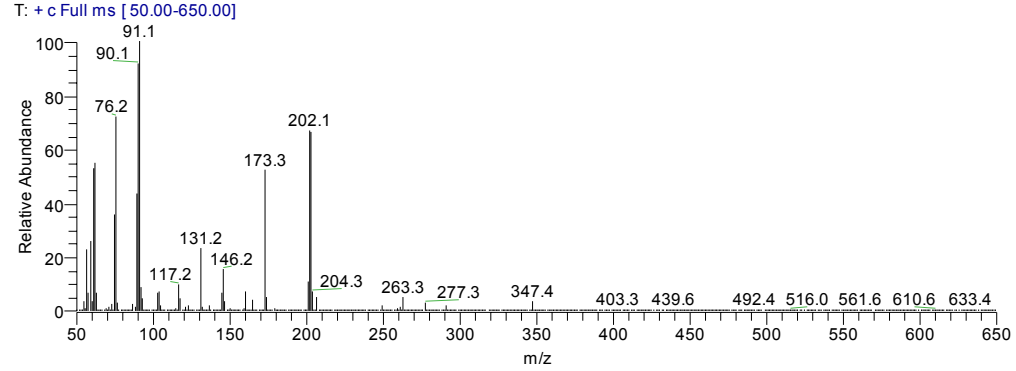


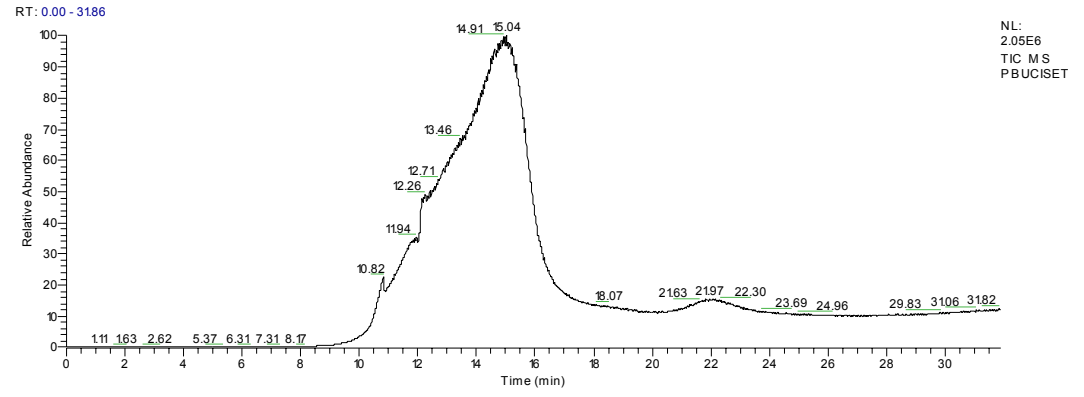
Figure 8: EGA: Mass Spec data from TGA for [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$], **1**.

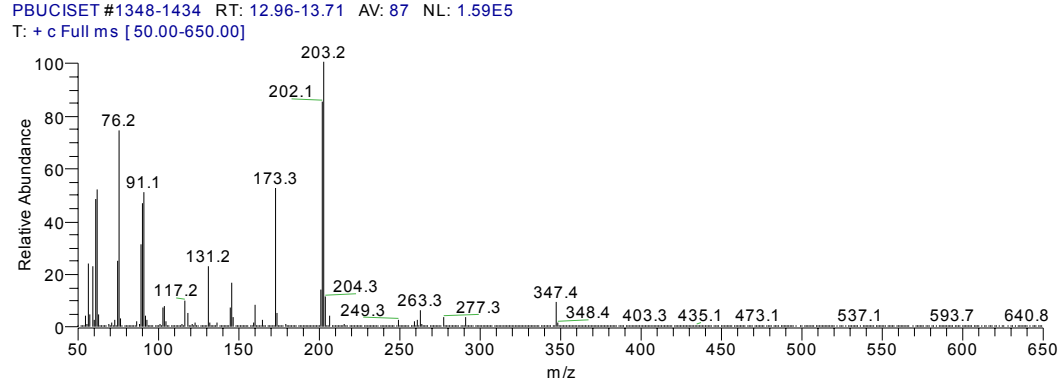


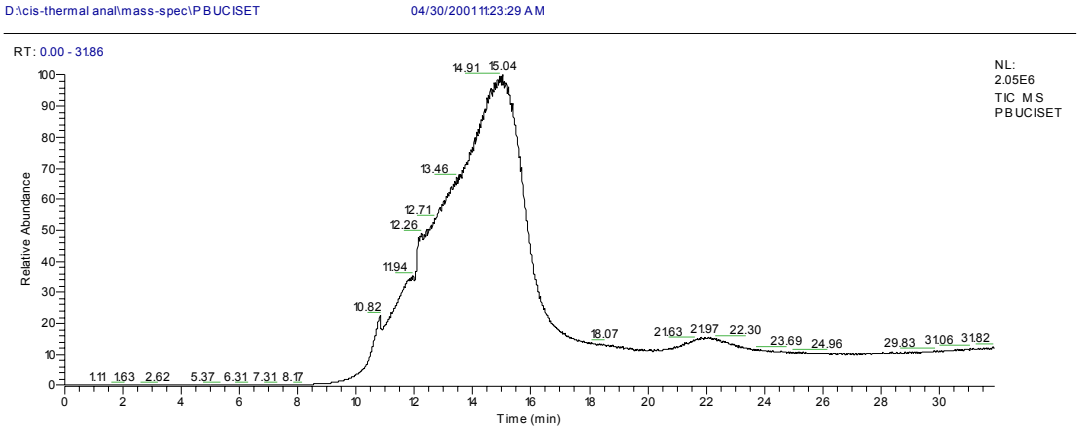

D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 31.86
NL: 2.05E6 TIC MS PBUCISET
Relative Abundance
Time (min)
PBUCISET #1102-1262 RT: 10.82-12.21 AV: 161 NL: 1.30E5
T: + c Full ms [50.00-650.00]
91.1
89.2
92.1
131.2
173.2
202.1
207.2
263.3
291.2
347.3
370.9
414.8
439.9
482.2
533.0
566.2
595.4
613.3
m/z
D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 31.86
NL: 2.05E6 TIC MS PBUCISET
Relative Abundance
Time (min)
PBUCISET #1274 RT: 12.32 AV: 1 NL: 1.46E5
T: + c Full ms [50.00-650.00]
91.1
76.2
92.1
131.2
173.2
203.2
207.2
263.3
291.3
347.4
372.3
412.9
477.6
535.5
576.2
595.3
m/z

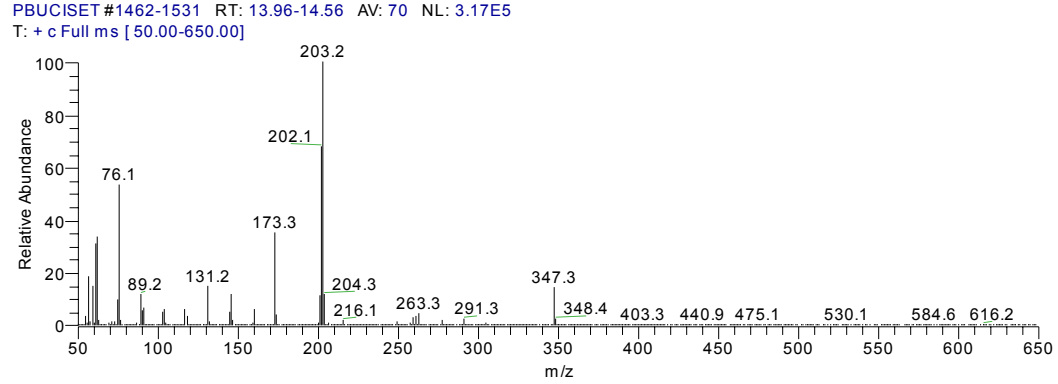

D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91 15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63 21.97 22.30
23.69 24.96
29.83 31.06 31.82
1.11 1.63 2.62 5.37 6.31 7.31 8.17

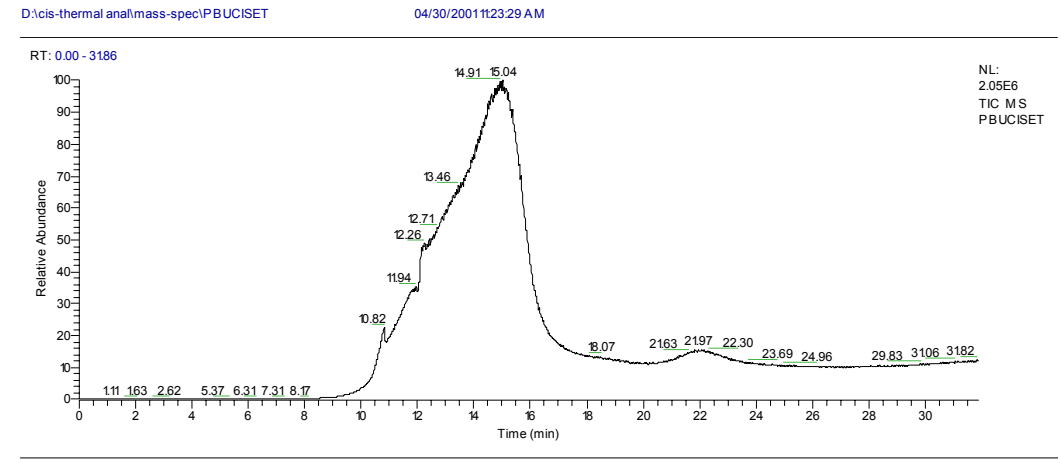

PBUCISET #1257-1371 RT: 12.17-13.16 AV: 115 NL: 1.23E5
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
91.1
90.1
76.2
202.1
173.3
131.2
146.2
117.2
204.3
263.3
277.3
347.4
403.3 439.6
492.4 516.0 561.6 610.6 633.4


D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91 15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63 21.97 22.30
23.69 24.96
29.83 31.06 31.82
1.11 1.63 2.62 5.37 6.31 7.31 8.17


PBUCISET #1348-1434 RT: 12.96-13.71 AV: 87 NL: 1.59E5
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
203.2
202.1
76.2
91.1
173.3
131.2
117.2
204.3
249.3
263.3
277.3
347.4
348.4
403.3 435.1 473.1
537.1
593.7
640.8


D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 3186
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91 15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63 21.97 22.30
23.69 24.96
29.83 31.06 31.82
1.11 1.63 2.62 5.37 6.31 7.31 8.17


PBUCISET #1462-1531 RT: 13.96-14.56 AV: 70 NL: 3.17E5
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
203.2
202.1
76.1
173.3
89.2
131.2
204.3
216.1
263.3
291.3
347.3
348.4
403.3 440.9 475.1
530.1
584.6 616.2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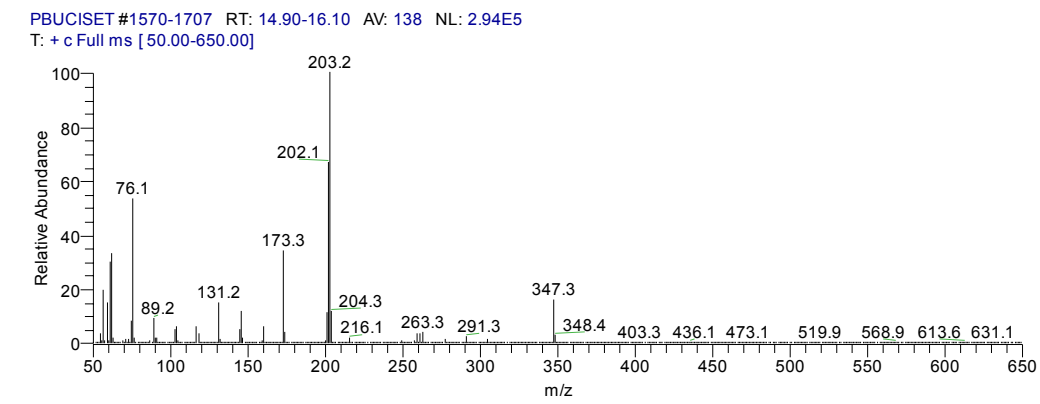
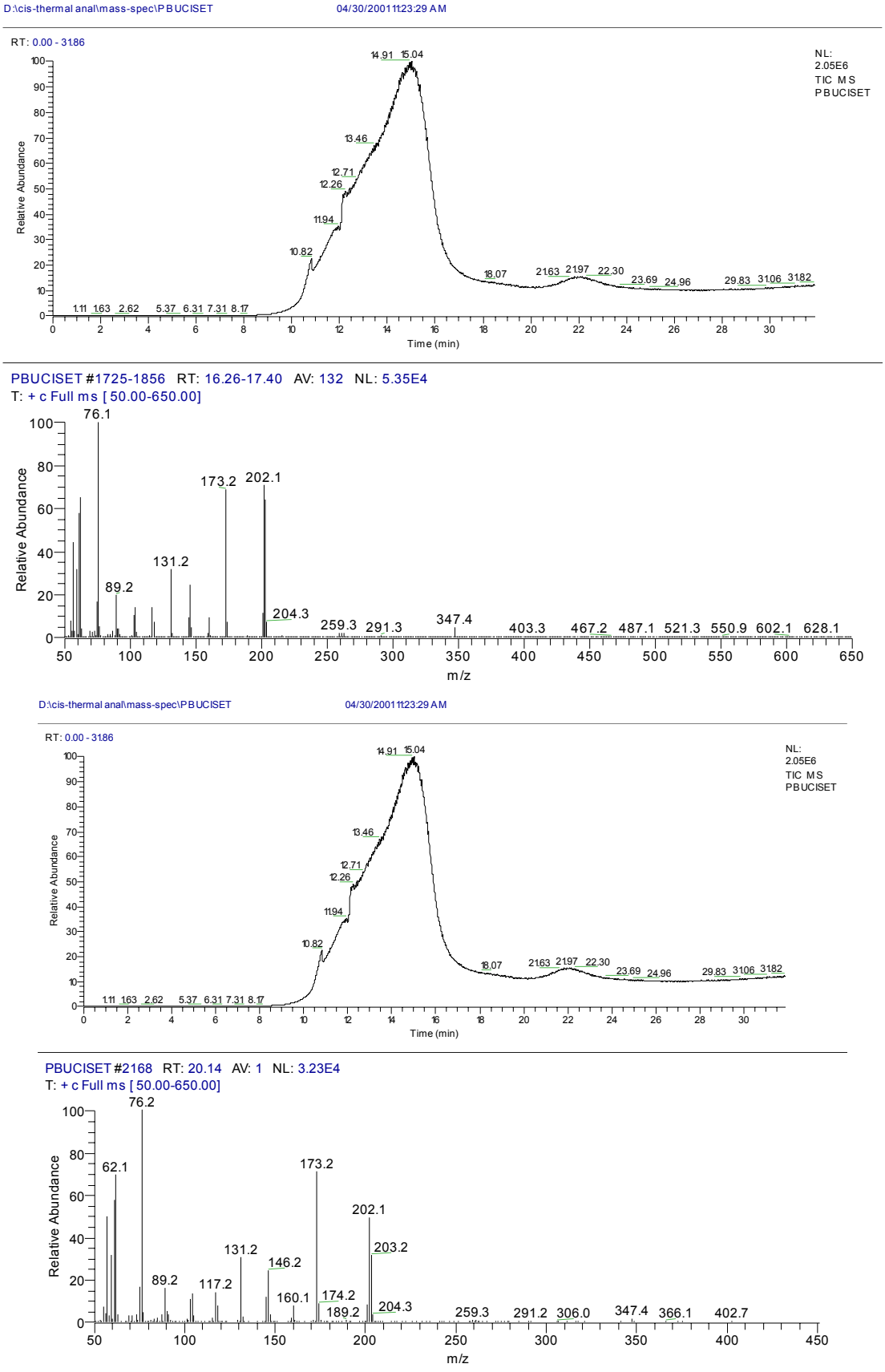
RT: 0.00 - 3186
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91 15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63 21.97 22.30
23.69 24.96
29.83 31.06 31.82
1.11 1.63 2.62 5.37 6.31 7.31 8.17


PBUCISET #1570-1707 RT: 14.90-16.10 AV: 138 NL: 2.94E5
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
203.2
202.1
76.1
173.3
89.2
131.2
204.3
216.1
263.3
291.3
347.3
348.4
403.3 436.1 473.1
519.9
568.9 613.6 631.1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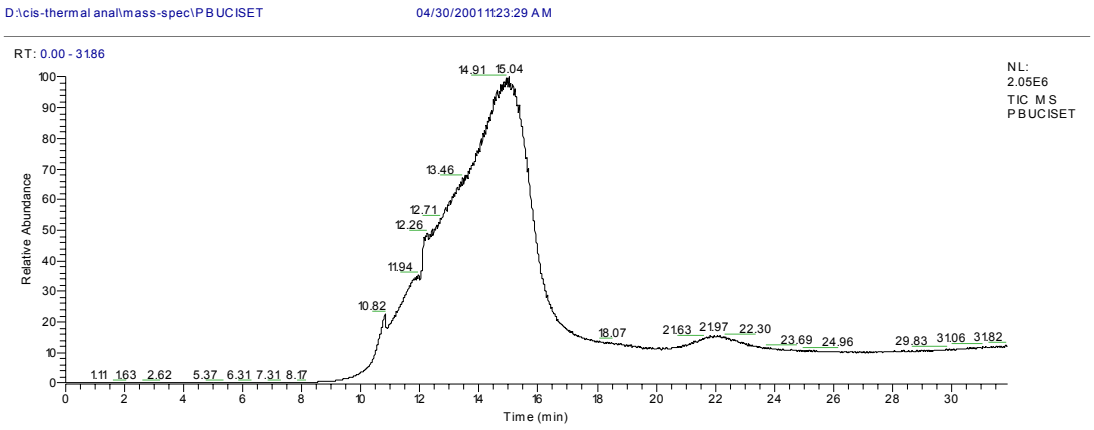
RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
PBUCISET #1725-1856 RT: 16.26-17.40 AV: 132 NL: 5.35E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
PBUCISET #2168 RT: 20.14 AV: 1 NL: 3.23E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z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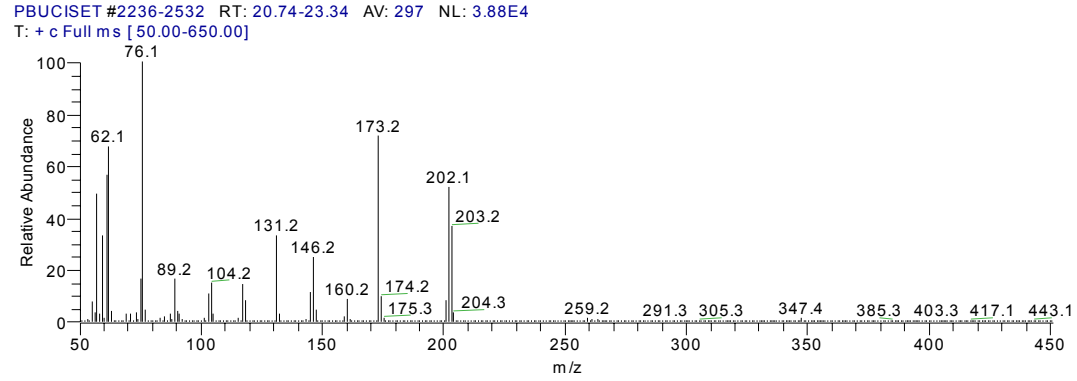
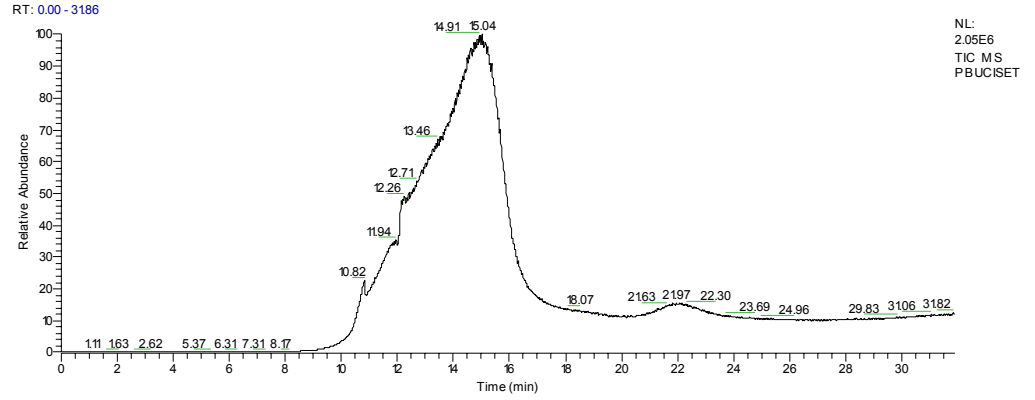
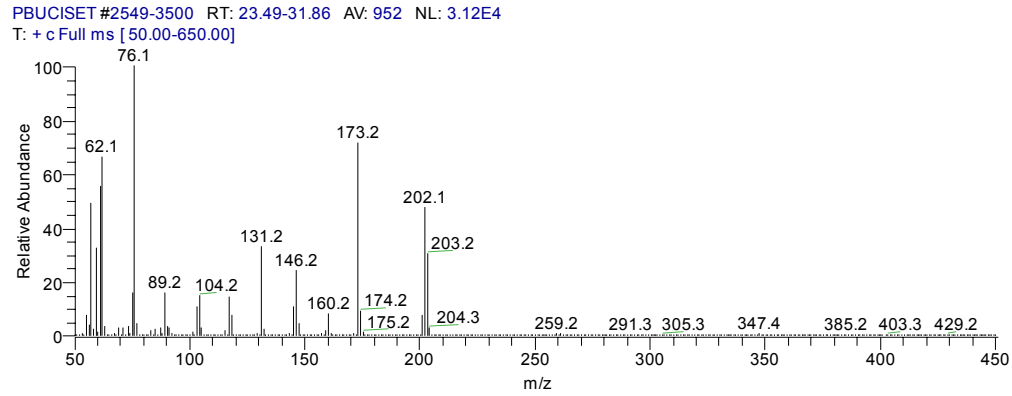
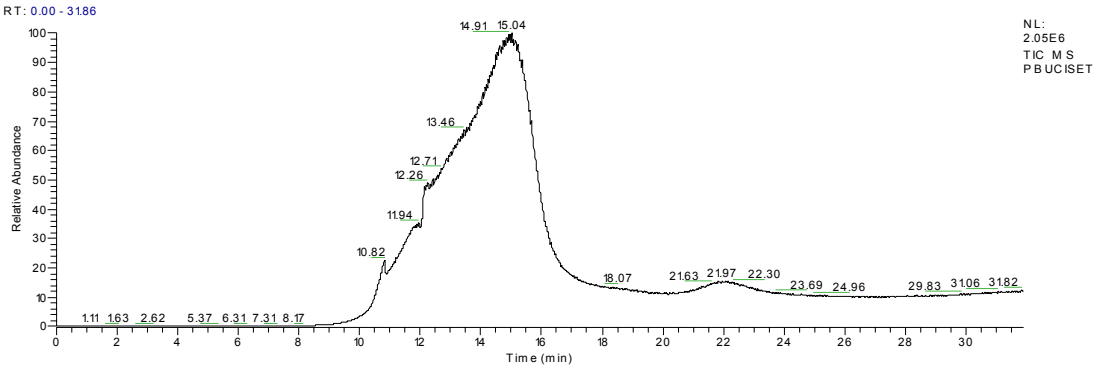
RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91 15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63 21.97 22.30
23.69 24.96
29.83 31.06 31.82
1.11 1.63 2.62 5.37 6.31 7.31 8.17


PBUCISET #2236-2532 RT: 20.74-23.34 AV: 297 NL: 3.88E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
76.1
62.1
173.2
202.1
203.2
131.2
146.2
89.2
104.2
160.2
174.2
175.3
204.3
259.2
291.3 305.3
347.4
385.3 403.3 417.1 443.1


D:\cis-thermal anal\mass-spec\PBUCISET 04/30/2001 11:23:29 AM
RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91 15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63 21.97 22.30
23.69 24.96
29.83 31.06 31.82
1.11 1.63 2.62 5.37 6.31 7.31 8.17


PBUCISET #2549-3500 RT: 23.49-31.86 AV: 952 NL: 3.12E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
76.1
62.1
173.2
202.1
203.2
131.2
146.2
89.2
104.2
160.2
174.2
175.2
204.3
259.2
291.3 305.3
347.4
385.2 403.3 429.2


RT: 0.00 - 31.86
NL:
2.05E6
TIC MS
PBUCISET
Relative Abundance
Time (min)
14.91
15.04
13.46
12.71
12.26
11.94
10.82
18.07
21.63
21.97
22.30
23.69
24.96
29.83
31.06
31.82
1.11
1.63
2.62
5.37
6.31
7.31
8.17

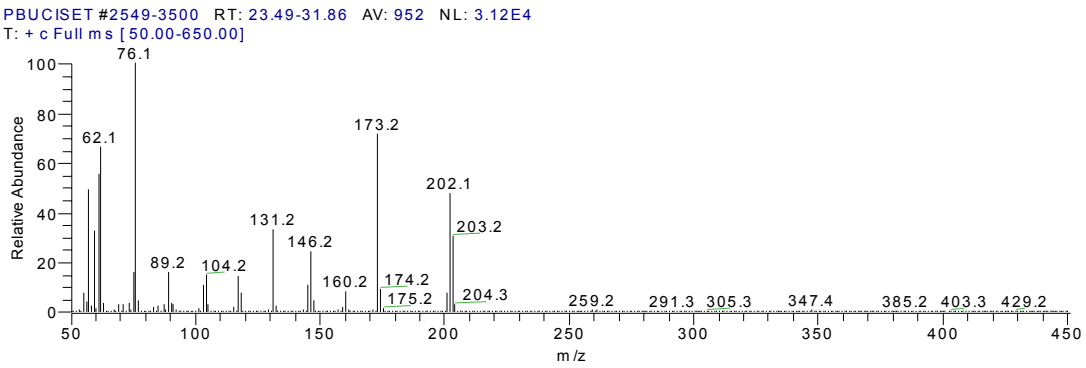
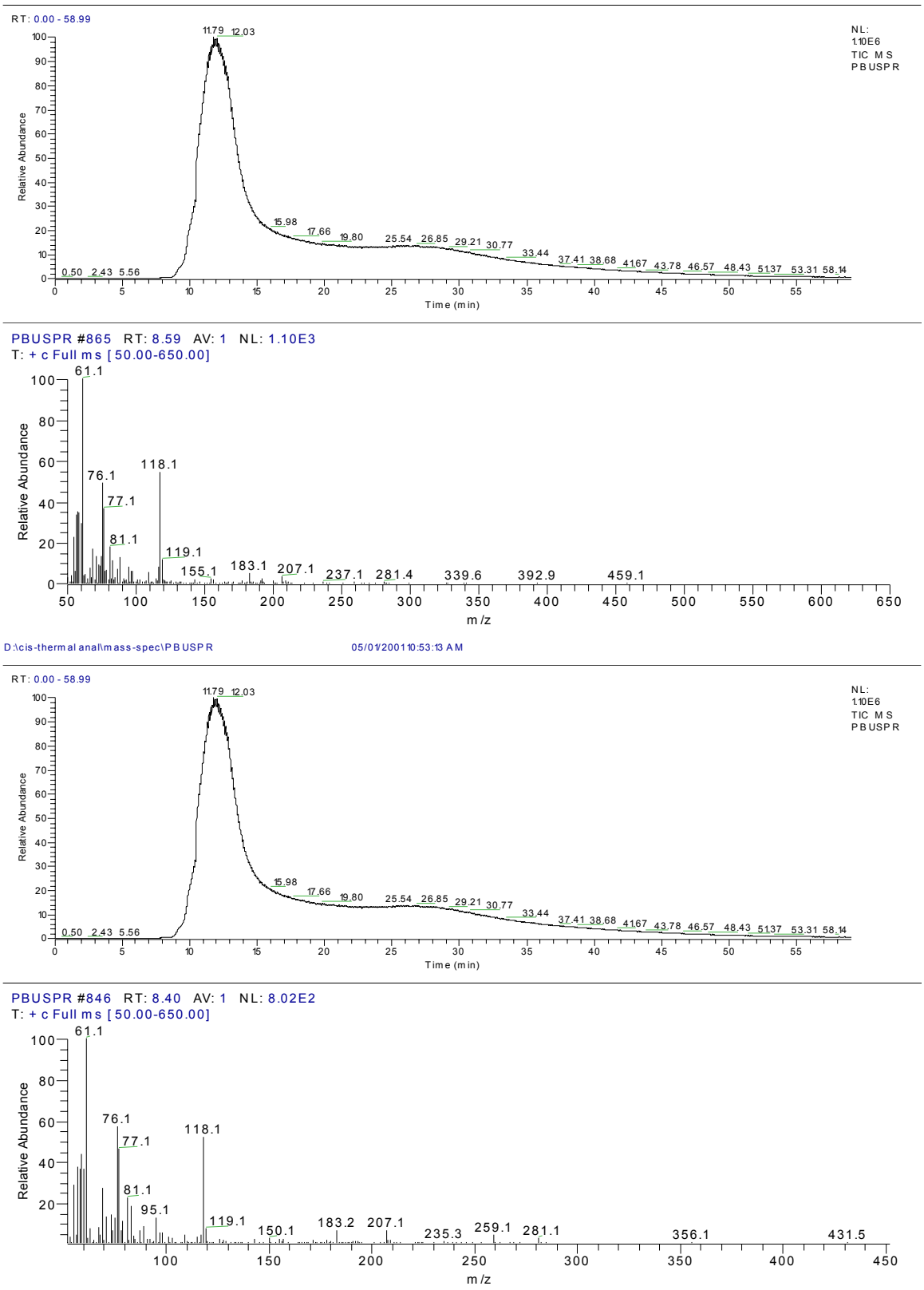

PBUCISET #2549-3500 RT: 23.49-31.86 AV: 952 NL: 3.12E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
76.1
62.1
173.2
202.1
203.2
131.2
146.2
89.2
104.2
160.2
174.2
175.2
204.3
259.2
291.3
305.3
347.4
385.2
403.3
429.2

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



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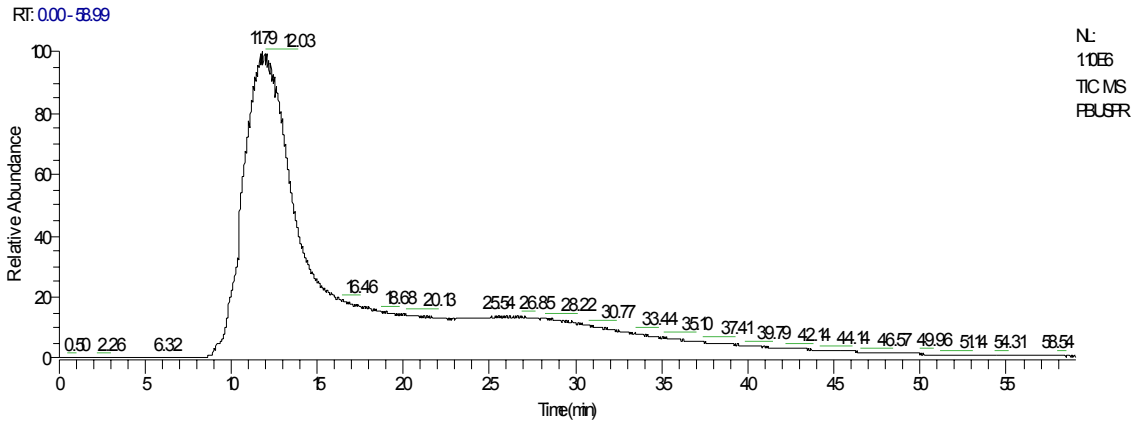

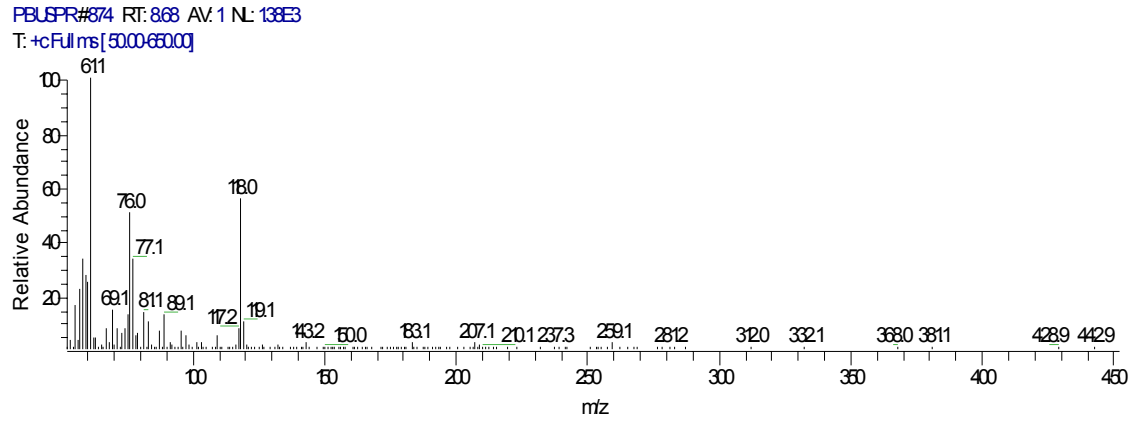

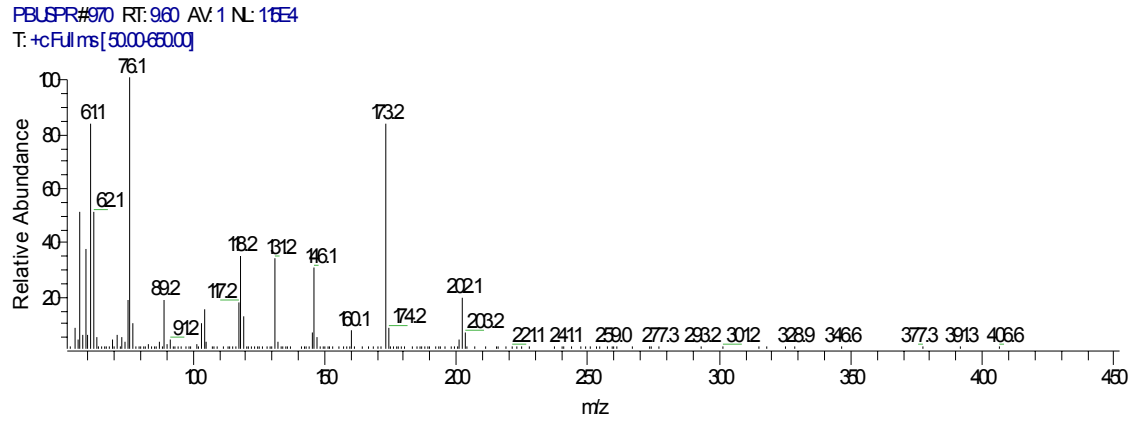

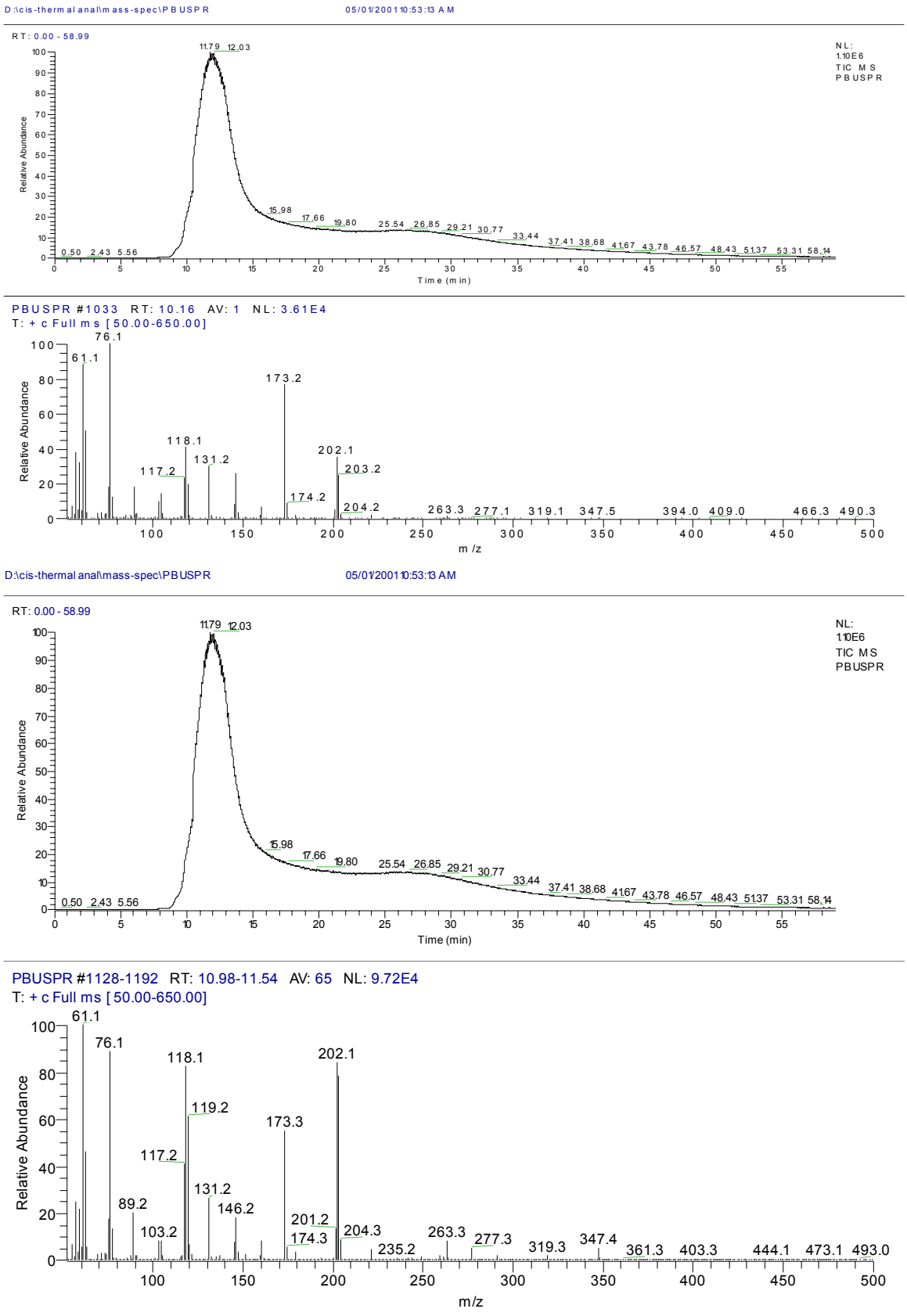
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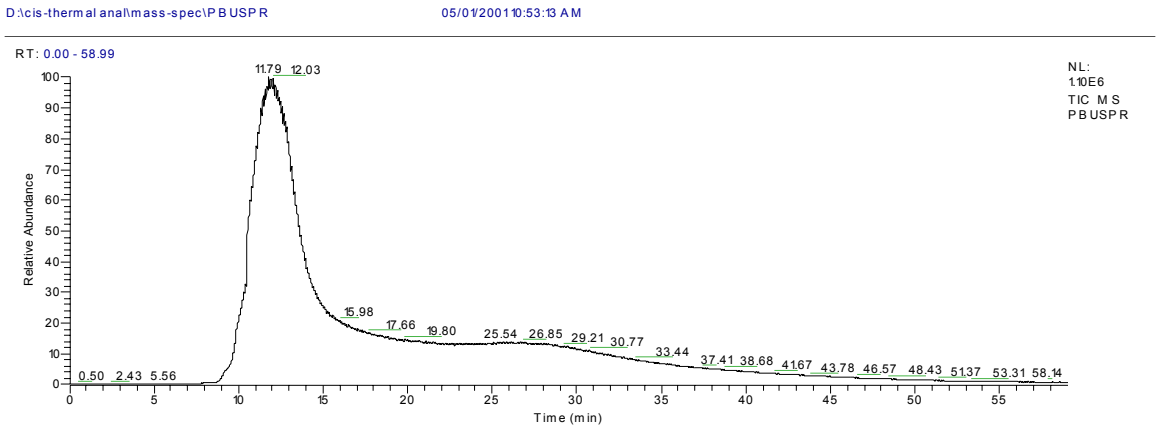
RT: 0.00 - 58.99
NL: 1.10E6 TIC MS PBUSPR
Relative Abundance
Time (min)
PBUSPR #1033 RT: 10.16 AV: 1 NL: 3.61E4
T: + c Full ms [50.00-650.00]
m/z
D:\cis-thermal anal\mass-spec\PBUSPR 05/01/2001 10:53:13 AM
RT: 0.00 - 58.99
NL: 1.10E6 TIC MS PBUSPR
Relative Abundance
Time (min)
PBUSPR #1128-1192 RT: 10.98-11.54 AV: 65 NL: 9.72E4
T: + c Full ms [50.00-650.00]
m/z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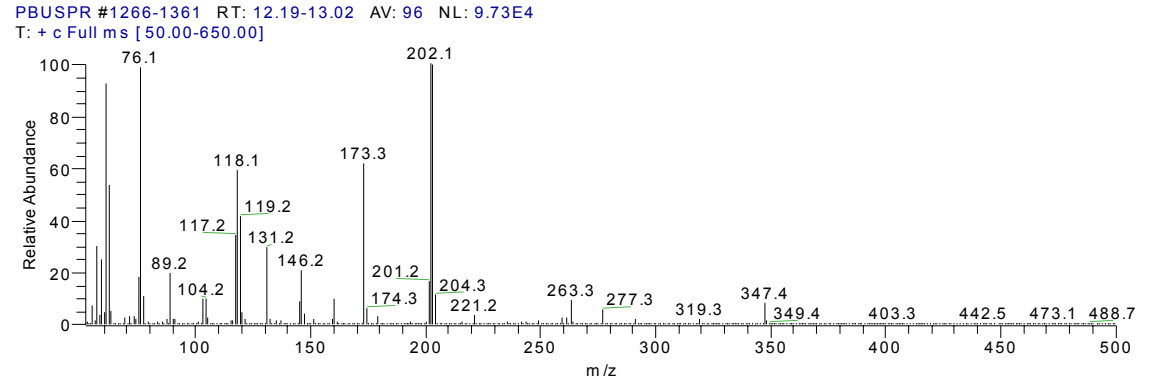
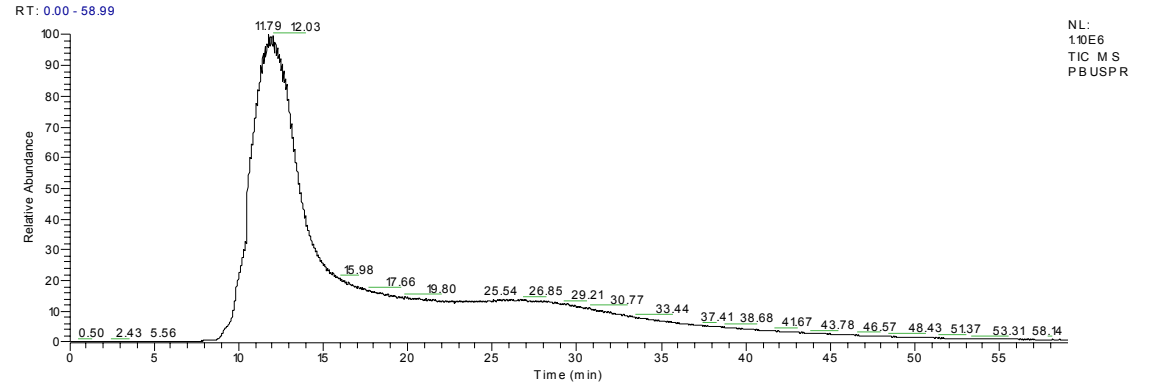
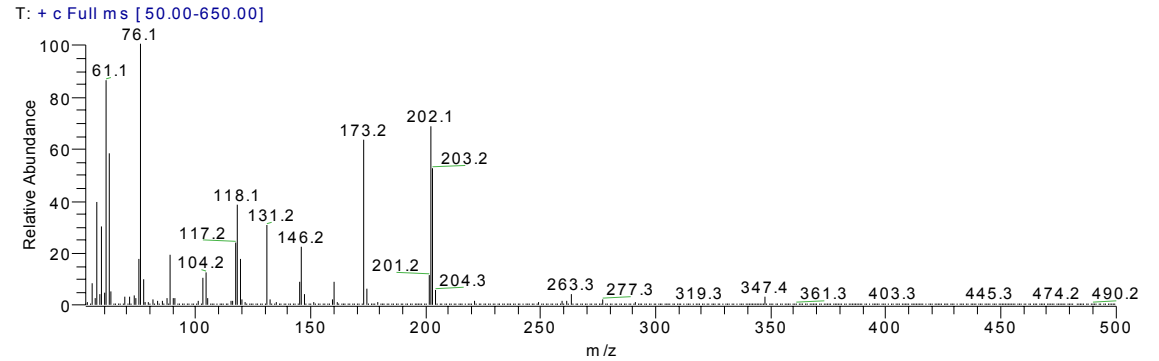
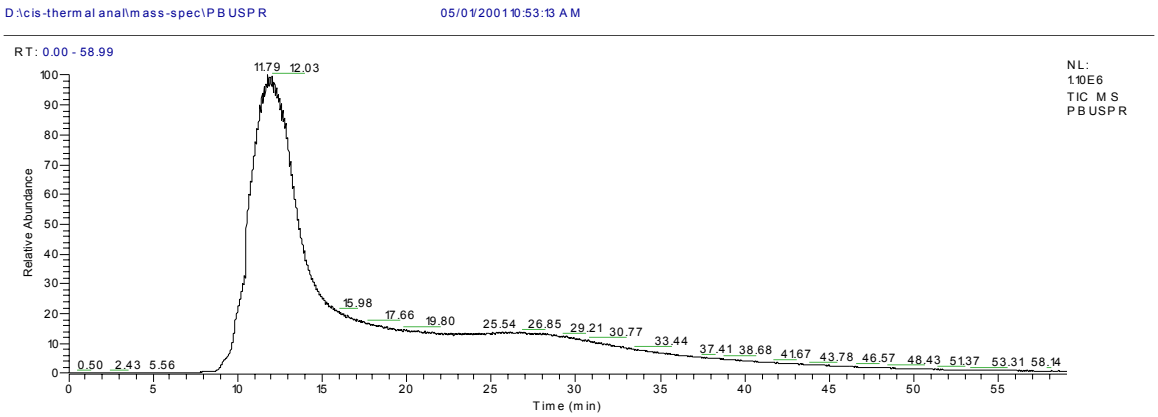
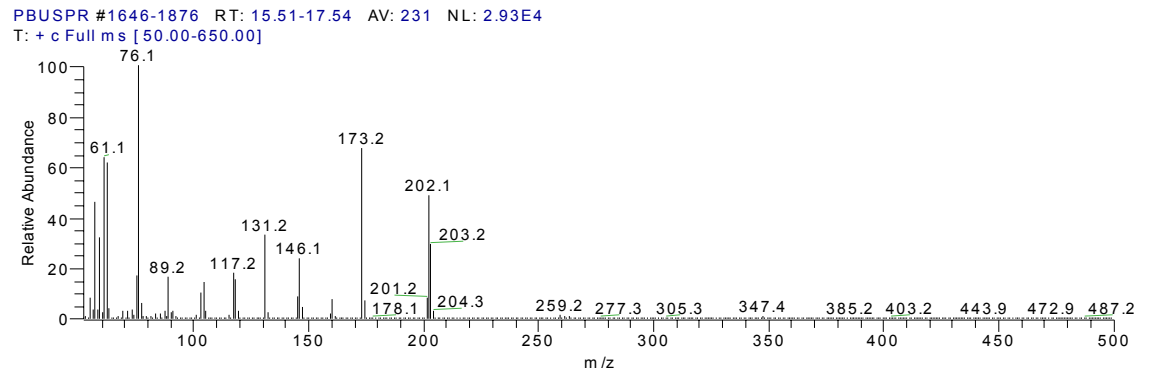
RT: 0.00 - 58.99
NL: 1.10E6 TIC MS PBUSPR
Relative Abundance
Time (min)
11.79 12.03
15.98 17.66 19.80 25.54 26.85 29.21 30.77 33.44 37.41 38.68 41.67 43.78 46.57 48.43 51.37 53.31 58.14
0.50 2.43 5.56

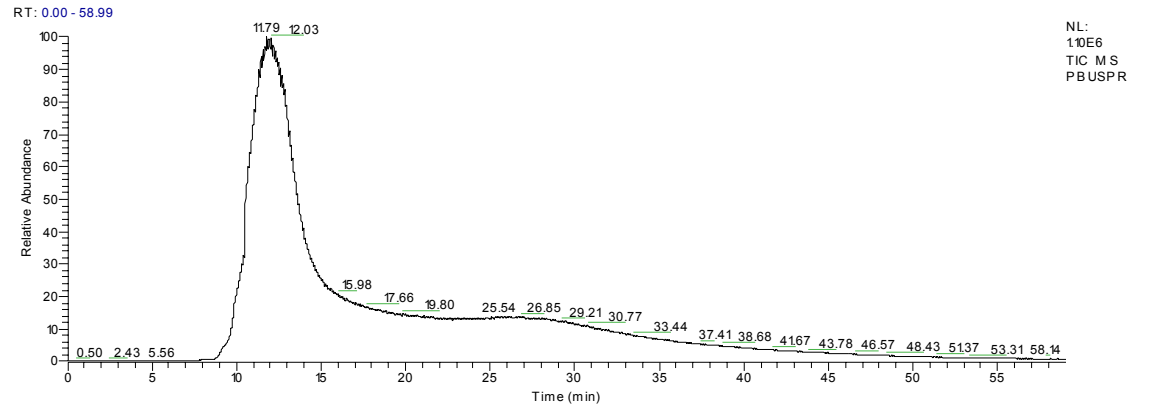

PBUSPR #1266-1361 RT: 12.19-13.02 AV: 96 NL: 9.73E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
76.1 202.1 173.3 118.1 119.2 117.2 131.2 146.2 89.2 104.2 201.2 204.3 174.3 221.2 263.3 277.3 319.3 347.4 349.4 403.3 442.5 473.1 488.7


D:\cis-thermal anal\mass-spec\PBUSPR 05/01/2001 0:53:13 AM
RT: 0.00 - 58.99
NL: 1.10E6 TIC MS PBUSPR
Relative Abundance
Time (min)
11.79 12.03
15.98 17.66 19.80 25.54 26.85 29.21 30.77 33.44 37.41 38.68 41.67 43.78 46.57 48.43 51.37 53.31 58.14
0.50 2.43 5.56


PBUSPR #1414-1583 RT: 13.48-14.96 AV: 170 NL: 4.82E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
76.1 61.1 173.2 202.1 203.2 118.1 131.2 117.2 146.2 104.2 201.2 204.3 263.3 277.3 319.3 347.4 361.3 403.3 445.3 474.2 490.2


D:\cis-thermal anal\mass-spec\PBUSPR 05/01/2001 0:53:13 AM
RT: 0.00 - 58.99
NL: 1.10E6 TIC MS PBUSPR
Relative Abundance
Time (min)
11.79 12.03
15.98
17.66
19.80
25.54 26.85 29.21 30.77
33.44
37.41 38.68 41.67 43.78 46.57 48.43 51.37 53.31 58.14
0.50 2.43 5.56


PBUSPR #1646-1876 RT: 15.51-17.54 AV: 231 NL: 2.93E4
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
76.1
61.1
173.2
202.1
203.2
131.2
146.1
89.2
117.2
201.2
178.1
204.3
259.2 277.3 305.3 347.4 385.2 403.2 443.9 472.9 487.2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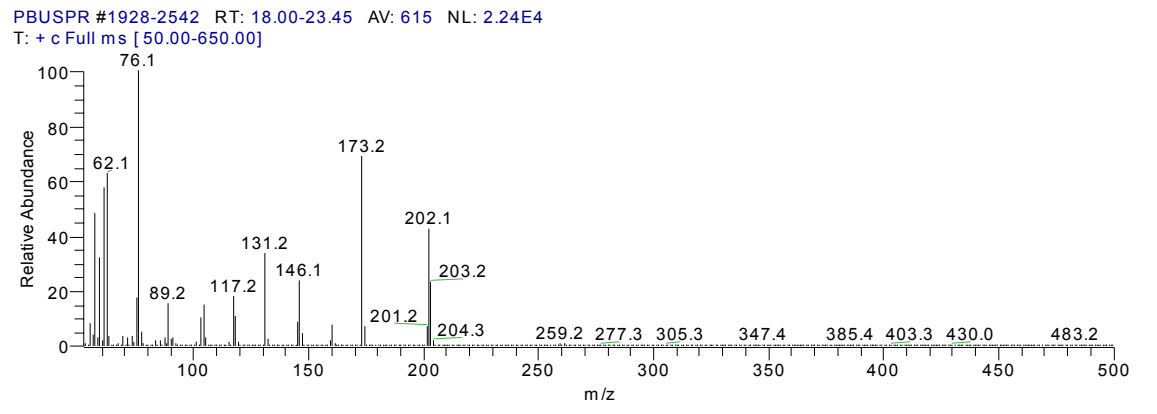
Relative Abundance
Time (min)
11.79 12.03
15.98
17.66
19.80
25.54 26.85 29.21 30.77
33.44
37.41 38.68 41.67 43.78 46.57 48.43 51.37 53.31 58.14
0.50 2.43 5.56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Relative Abundance
m/z
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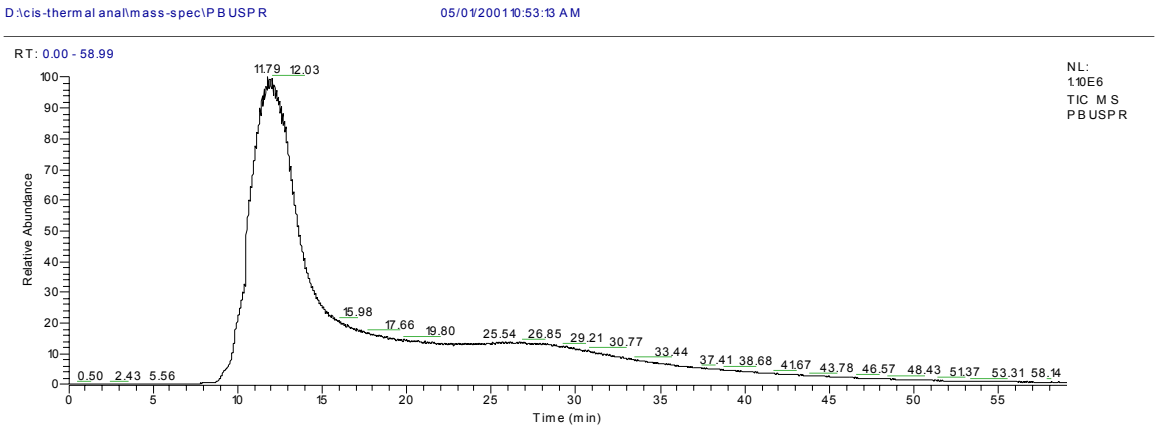
62.1
173.2
202.1
203.2
131.2
146.1
89.2
117.2
201.2
204.3
259.2 277.3 305.3 347.4 385.4 403.3 430.0 483.2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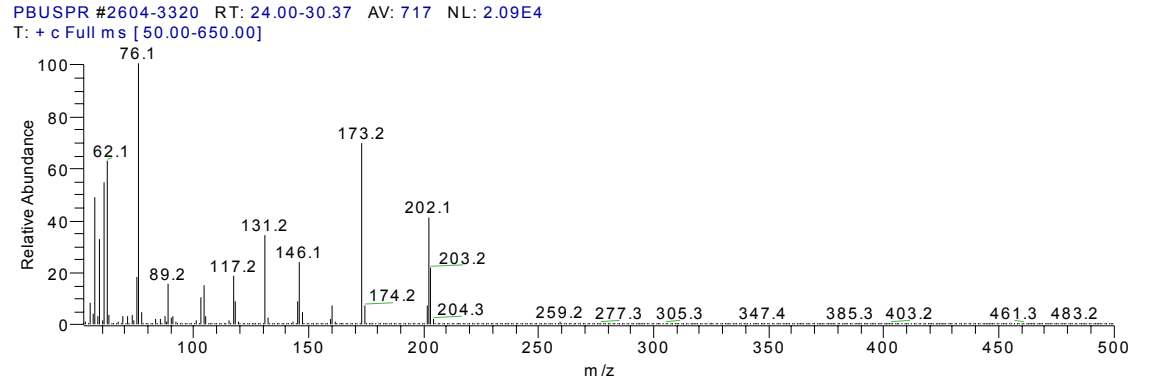
NL:
1.10E6
TIC MS
PBUSPR
Relative Abundance
Time (min)
11.79 12.03
15.98
17.66
19.80
25.54 26.85 29.21 30.77
33.44
37.41 38.68
41.67 43.78 46.57 48.43 51.37 53.31 58.14
0.50 2.43 5.56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Relative Abundance
m/z
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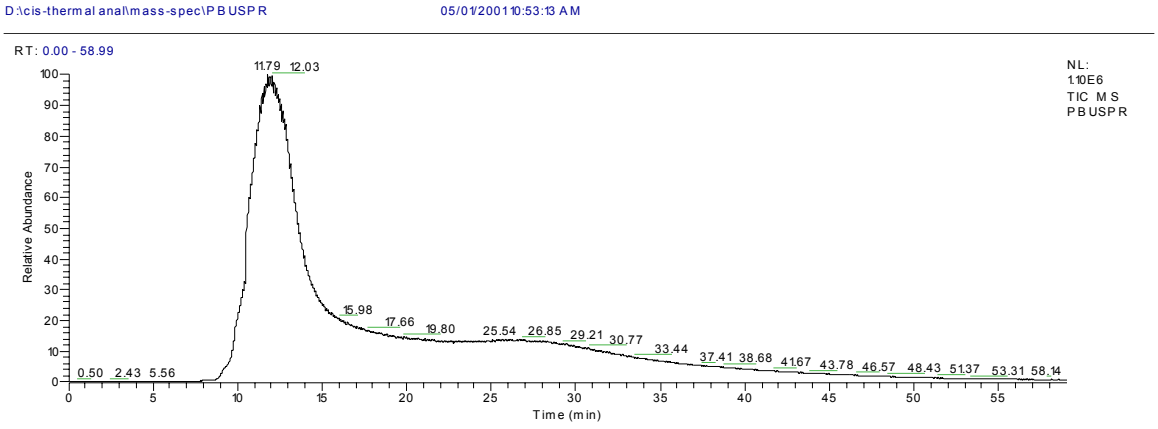
62.1
89.2
117.2
131.2
146.1
173.2
174.2
202.1
203.2
204.3
259.2 277.3 305.3 347.4 385.3 403.2 461.3 483.2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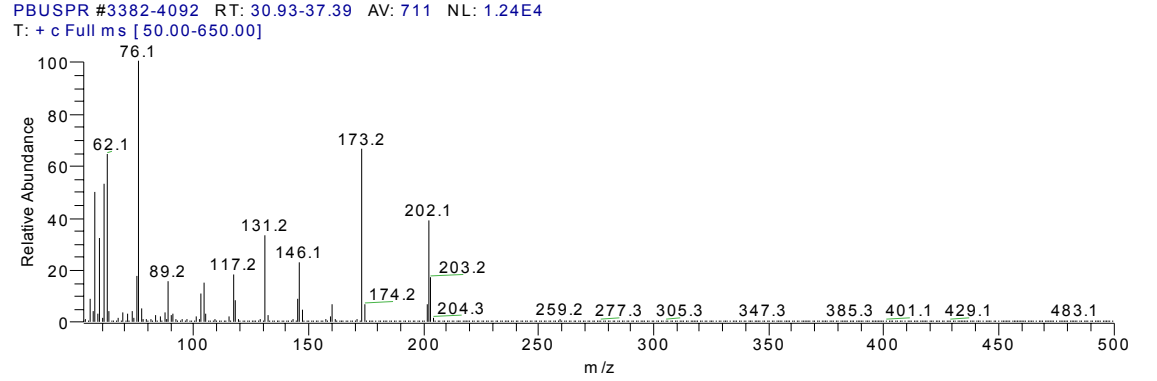
NL:
1.10E6
TIC MS
PBUSPR
Relative Abundance
Time (min)
11.79 12.03
15.98
17.66
19.80
25.54 26.85 29.21 30.77
33.44
37.41 38.68
41.67 43.78 46.57 48.43 51.37 53.31 58.14
0.50 2.43 5.56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Relative Abundance
m/z
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62.1
89.2
117.2
131.2
146.1
173.2
174.2
202.1
203.2
204.3
259.2 277.3 305.3 347.3 385.3 401.1 429.1 483.1

Figure 10. ^{1}H, ^{13}C & ^{31}P NMR data for **1**, **2**, and $[\{P(nBu_3)_3\}Cu\{MeCN\}_2]PF_6$.

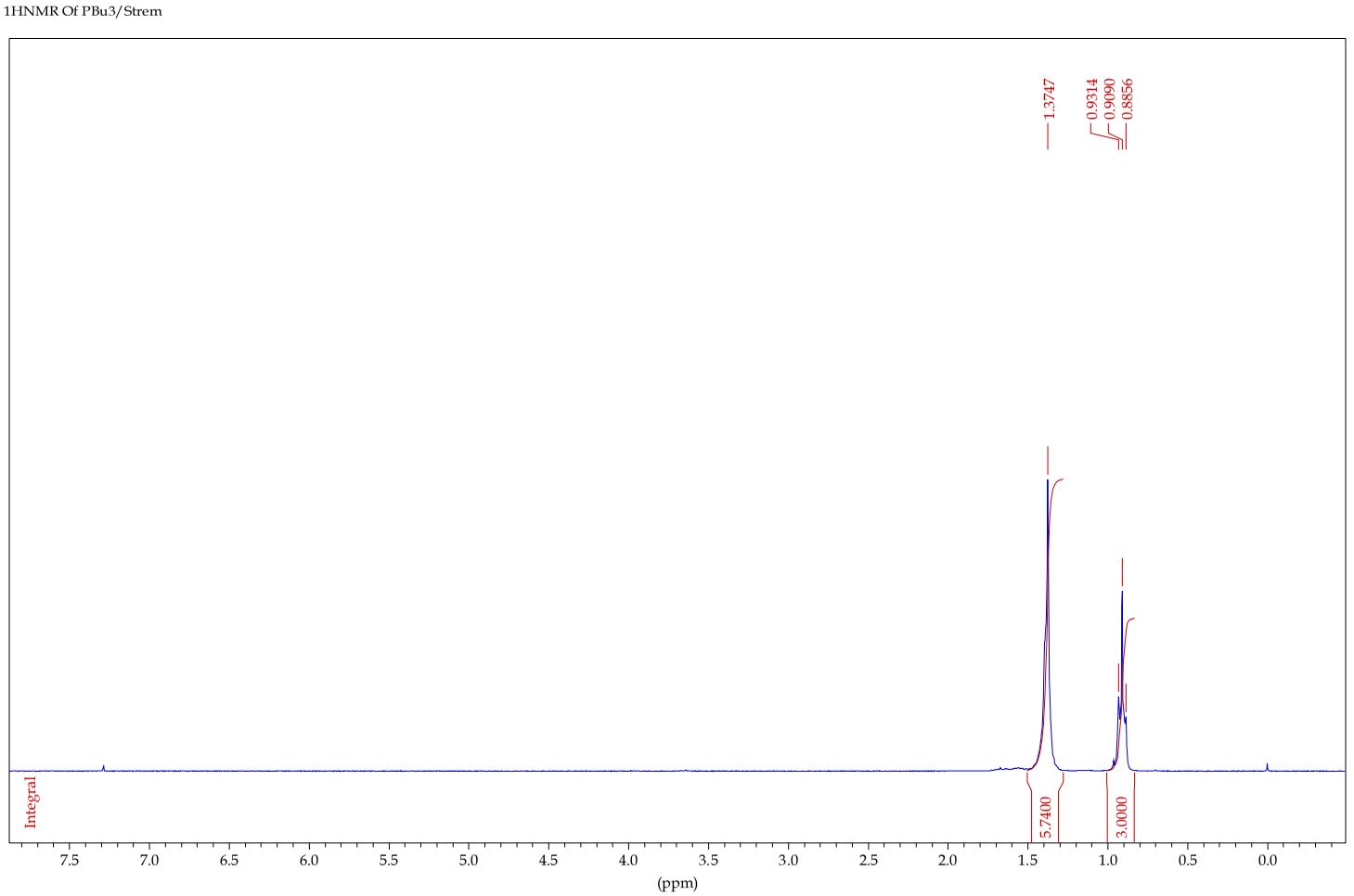
NOTE

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}P NMR spectra of a mixture of 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" PBu_3 in both precursors. ^{1}H, ^{13}C, NMR spectra for both precursors show the absence of a signal associated with a nitrile group, thus confirming that the intermediate $[\{PBu_3\}_2Cu\{MeCN\}_2]^{+}PF_6^{-}$ (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.

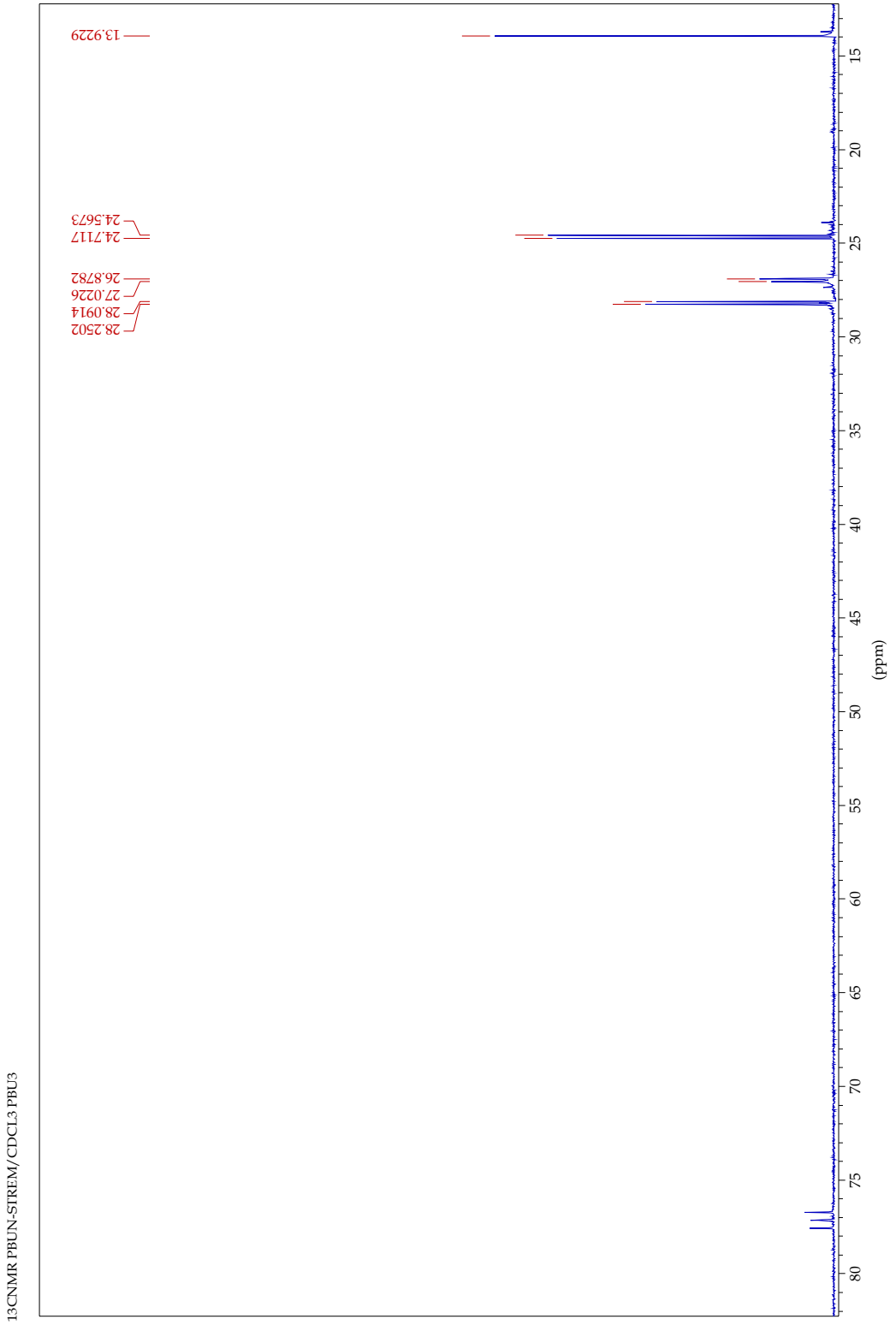
For $[\{P(nBu_3)_3\}Cu\{MeCN\}_2]PF_6$: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 2.25 ppm (s, CH_3CN); δ 1.62 ppm (br, $P(CH_2C_3H_7)_3$); δ 1.42 ppm (br, $P(CH_2C_2H_4CH_3)_3$) ; δ 0.94 ppm (t, $P(C_3H_6CH_3)_3$); ^{13}C NMR 75 MHz; $CDCl_3$; δ 119.68 ppm (CH_3CN); δ 27.15 ppm ($P(CH_2C_3H_7)_3$); δ 24.55 ppm ($P(CH_2CH_2C_2H_5)_3$); δ 24.12 ppm ($P(C_2H_4CH_2CH_3)_3$); δ 13.85 ppm, ($P(C_2H_4CH_2CH_3)_3$); ^{31}P NMR: 121 MHz; $CDCl_3$; δ -19.26 ppm, (br s, $-Cu\{P(Bu_3)\}_2$); δ -145.92 ppm, (sep, $^{-}PF_6$).

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

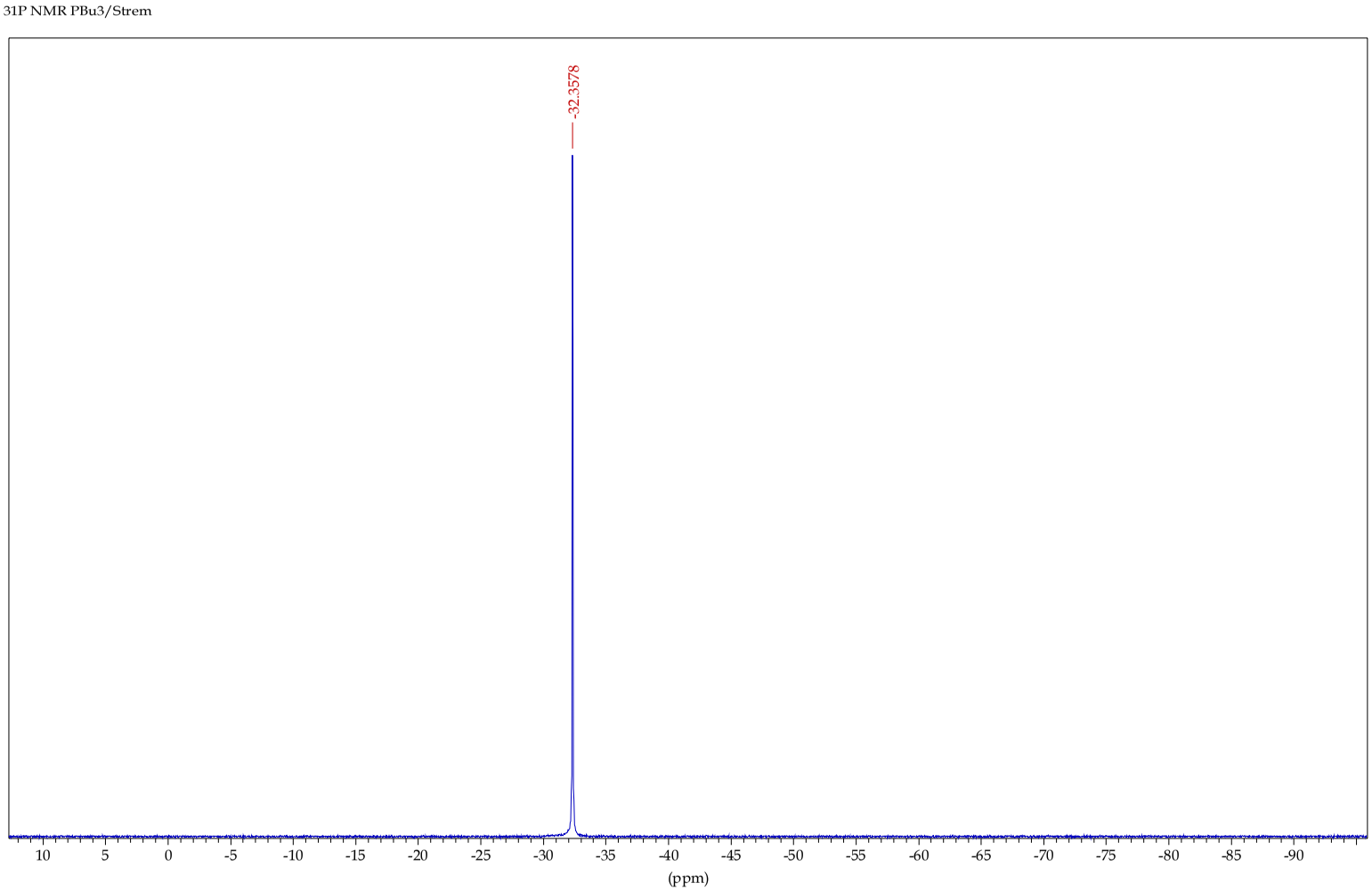
1H NMR: PBu_3



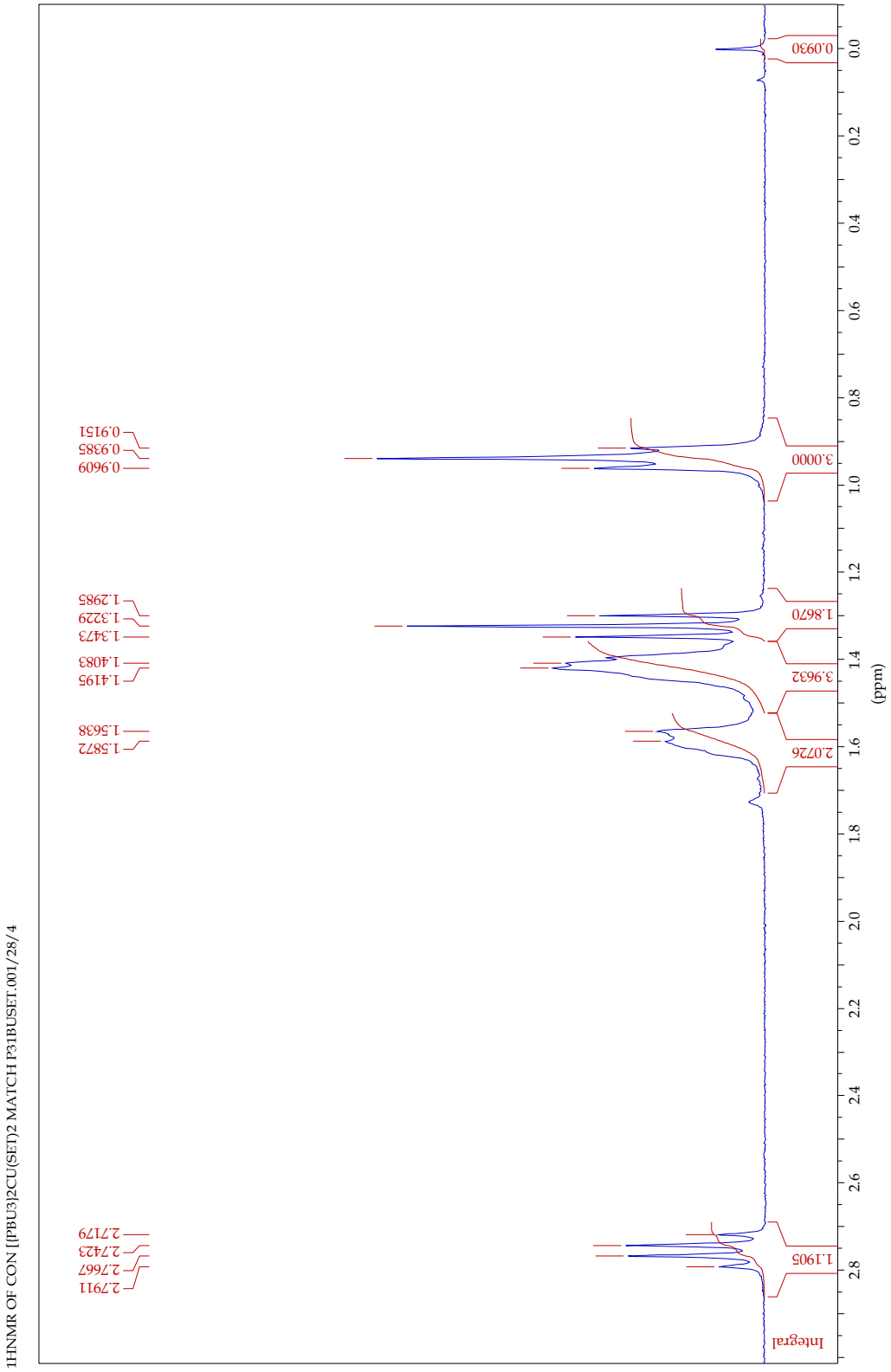
13 C NMR: PBu_3


13CNMR PBUN-STREM/CDCL3 PBU3
13.9229
24.5673
24.7117
26.8782
27.0226
28.0914
28.2502
15
20
25
30
35
40
45
50
55
60
65
70
75
80
(ppm)

31P NMR: PBu_3



IH NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$] 1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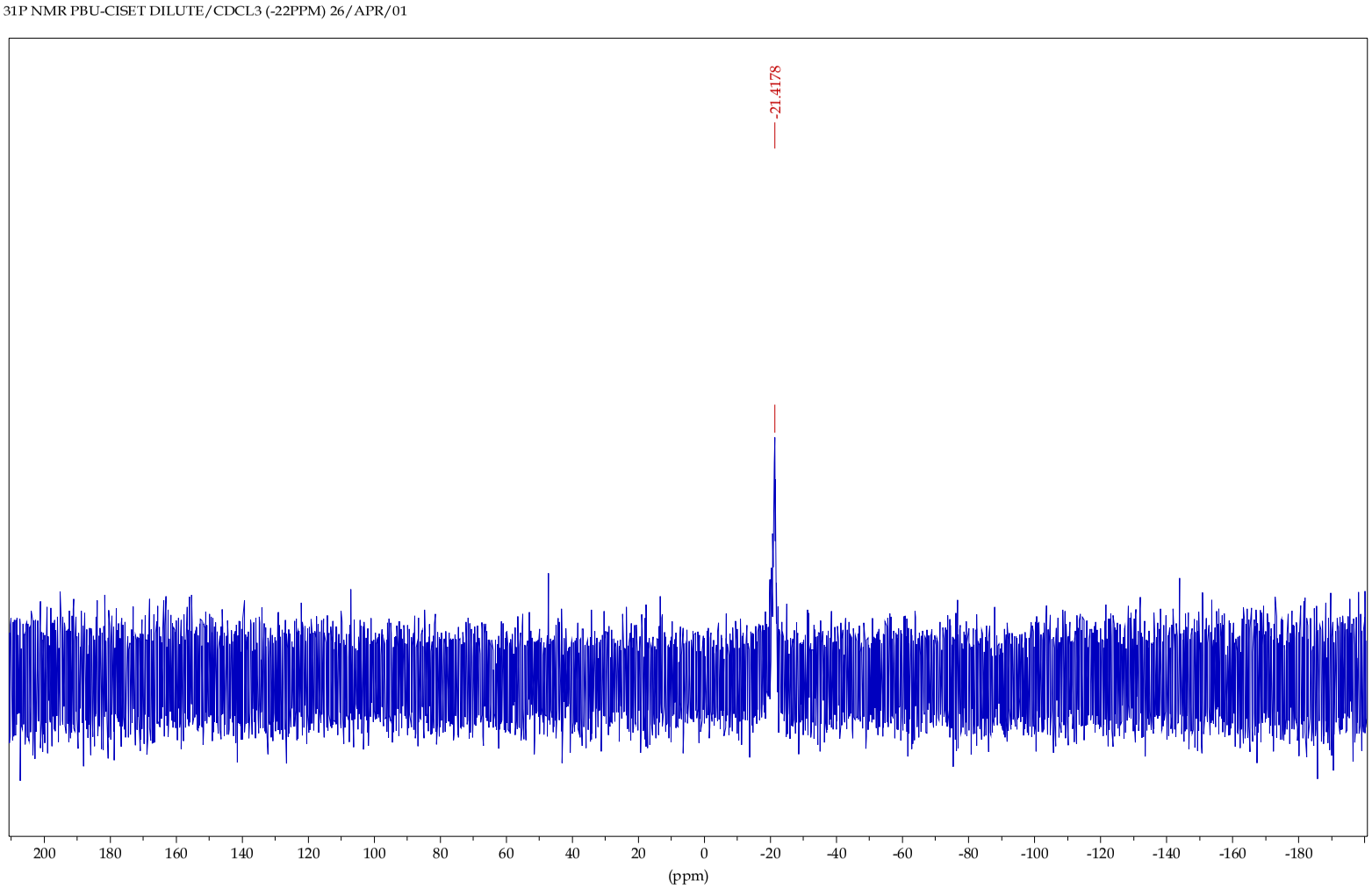
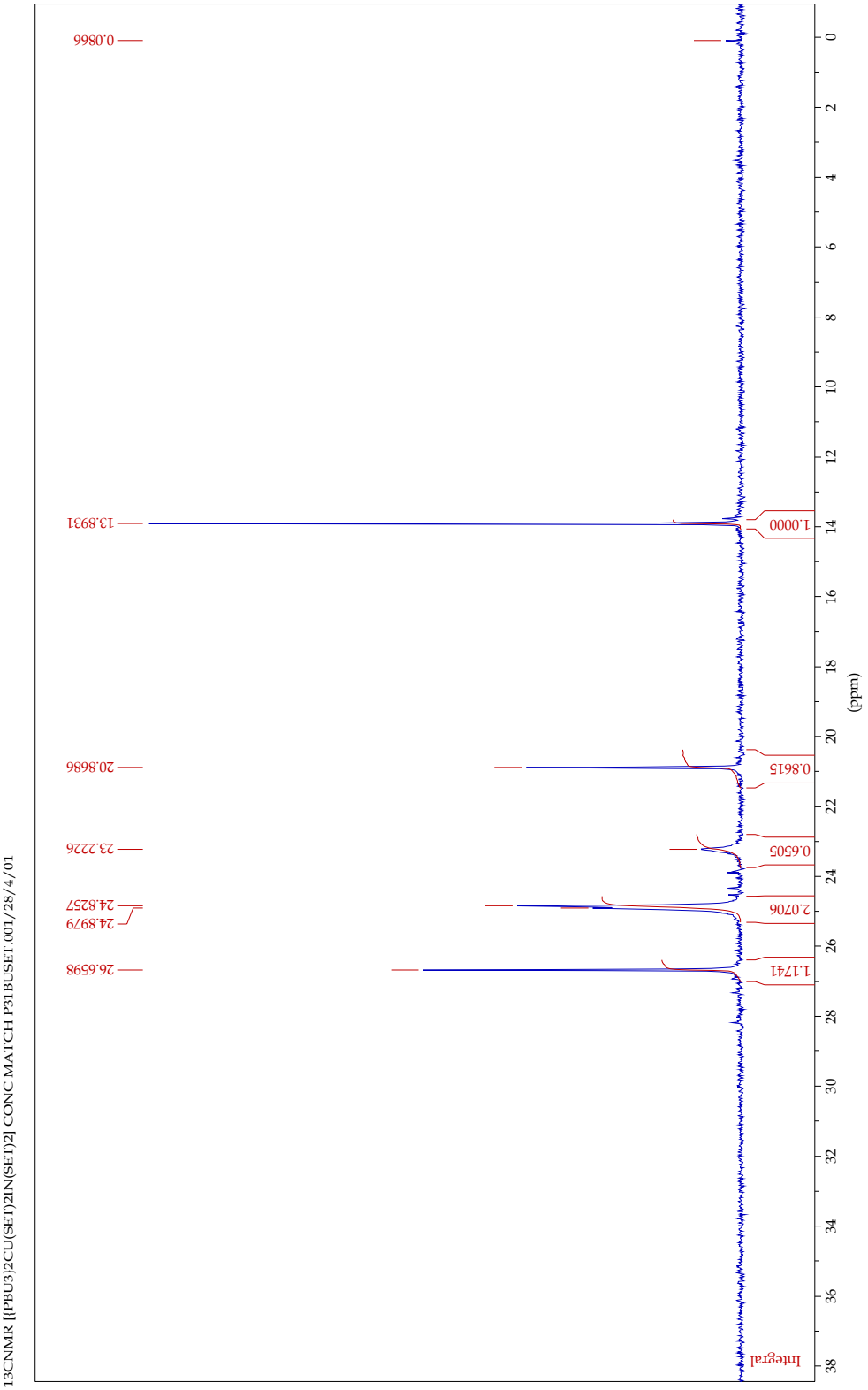
Integral
0.0930
3.0000
1.8670
3.9632
2.0726
1.1905
0.9151
0.9385
0.9609
1.2985
1.3229
1.3473
1.4083
1.4195
1.5638
1.5872
2.7179
2.7423
2.7667
2.7911
(ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8

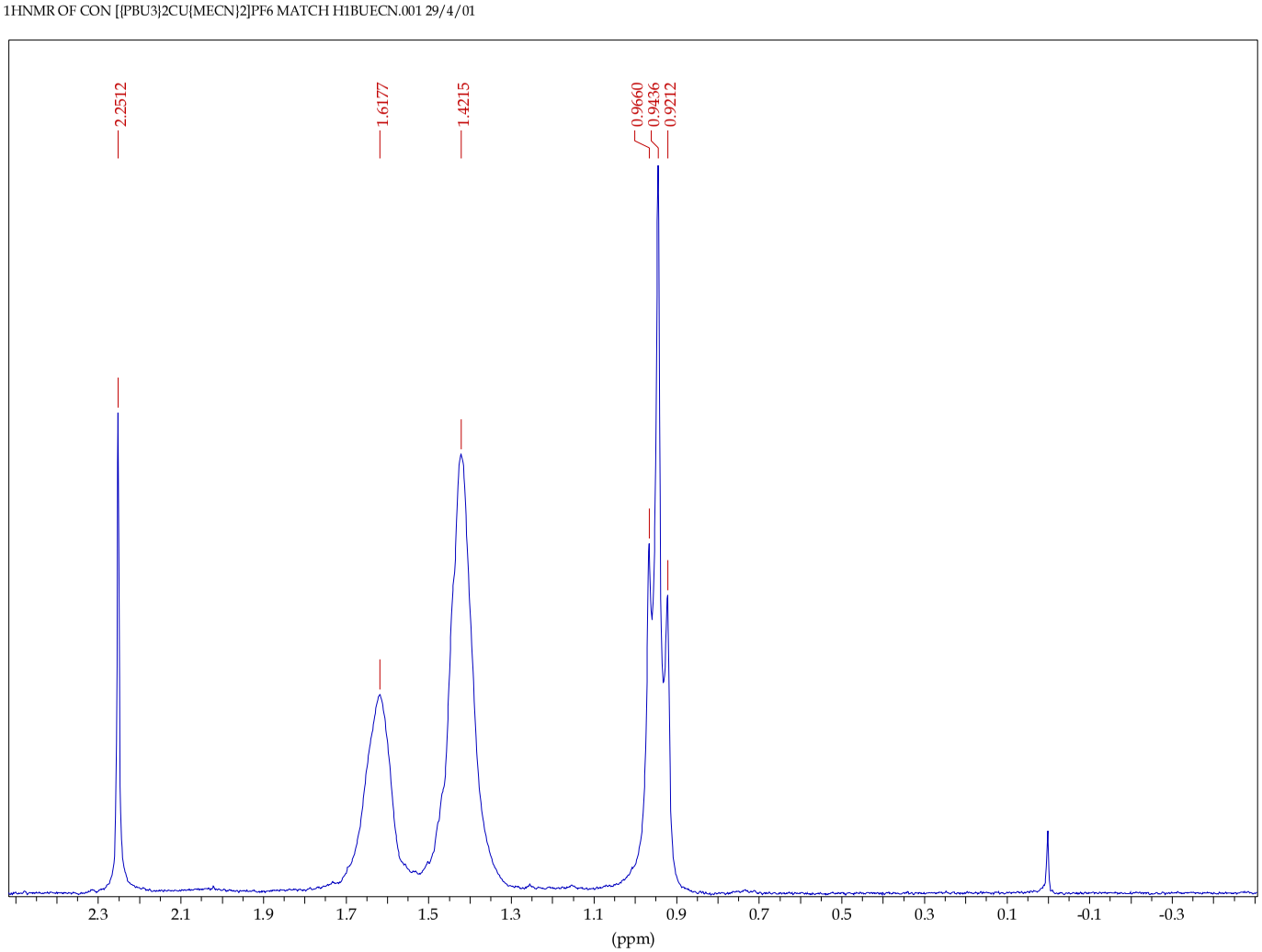
31P NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$] (1)



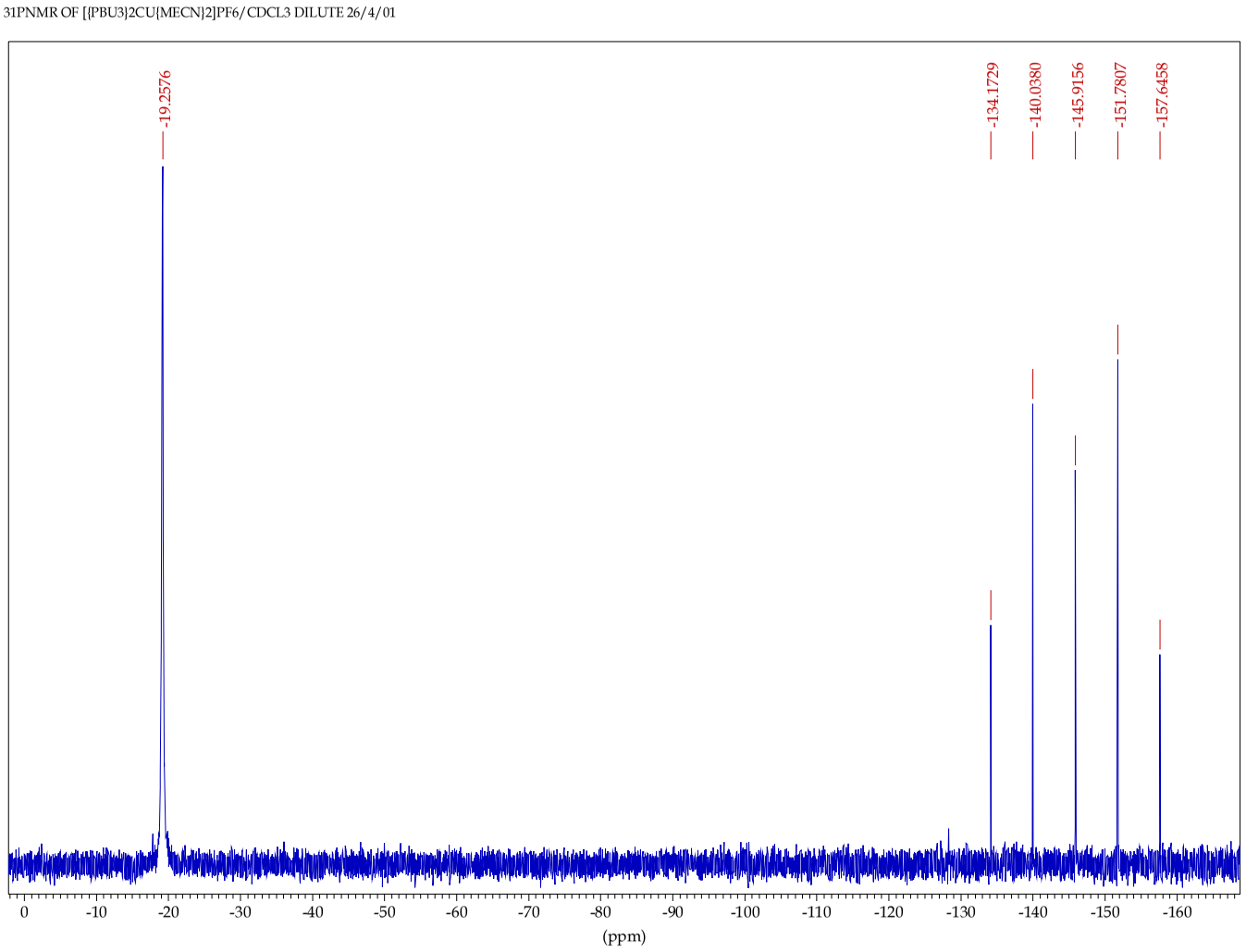
13C NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$]



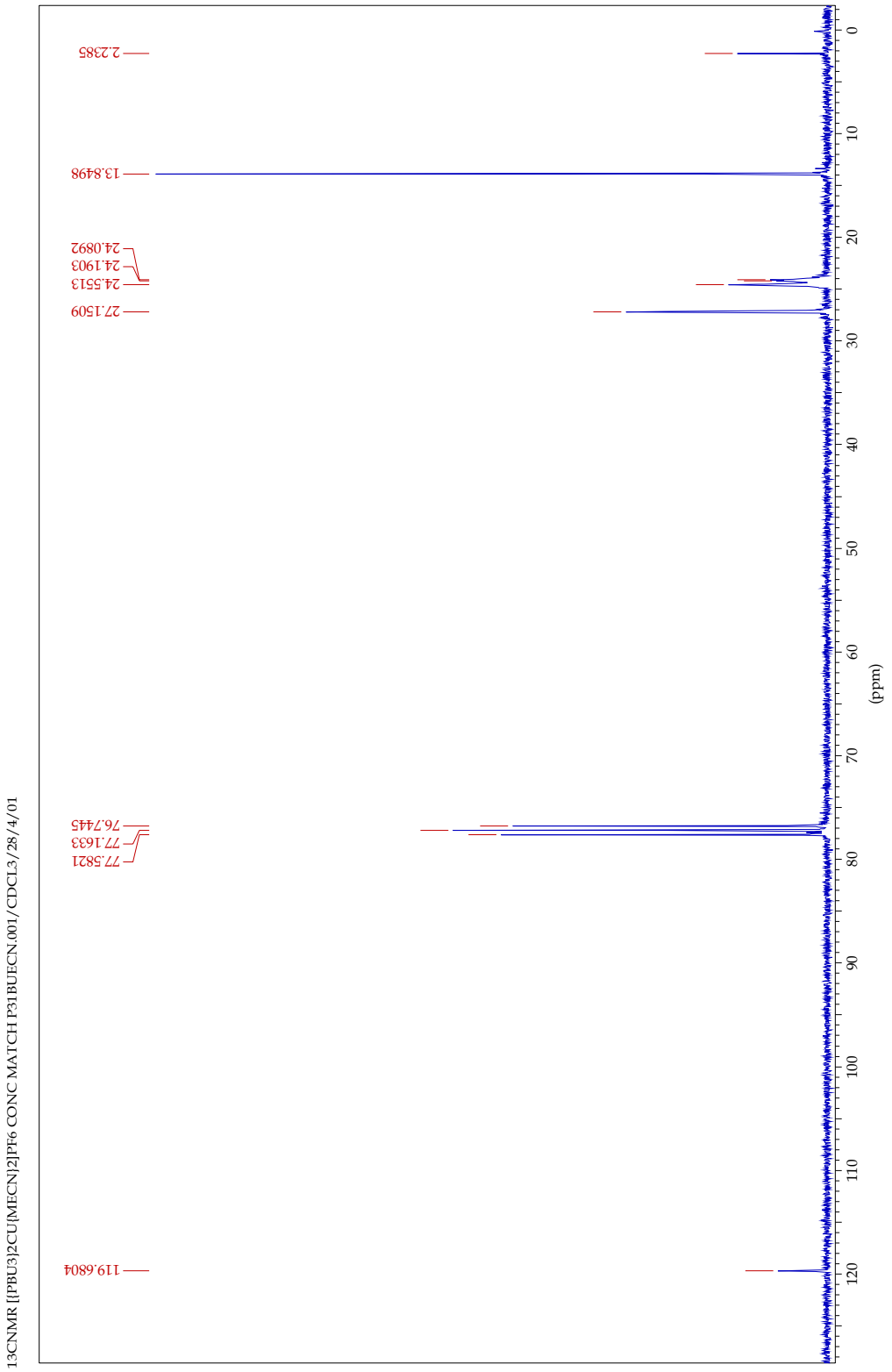
1H NMR: [{PBu_3}$_2$Cu{MeCN}$_2$]PF_6

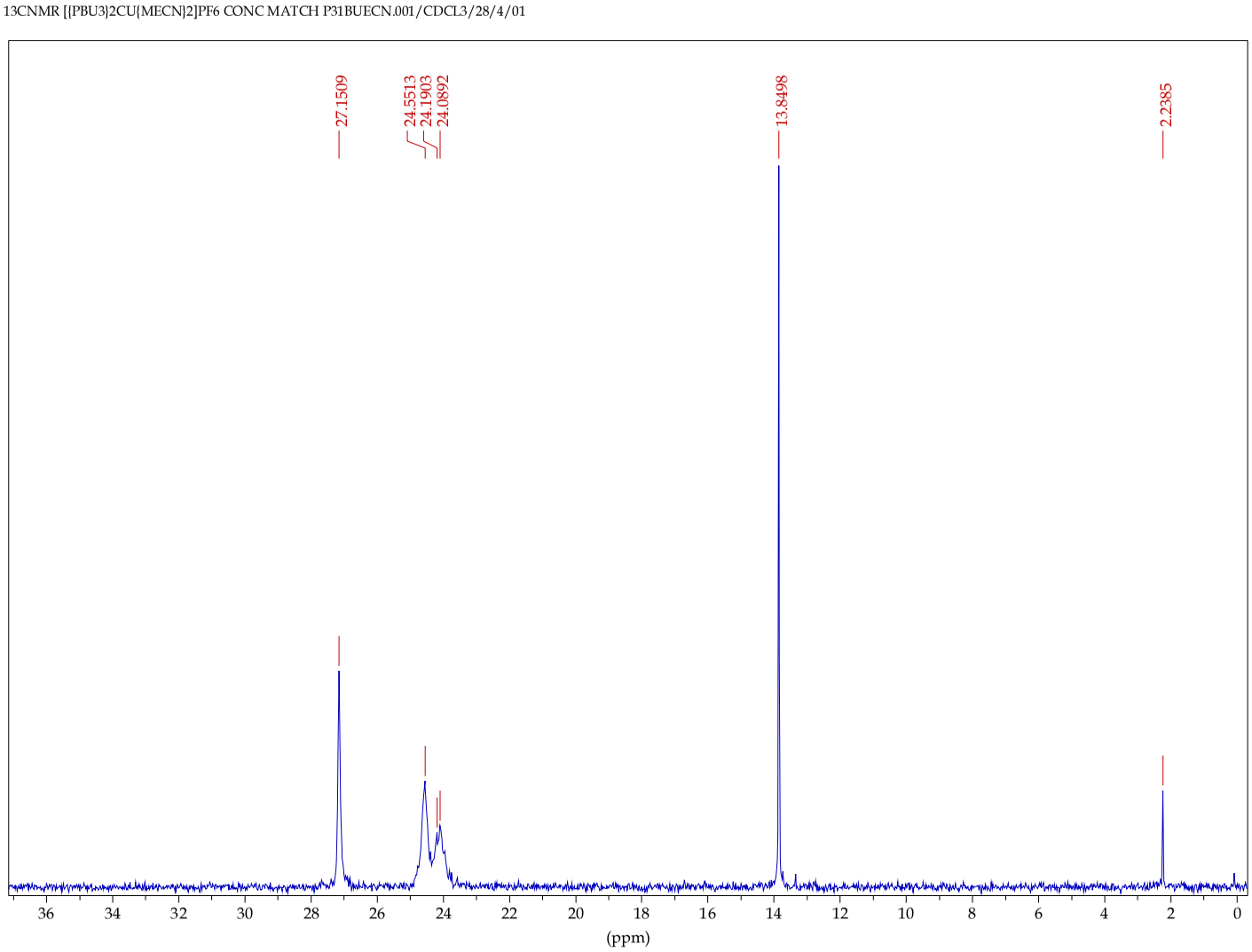


31P NMR: [{PBu_3}$_2$Cu{MeCN}$_2$]PF_6

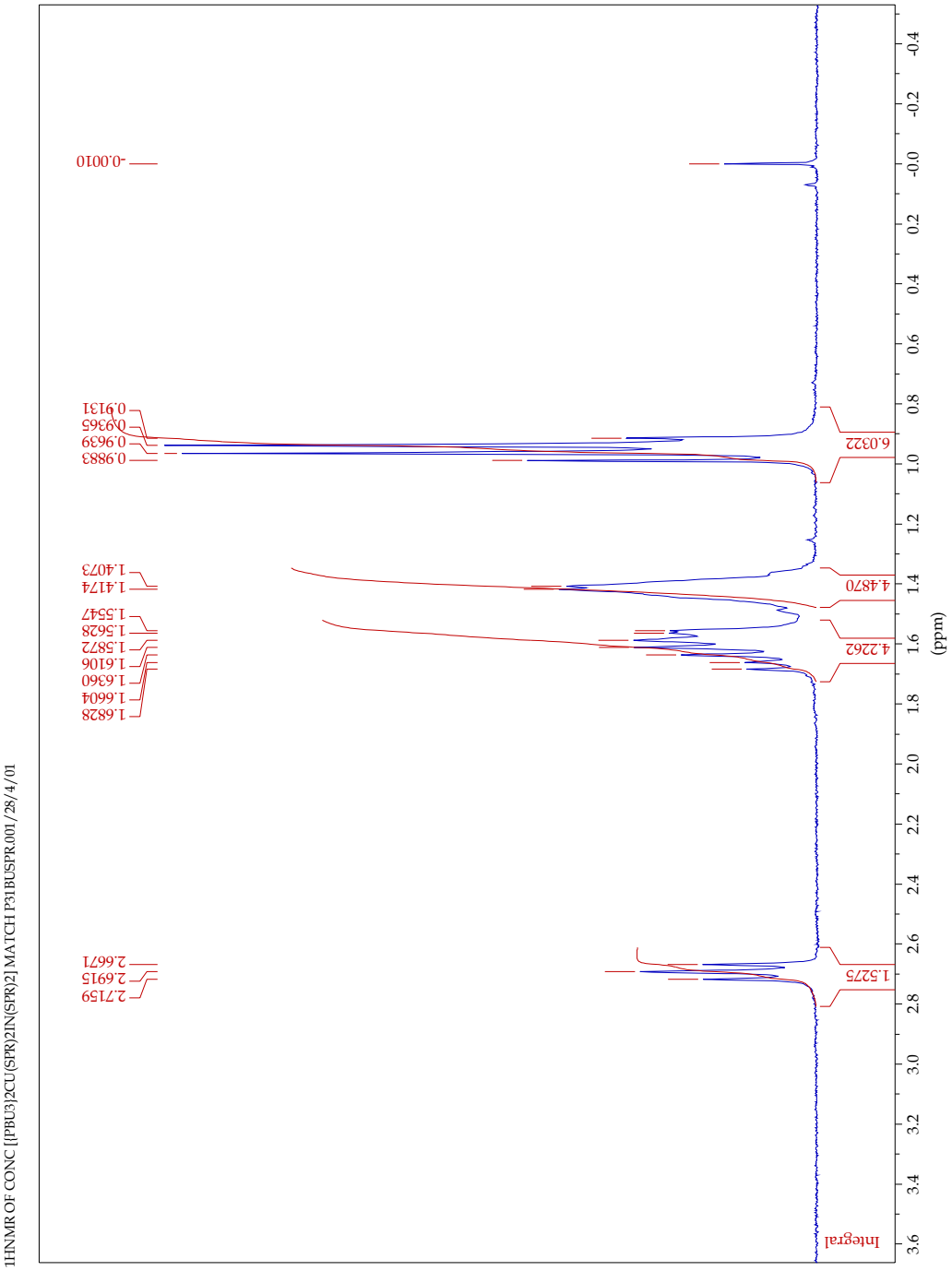


13C NMR: $[\{PBu_3\}_2Cu\{MeCN\}_2]PF_6$

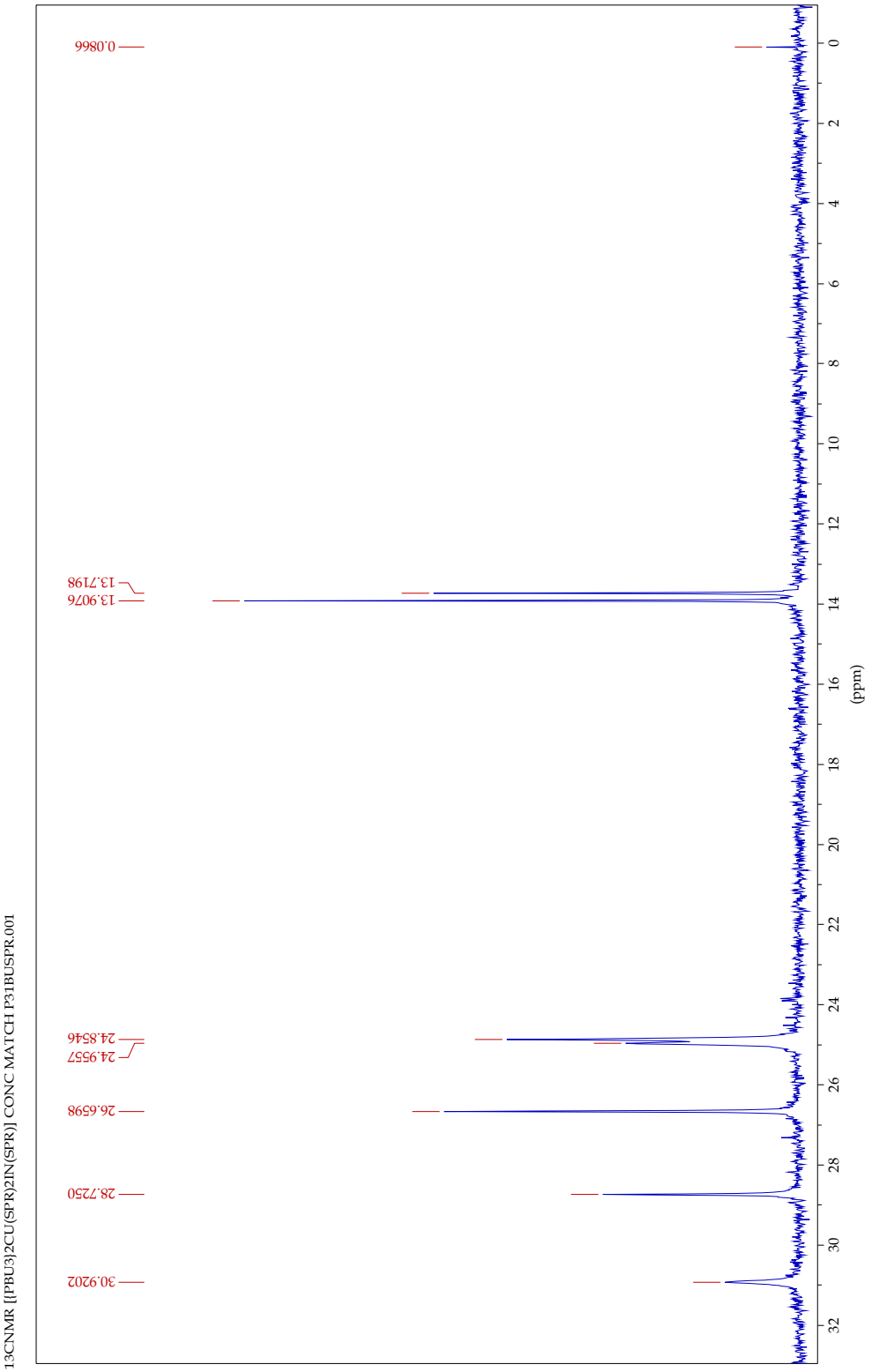

13CNMR [[PBU3]2CU[MECN]2]PF6 CONC MATCH P31BUECN.001/CDCL3/28/4/01
2.2385
13.8498
24.0892
24.1903
24.5513
27.1509
76.7445
77.1633
77.5821
119.6804
0
10
20
30
40
50
60
70
80
90
100
110
120
(ppm)



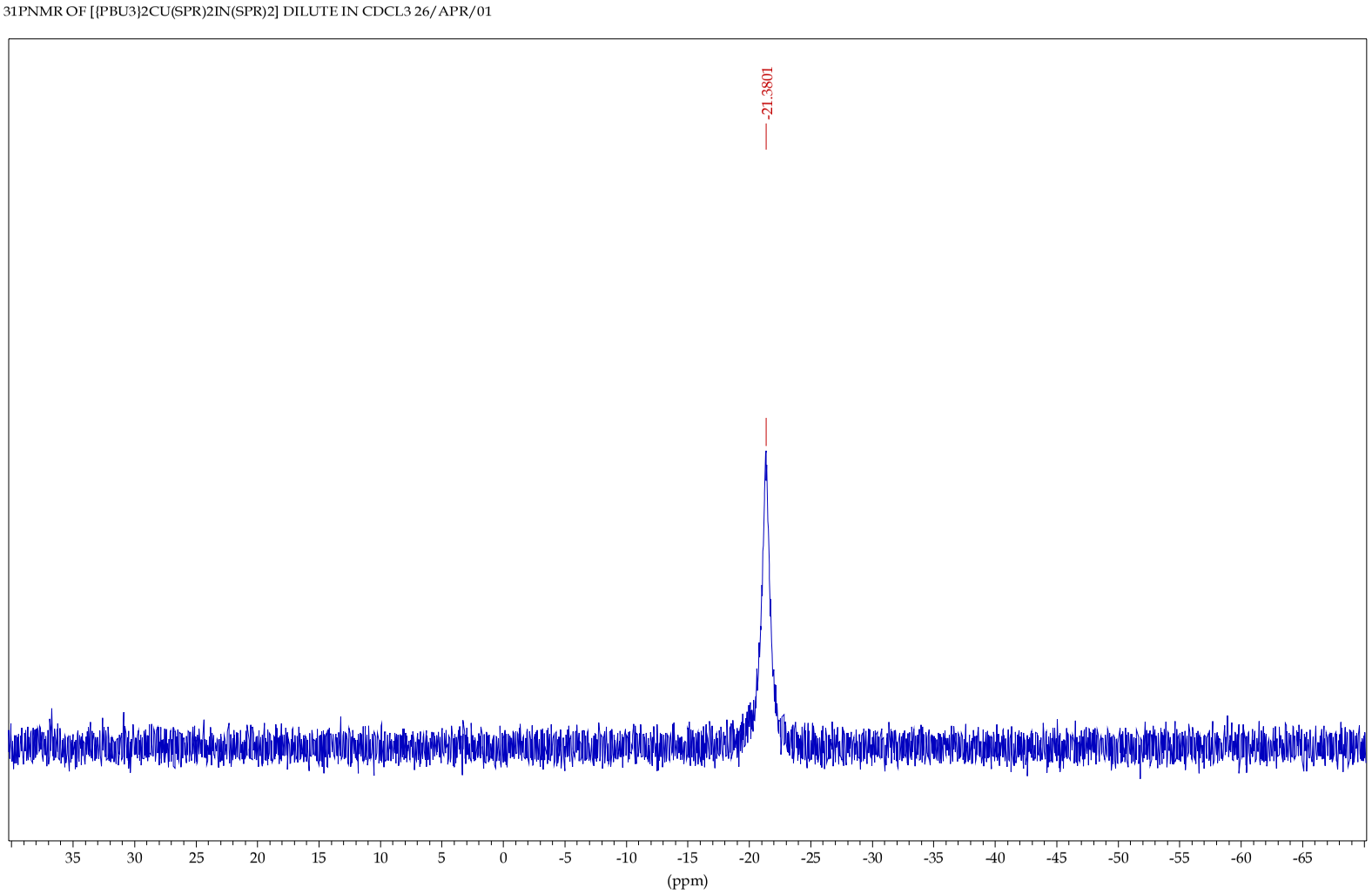
1H NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SPr)$_2$In(SPr)$_2$]


1HNMR OF CONC [(PBU3)2CU(SPR)2IN(SPR)2] MATCH P31BUSPR.001/28/4/01
-0.0010
0.9883
0.9639
0.9365
0.9131
1.4174
1.4073
1.5547
1.5628
1.5872
1.6106
1.6360
1.6604
1.6828
2.7159
2.6915
2.6671
Integral
6.0322
4.4870
4.2262
1.5275
(ppm)

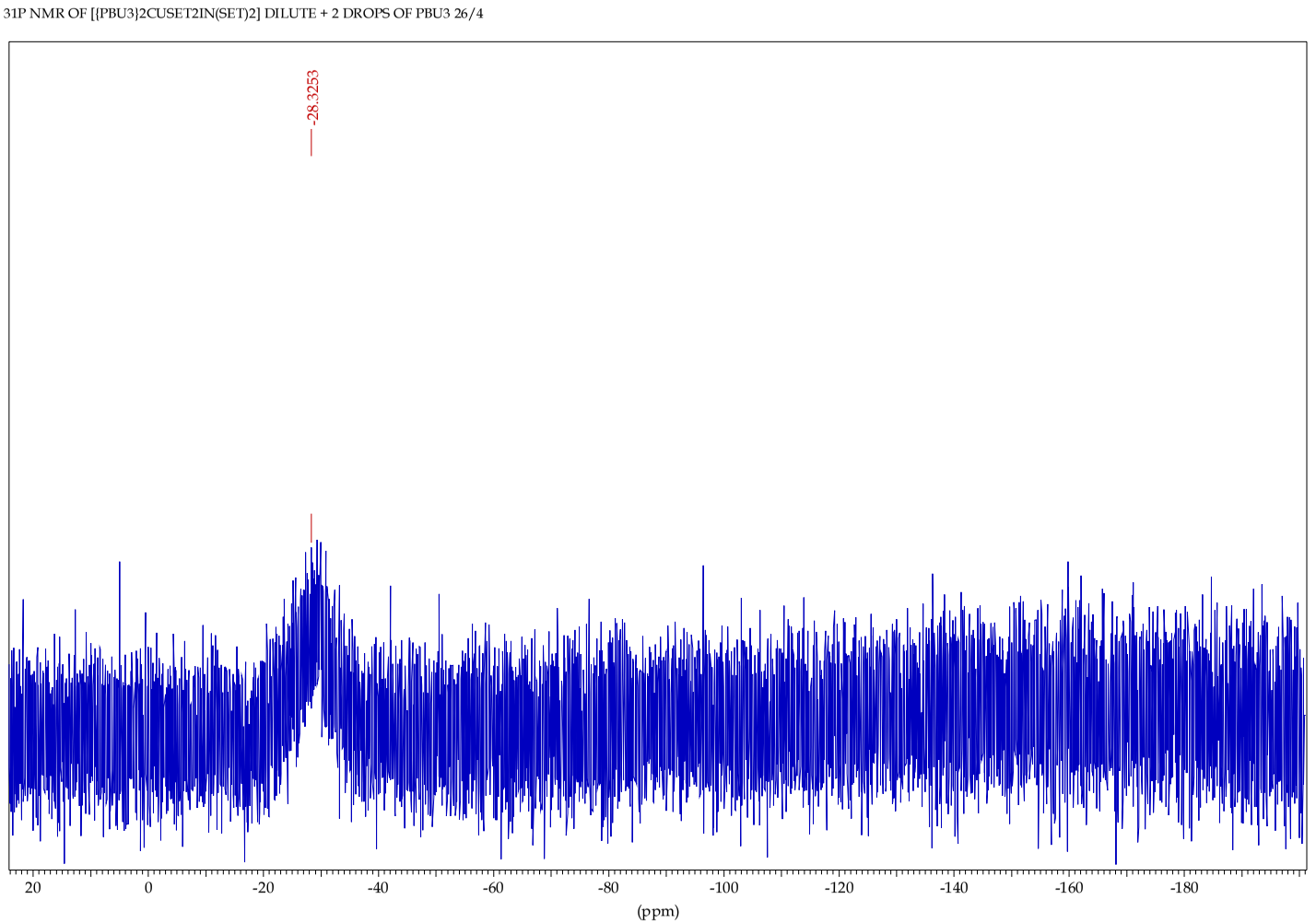
13C NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SPr^n)$_2$In(SPr^n)$_2$]



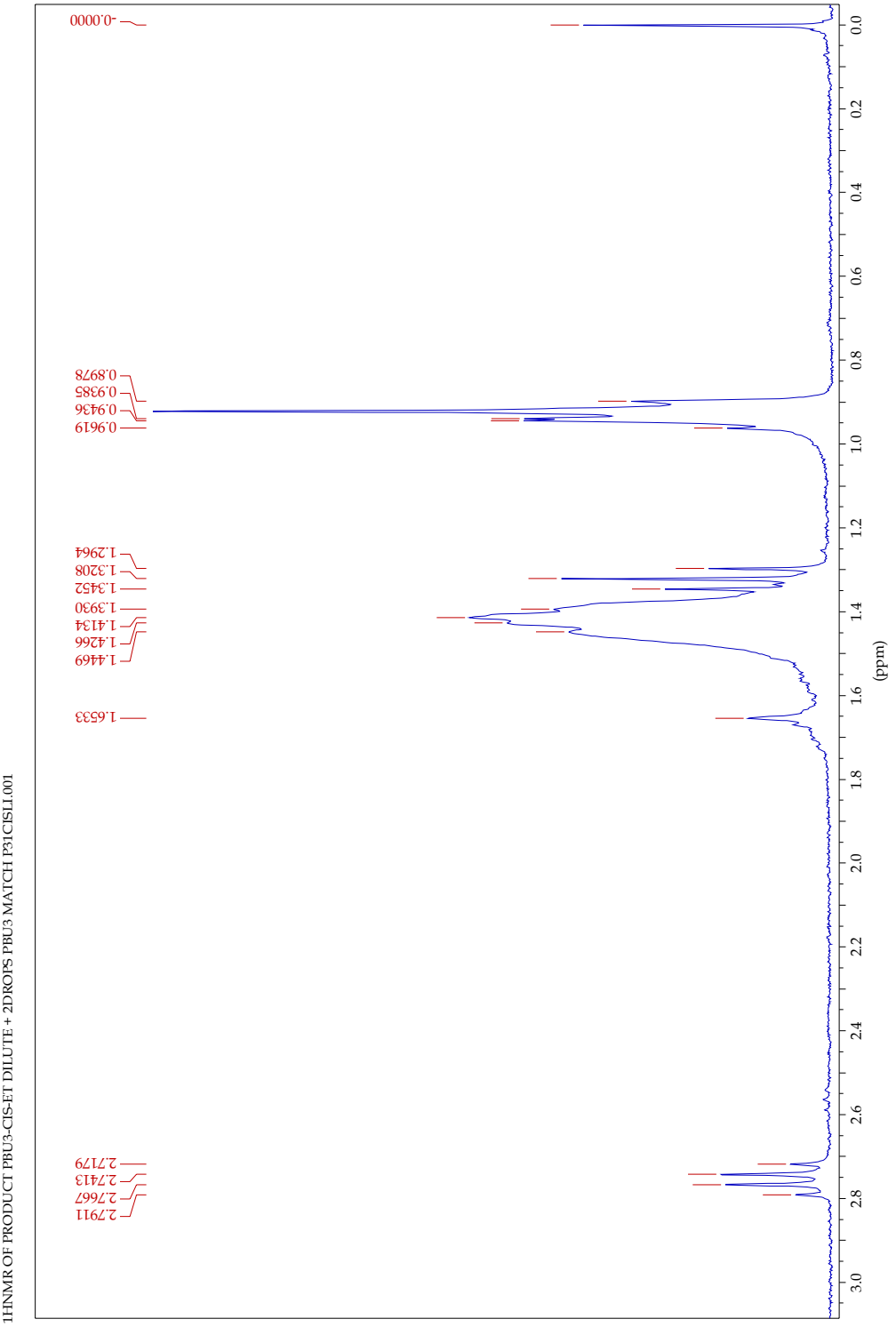
31 P NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SPr)$_2$In(SPr)$_2$]



31P NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$] & PBu$_3$



1H NMR: [{P(*n*-Bu)$_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$] & PBu$_3$



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13. ABSTRACT ***(Maximum 200 words)***

Molecular engineering of ternary single source precursors based on the $[\{PBu_3\}_2Cu(SR')_2In(SR')_2]$ 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 $CuInS_2$ at low temperatures.

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