INVESTIGATION OF THE MECHANISM OF NUCLEOPHILIC ATTACK ON THE [*trans*-$B_{20}H_{18}$]$^{2-}$ ANION

THESIS

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DEDICATION

Dedicated to my grandfather, Richard Schneider.

Your love of science and enthusiasm for chemistry has always been influential.

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ABSTRACT

INVESTIGATION OF THE MECHANISM OF NUCLEOPHILIC ATTACK ON THE [*trans*-$B_{20}H_{18}$]$^{2-}$ ANION

by

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August 2006

SUPERVISING PROFESSOR: DEBRA A. FEAKES

The substitution chemistry of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion was first investigated by Hawthorne and coworkers. The product formed from the reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion with the hydroxide ion is an apical-equatorial isomer of the $[B_{20}H_{17}OH]^{4-}$ ion with the hydroxide substituent located on the equatorial belt adjacent to the intercage linkage. Analogous reactions have been reported for the synthesis of alkoxy and ammonio derivatives. Previously, our laboratory reported the synthesis of an unexpected isomer of the $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ ion, characterized by an apical-apical boron atom intercage connection with the sulfur substituent located on the equatorial belt adjacent to the terminal boron apex. In an effort to investigate the factors which lead to the formation of the unusual isomer, our laboratory initiated an investigation of the reaction

of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion with sterically demanding nucleophiles. During the initial investigation, a novel THP solvent-coordinated species, analogous to that proposed by Hawthorne and coworkers for CH_3CN and THF, was isolated.

Therefore, the specific goals of the current research project are:

1) Develop a synthetic route to evaluate the reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion with the original proposed nucleophiles,
2) Evaluate the role of nucleophile in the formation of the THP-coordinated product, and
3) Evaluate the potential chemistry of the THP-coordinated product.

Synthesis of the proposed nucleophile derivatives has been accomplished and the products have been isolated and characterized. Isomeric designations (*ae* or a^2) have been made and the location of the substituent has been predicted for each of the products. The direct formation of the a^2 isomer appears to be the result of the electronics associated with the nucleophiles containing the sulfur atom. The location of the substituent on the equatorial belt adjacent to the terminal boron apex appears to be the result of the carbamate functionality; however, the result should be verified with two-dimensional ^{11}B NMR spectroscopy.

The reactivity of the solvent-coordinated intermediate has been studied and the reaction conditions required for the formation of the anion have been determined. Although the absolute role of the nucleophile has not been determined, the nucleophile is required for the formation of the THP-coordinated compound. The nucleophile does not act as a catalyst in the reaction nor is the reaction base-mediated. The reaction does not occur unless THP is the solvent for the reaction. Therefore, the results suggest that the

formation of the solvent-coordinated intermediate is a result of mass action.

Preliminary investigations have been completed using sulfur and nitrogen analogues of THF and THP. The sulfur analogues, like THP, require the presence of a nucleophile for any type of reaction to occur. Although the nitrogen analogues will eventually react with the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion in the absence of the nucleophile, the presence of the nucleophile significantly reduces the reaction time. Results suggest that continued investigation of the sulfur and nitrogen derivatives is warranted.

1.0 INTRODUCTION

1.1 Boranes

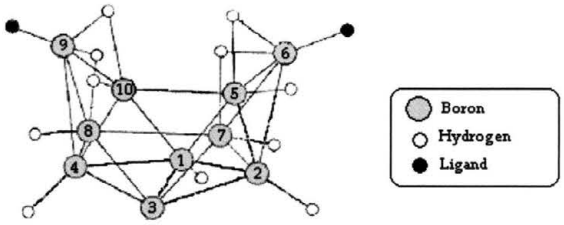
Boron and boron-containing compounds have been the foundation of investigation for a variety of applications ranging from the use as jet fuels to the development of new medicinal compounds.[1-3] The isoelectronic and isostructural similarities between the BH_2^- ion and the CH_2 moiety serves as the basis for the expectation that boron will, like carbon, have an unusual and sophisticated chemistry. Similar to catenation reactions in carbon species, boron has the ability to bond to other boron atoms in intricate arrangements.[4] Some polyhedral boranes, such as the $[B_{10}H_{10}]^{2-}$ ion and the $[B_{12}H_{12}]^{2-}$ ion, even possess the characteristic of aromaticity.[5] The prospect of boron having a profoundly complex and diverse chemistry has become a reality over the course of the past century. The capacity of boron to bond in a magnitude of arrangements and unexpected orientations has become the center of investigative work yielding considerable discoveries encompassing all areas of chemistry.

Professor William Lipscomb received the 1976 Noble Prize in Chemistry for his research on the structure and bonding of boron compounds.[6] Lipscomb's investigations of boron compounds containing three-center two-electron bonds have been quintessential to the development and understanding of boron hydride chemistry. He developed the theory which has been used to explain the types of bonds within the boron framework of a borane structure, ultimately leading to the evolution of new reaction mechanisms.[6] His

molecular orbital studies of boranes set forth vital guidelines for chemists dealing with boron hydride compounds and the enigmatic ability of boron to bond through unconventional means.[6]

Lipscomb's theoretical investigations were preceded by the work of Alfred Stock, who pioneered the synthesis of boron hydrides.[4] Stock has been attributed with the development of air-sensitive techniques which were essential in the preparation of the volatile and potentially explosive borane compounds B_2H_6, B_4H_6, B_5H_{11}, and B_6H_{10}.[6] The synthesis of the relatively stable, yet extremely hazardous, $B_{10}H_{14}$, commonly referred to as decaborane, is also attributed to Stock.[6,7]

Decaborane is characterized by ten B-H vertices linked through a series of B-B-B and B-H-B bonds in an *arachno* structure (Figure 1).[1,6] The compound is produced by the pyrolysis of smaller boron hydride clusters under vacuum and is sublimed to a white crystalline solid.[7] Decaborane can undergo a ligand-mediated cage rearrangement reaction with triethylamine in xylene to produce the decahydrodecaborate 2- anion $[B_{10}H_{10}]^{2-}$ (Figure 1).[8] In the first step of the reaction, two electron donor ligands, such as dimethylsulfide or triethylamine, replace two exo hydrogen atoms to form the $B_{10}H_{12}X_2$ intermediate. The intermediate undergoes an internal interconversion requiring rearrangements of the original boron configuration present in the $B_{10}H_{12}X_2$ compounds, resulting in the formation of the $[B_{10}H_{10}]^{2-}$ anion . Hawthorne reported the proposed mechanism based on the rearrangement of the 5(7) boron atom to the 9 boron atom in decaborane as well as the attachment of the 8(10) boron atom to the 6 position, resulting in the formation of the polyhedral bicapped square antiprism, $[B_{10}H_{10}]^{2-}$.[9,10]



$$B_{10}H_{14} + 2\,Et_3N \rightarrow (Et_3NH)_2[B_{10}H_{10}] + H_2$$

Figure 1: Structure of decaborane and the reaction of decaborane and triethylamine to form the $[B_{10}H_{10}]^{2-}$ anion.

Oxidation of the $[B_{10}H_{10}]^{2-}$ anion by a suitable oxidizing agent, such as Fe^{3+} or Ce^{4+}, in dilute aqueous solutions under refluxing conditions results in the formation of a centrosymmetric $[B_{20}H_{18}]^{2-}$ anion (Figure 2).[11,12]

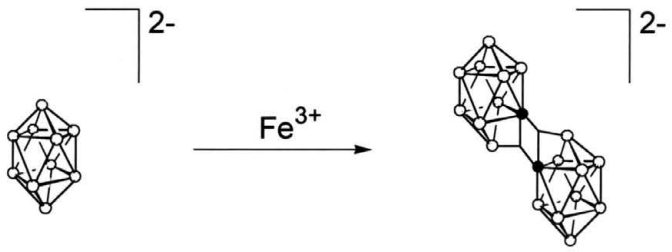


Figure 2: Oxidation of the $[B_{10}H_{10}]^{2-}$ anion to form the $[B_{20}H_{18}]^{2-}$ anion. ● = B; ○ = BH.

Three isomers of the $[B_{20}H_{18}]^{2-}$ anion are known, each consisting of two polyhedral $[B_{10}H_9]^-$ anions linked by a pair of three-center two-electron bonds (Figure 3).[11-14] The relative location and composition of the unique bonding region determines the isomeric assignment of the polyhedral borane isomer. The [*trans*-$B_{20}H_{18}]^{2-}$ and the

[*cis*-$B_{20}H_{18}]^{2-}$ isomers are both characterized by the presence of B-B-B linkages at the intercage region while the [*iso*-$B_{20}H_{18}]^{2-}$ isomer is characterized by a set of B-H-B linkages between two parallel $[B_{10}H_9]^-$ cages.[11-14]

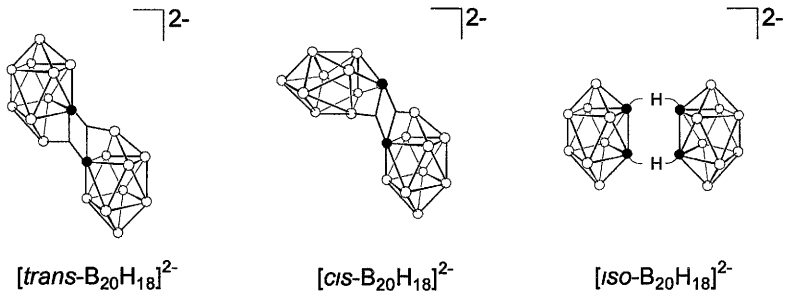


Figure 3: Structures of the three known isomers of the $[B_{20}H_{18}]^{2-}$ anion. ● = B; ○ = BH.

The known isomers of the $[B_{20}H_{18}]^{2-}$ anion are produced by different means. The [*trans*-$B_{20}H_{18}]^{2-}$ isomer, first reported in 1962, was produced by the oxidation of the $[B_{10}H_{10}]^{2-}$ anion with the Fe^{3+} ion.[11,12] Irradiation of the [*trans*-$B_{20}H_{18}]^{2-}$ anion with ultraviolet light in acetonitrile results in the production of the symmetric [*iso*-$B_{20}H_{18}]^{2-}$ species, a photoisomer of [*trans*-$B_{20}H_{18}]^{2-}$.[13] Salts of the photoiosomer will revert to the normal isomer by thermal soaking at 110°C for 36 hours.[13] The most recently determined isomer is the [*cis*-$B_{20}H_{18}]^{2-}$ anion.[14] The cis isomer can be converted either to the [*trans*-$B_{20}H_{18}]^{2-}$ ion, by heating or by adding catalytic amounts of HCl, or it can be converted to the [*iso*-$B_{20}H_{18}]^{2-}$ anion, through a photoisomerization process.[4] The cis isomer can be produced directly by oxidation of the $[B_{10}H_{10}]^{2-}$ anion with two equivalents of Ce^{4+} ion in acidified aqueous solutions or by the low temperature oxidation of an [*ae*-$B_{20}H_{18}]^{4-}$ anion with Fe^{3+}.[4]

The reactivity of the known isomers follows an established order of reactivity based on the relative thermodynamic stabilities of the three isomers.[4] The [*trans*-$B_{20}H_{18}]^{2-}$ ion is more stable than the [*cis*-$B_{20}H_{18}]^{2-}$ isomer which has a greater stability than the [*iso*-$B_{20}H_{18}]^{2-}$ ion (Figure 4).

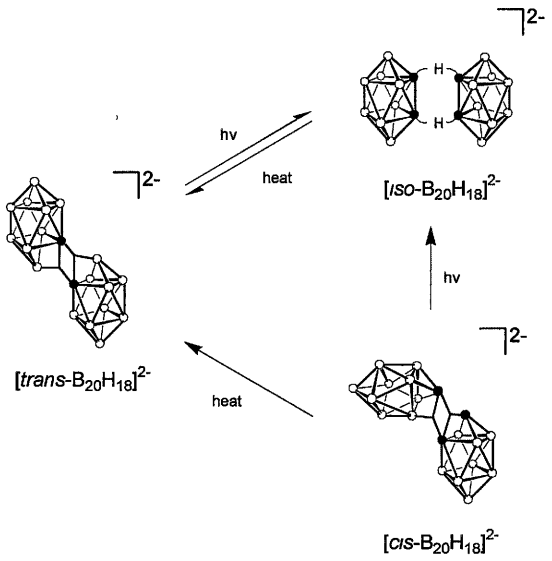


Figure 4: Conversion reactions of the *trans*, *cis* and *iso* isomers of the $[B_{20}H_{18}]^{2-}$ ion. ● = B; ○ = BH.

Reduction of the [*trans*-$B_{20}H_{18}]^{2-}$ anion in a solution of sodium metal in liquid ammonia results in the formation of a $[B_{20}H_{18}]^{4-}$ anion.[15] The $[B_{20}H_{18}]^{4-}$ anion is characterized as two fragments of the $[B_{10}H_9]^{2-}$ polyhedra linked by a two center B-B bond. The isomeric designation of the reduced species is determined by the location of the two boron atoms involved in the intercage connection. Based on the possible orientations of the linkages, three formal isomers can be derived (Figure 5). A pair of $[B_{10}H_9]^{2-}$ anions linked through the cage apices are designated apical-apical or a^2. When the $[B_{10}H_9]^{2-}$anions are linked through equatorial boron atoms, the isomer is designated

equatorial-equatorial or e^2. Anions linked through one apical boron atom and one equatorial boron atom produces an isomer designated as apical-equatorial or *ae*.

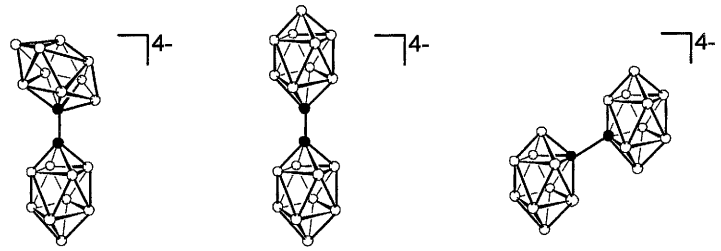


Figure 5: Isomers of the reduced $[B_{20}H_{18}]^{4-}$ anion. ● = B; ○ = BH.

1.2 Nucleophilic Attack of the $[B_{20}H_{18}]^{2-}$ Anion

The intercage linkages in all three of the known isomers of the $[B_{20}H_{18}]^{2-}$ anion provide an electron-deficient region which is susceptible to reactions with nucleophiles.[4] The nucleophilic attack of the electron-deficient region linking the cages results in a reductive substitution reaction. Nucleophilic attack of the $[B_{20}H_{18}]^{2-}$ isomers allows for a wide variety of substituted derivatives.[16-20] A mechanism for the nucleophilic attack of the normal isomer was proposed using the hydroxide ions as a representative nucleophile (Figure 6).[17]

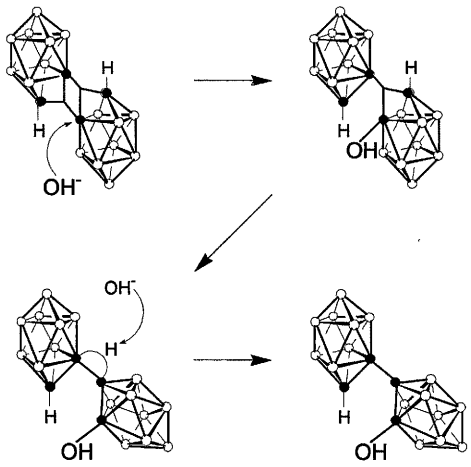


Figure 6: Original mechanism of nucleophilic attack proposed by Hawthorne in 1965. ● = B; ○ = BH.

The first step of the mechanism is attack of the apical boron atom involved in the electron-deficient three-center two-electron bond by the hydroxide ion. The second step is the migration of one of the boron cages by displacement of an apical proton. After the addition of a second equivalent of the hydroxide ion, the residual proton is removed, resulting in the formation of the kinetic, apical-equatorial isomer of $[B_{20}H_{17}OH]^{4-}$, designated $[ae\text{-}B_{20}H_{17}OH]^{4-}$. The hydroxide substituent is located on the equatorial belt near the intercage linkage. The $[ae\text{-}B_{20}H_{17}OH]^{4-}$ isomer is susceptible to subsequent acid-catalyzed rearrangement to form the thermodynamically stable, apical-apical isomer, designated $[a^2\text{-}B_{20}H_{17}OH]^{4-}$ (Figure 7).[17]

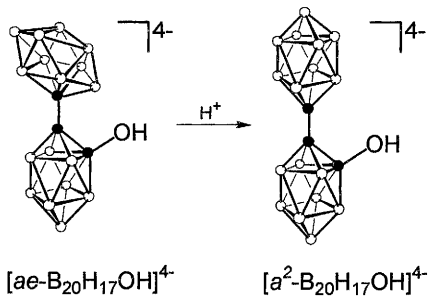


Figure 7: Acid-catalyzed rearrangement of the *ae*-isomer to the a^2-isomer. ● = B; ○ = BH.

Both the $[cis\text{-}B_{20}H_{18}]^{2-}$ and the $[iso\text{-}B_{20}H_{18}]^{2-}$ isomers also possess an electron-deficient region and are also susceptible to nucleophilic attack.[4] Reductive substitution of the $[iso\text{-}B_{20}H_{18}]^{2-}$ isomer results in the formation of a substituted $[e^2\text{-}B_{20}H_{17}X]^{4-}$ isomer, where X represents a generic nucleophile, with the substituent located on the equatorial belt adjacent to the terminal boron apex (Figure 8). Acid catalyzed rearrangement yields the $[a^2\text{-}B_{20}H_{17}X]^{4-}$ ion.

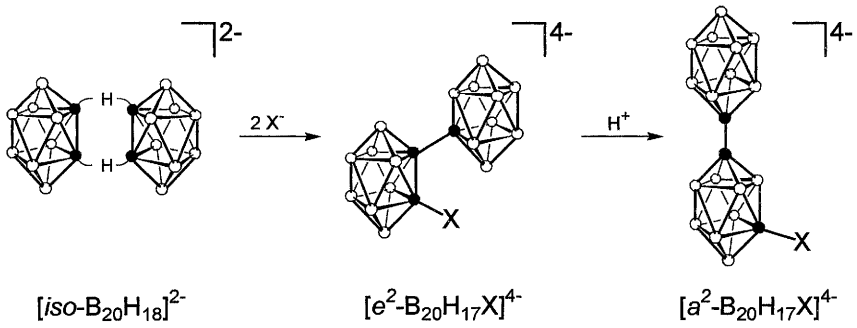


Figure 8: Conversion of the $[iso\text{-}B_{20}H_{18}]^{2-}$ ion to the $[a^2\text{-}B_{20}H_{17}X]^{4-}$ ion. ● = B; ○ = BH.

Nucleophilic attack of the $[cis\text{-}B_{20}H_{18}]^{2-}$ isomer results in the direct formation of a substituted $[a^2\text{-}B_{20}H_{17}X]^{4-}$ isomer with the substituent located on the equatorial belt near the intercage linkage (Figure 9).[21]

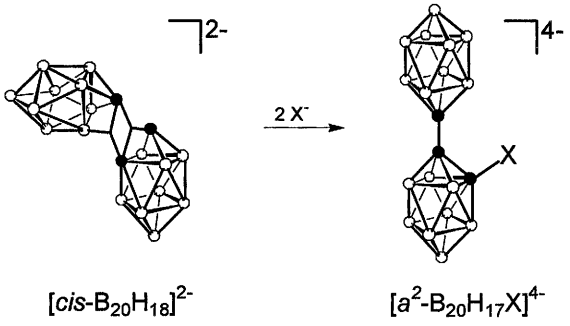


Figure 9: Conversion of the $[cis\text{-}B_{20}H_{18}]^{2-}$anion to form the $[a^2\text{-}B_{20}H_{17}X]^{4-}$anion. ● = B; ○ = BH.

Reaction of the $[B_{20}H_{18}]^{2-}$ isomers with nucleophiles is monitored by boron–11, or ^{11}B, nuclear magnetic resonance (NMR) spectroscopy. The starting material for the current investigations, $[trans\text{-}B_{20}H_{18}]^{2-}$ ion, has a characteristic seven peak proton-decoupled ^{11}B NMR spectrum (Figure 10).

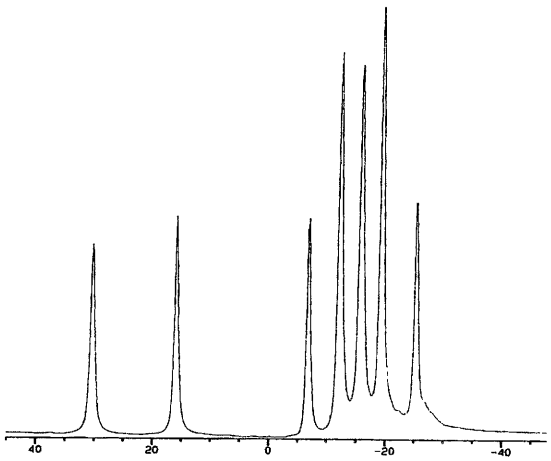


Figure 10: $\{^1H\}^{11}B$ NMR spectrum of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion.

Isomeric assignment of the product (*ae*, a^2, or e^2) can easily be made from the ^{11}B NMR spectrum. The peaks associated with apical boron atoms and substituted boron atoms appear in the region above -15 ppm in the ^{11}B NMR spectrum. The peaks associated with equatorial boron atoms appear upfield. An apical-equatorial isomer is characterized by three apical B-H vertices (Figure 11). The signals associated with the apical vertices will appear as singlets in the proton-decoupled ^{11}B NMR spectrum.

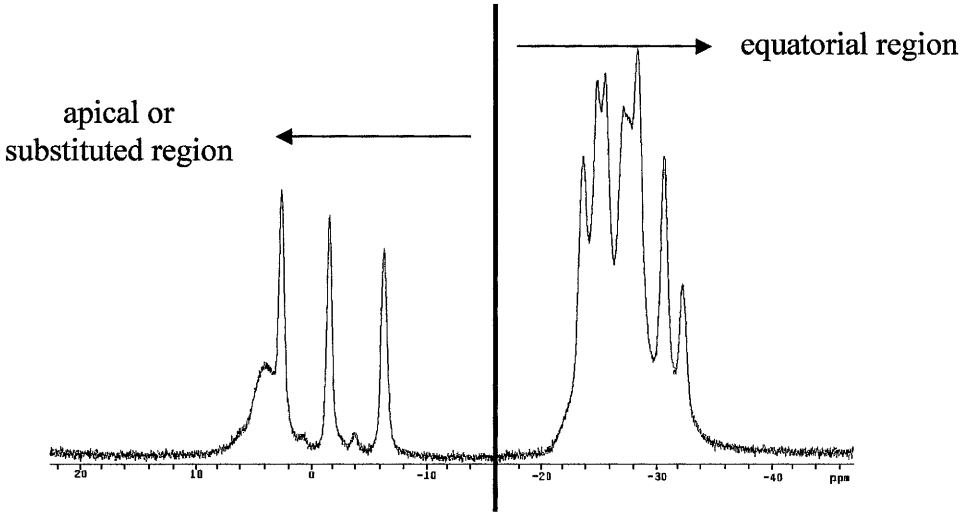


Figure 11: Representative ^{11}B NMR spectrum of an apical-equatorial isomer of $[B_{20}H_{17}X]^{4-}$ (X is a generic nucleophile) indicating the apical or substituted region and the equatorial region of the spectrum.

An apical-apical isomer is characterized by the presence of two apical B-H vertices (Figure 12). Two sharp peaks are present in the apical region of the spectrum. The peaks are singlets in the proton-decoupled.

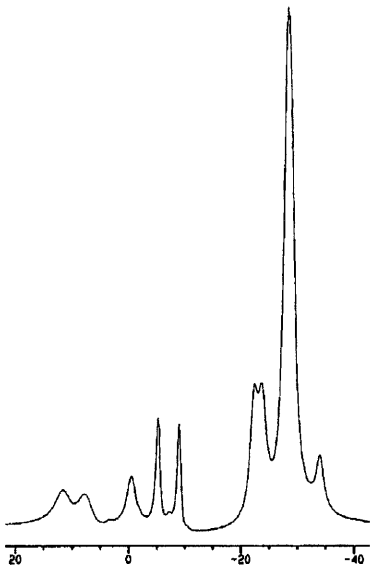


Figure 12: Representative ^{11}B NMR spectrum of an apical-apical isomer of $[B_{20}H_{17}X]^{4-}$ (X is a generic nucleophile).

The $[e^2\text{-}B_{20}H_{17}X]^{4-}$ isomer is characterized by the presence of four apical B-H vertices. The ^{11}B NMR spectrum of an $[e^2\text{-}B_{20}H_{17}X]^{4-}$ isomer would have four sharp singlets in the apical or substituted region of the proton-decoupled spectrum.

The $[B_{20}H_{18}]^{2-}$ ions and the substituted $[B_{20}H_{17}X]^{4-}$ derivatives have gained recent interest because of their potential application in boron neutron capture therapy (BNCT), a binary cancer therapy proposed for the treatment of metastatic melanoma and *glioblastoma multiforme*, a particularly lethal brain tumor.[2,3] Researchers have proposed that intracellular protein moieties could serve as nucleophiles and covalently bind the boron-containing compounds in the interior of the tumor cell.[18,20,22] The thiol derivative, $[B_{20}H_{17}SH]^{4-}$, was of considerable interest for application to BNCT chemistry because of the potential of the anion to form disulfide bonds with intracellular thiol moieties.

The thiol anion, $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ was isolated in our laboratories in 1999 as an intermediate to the desired $[B_{20}H_{17}SH]^{4-}$ anion.[20] Nucleophilic attack of the

[*trans*-$B_{20}H_{18}$]$^{2-}$ isomer with the Bender's salt, $KSC(O)OC(CH_3)_3$, yielded an unexpected isomer of $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$, characterized by an apical-apical cage connection with the substituent located on the equatorial belt adjacent to the terminal boron apex (Figure 13). The unusual isomeric assignment is characteristic for the product of nucleophilic attack of the [*iso*-$B_{20}H_{18}$]$^{2-}$ anion. No reports of this type of arrangement using the [*trans*-$B_{20}H_{18}$]$^{2-}$ as a starting material have been made. However, the reaction of a sterically demanding nucleophile with [*trans*-$B_{20}H_{18}$]$^{2-}$ isomer had not been investigated.

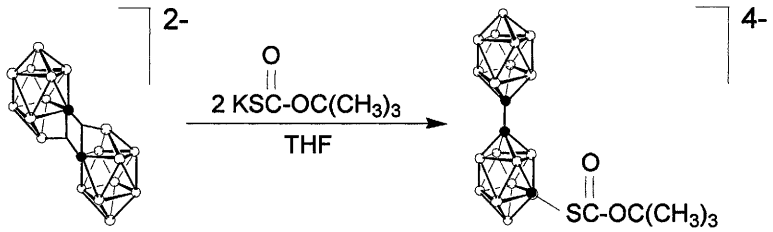


Figure 13 : Nucleophilic attack of the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion by the $[SC(O)OC(CH_3)_3]^-$ ion. ● = B; ○ = BH.

Although a single-crystal x-ray diffraction analysis of the product could not be obtained, the isomeric assignment was ascertained using one and two-dimensional ^{11}B NMR spectroscopy. The one-dimensional ^{11}B NMR spectrum exhibited two sharp peaks in the apical or substituted boron atom region, indicating the formation of an a^2 isomer. The two-dimensional ^{11}B NMR spectrum exhibited cross-coupling peaks between the two broad signals at approximately 10 ppm, assigned to the boron atoms in the intercage connection, and also exhibited a cross-coupling peak between the signal for the substituted boron atom (at approximately –2 ppm) and one of the apical boron atom

signals, indicating the location of the substituent on the equatorial band adjacent to the terminal boron apex (Figure 14). The signal associated with the boron-boron intercage connection also provides indirect evidence for the location of the substituent (Figure 15). When the substituent is located on the equatorial band adjacent to the intercage connection, only one signal is typically observed in the 10 ppm region. In contrast, when the substituent is located on the equatorial band adjacent to the intercage connection, two signals are typically observed in the 10 ppm region.

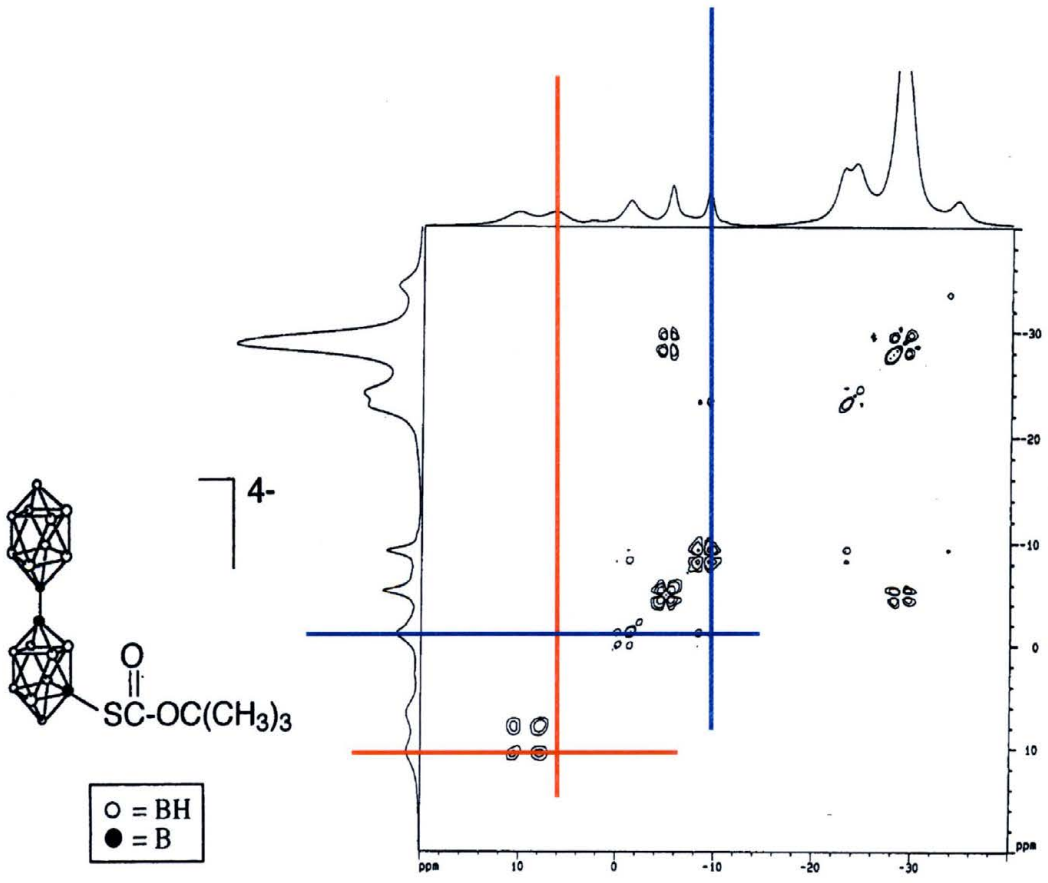


Figure 14: Two-dimensional ^{11}B NMR spectrum of $[a^2\text{-}B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ showing the relevant cross-coupling peaks. ● = B; ○ = BH.

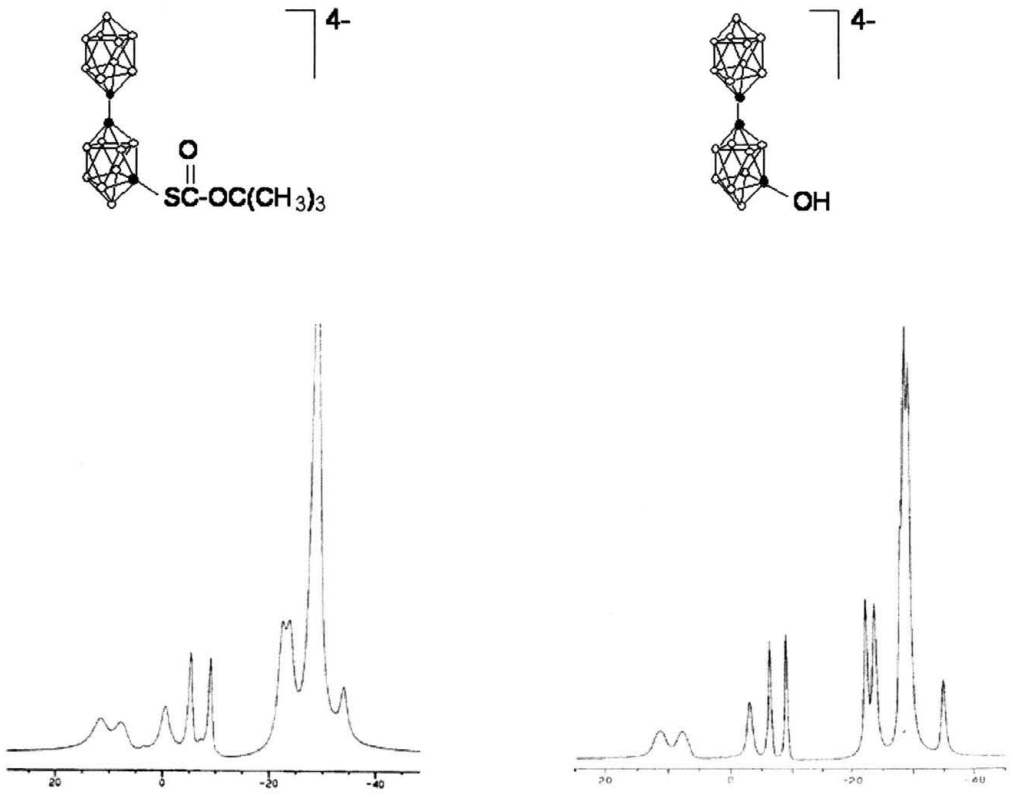


Figure 15: One-dimensional ^{11}B NMR spectrum of $[a^2\text{-}B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ and one-dimensional ^{11}B NMR spectrum of $[a^2\text{-}B_{20}H_{17}OH]^{4-}$. Both substituents are located on the equatorial belt adjacent to the terminal boron apex. ● = B; ○ = BH.

The unusual isomeric arrangement was hypothesized to be the result of the steric requirements of the nucleophile. No evidence of the formation of the kinetic, apical-equatorial isomer, or the expected substitution pattern on the equatorial belt adjacent to the intercage connection was observed while monitoring the reaction. An investigation of the reaction between the $[trans\text{-}B_{20}H_{18}]^{2-}$ isomer and a series of sterically demanding nucleophiles was initiated. The compounds that were selected for investigation are depicted in Figure 16.

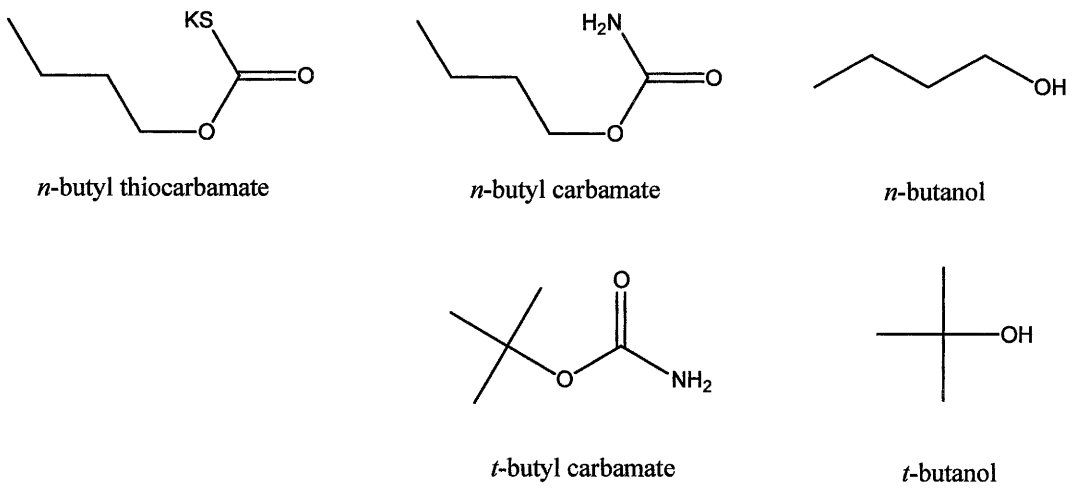


Figure 16: Starting materials for the investigation of the reactivity of the [*trans*-$B_{20}H_{18}]^{2-}$ ion.

The *n*-butyl derivate of the previously investigated Bender's salt, $KSC(O)O(CH_2)CH_3$, was selected to compare the steric factors of the alkyl group. In addition to the Bender's salt, *t*-butyl and *n*-butyl alkoxide and *t*-butyl and *n*-butylcarbamate nucleophiles were selected for investigation. The oxygen and nitrogen analogs were selected because of the expectation that they would react as strong nucleophiles and the steric factors could be evaluated in both cases. The selection of the nucleophiles provided a basis to evaluate whether the unusual isomer product could be observed with heteroatom nucleophiles having a similar structure to the original Bender's salt derivative or if the phenomenon is due solely to the steric requirements of the substituent.

If steric effects where the primary factor contributing to the isomeric and substitution pattern, both the *t*-butoxide and the *t*-butylcarbamate should form an a^2 isomer and the substituent should be located on the equatorial belt adjacent to the

terminal boron apex. Alternatively, if the substitution was attributed to the electronic effects of the substituent, only the sulfur derivatives would form the a^2 isomer and the nitrogen and oxygen nucleophiles should form the expected *ae* isomer with the substituent located on the equatorial belt adjacent to the intercage connection.

In the original synthesis of the $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ anion from [*trans*-$B_{20}H_{18}]^{2-}$ and the Bender's salt, $KSC(O)OC(CH_3)_3$, in THF, a ring-opened impurity, $[B_{20}H_{17}O(CH_2)_3CH_3]^{4-}$, was observed in ^1H and ^{13}C NMR spectra. The ability of THF and acetonitrile solvents to complex to the [*trans*-$B_{20}H_{18}]^{2-}$ anion was reported by Hawthorne.[4,23] Hawthorne proposed the possible coordination of a solvent molecule, such as tetrahydrofuran (THF), to the [*trans*-$B_{20}H_{18}]^{2-}$ anion. The coordination could result in a subsequent nucleophile-induced ring-opening. Consequently, ring opening could lead to potential impurities in a nucleophilic substitution reaction if THF is used as a solvent. As a result, a solvent that would be neither capable of coordination to the [*trans*-$B_{20}H_{18}]^{2-}$ anion nor susceptible to nucleophile-induced ring-opening became increasingly important to the development of the nucleophilic reactions.

Tetrahydropyran (THP) was used for the solvent in the nucleophile reactions because of the structural similarity to THF. THF and THP were expected to be similar in their ability to dissolve the desired starting materials. The six-membered ring in THP was expected to be more stable and, consequently, less susceptible to nucleophile-induced ring opening. The nucleophile for the reactions was created by deprotonating the appropriate starting materials using NaH in THP. The solution of deprotonated nucleophile was cannulated into a solution of $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] in THP and the

reactions monitored by ^{11}B NMR spectroscopy. The products were isolated by precipitation with a solution of the appropriate cation.

Regardless of the nucleophile used, the ^{1}H, ^{13}C and ^{11}B NMR spectra exhibited identical patterns (Figure 17). The product of the nucleophile reactions was the THP solvent-coordinated compound, an intermediate analogous to that proposed by Hawthorne.[4,23]

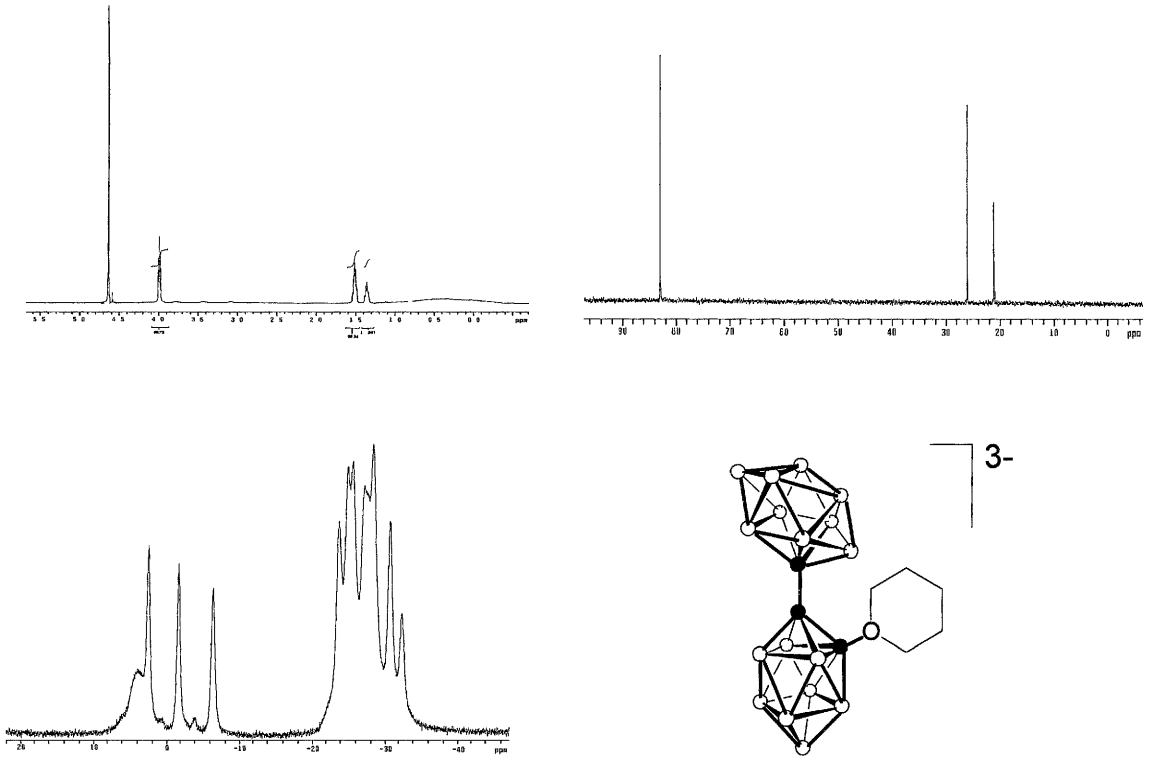


Figure 17: ^{1}H, ^{13}C, and ^{11}B NMR spectra of the product of the reaction of [*trans*-$B_{20}H_{18}]^{2-}$ and a nucleophile in THP and the structure of the product. ● = B; ○ = BH.

Isolation of a product resulting from the ring-opening of THF lead Hawthorne and coworkers to propose a modified mechanism involving three types of nucleophilic attack,

each of which depends not only on the identity of the nucleophilic species but also the solvent (Figure 18).[4] The type 3 mechanism involves the reversible coordination of a nucleophilic solvent molecule to the anion. The coordinated solvent molecule is activated for nucleophilic attack by an anionic nucleophile present in solution. Rearrangement of the intermediate, followed by deprotonation of an equatorial proton on the substituted cage by a second equivalent of nucleophile, yields the product.

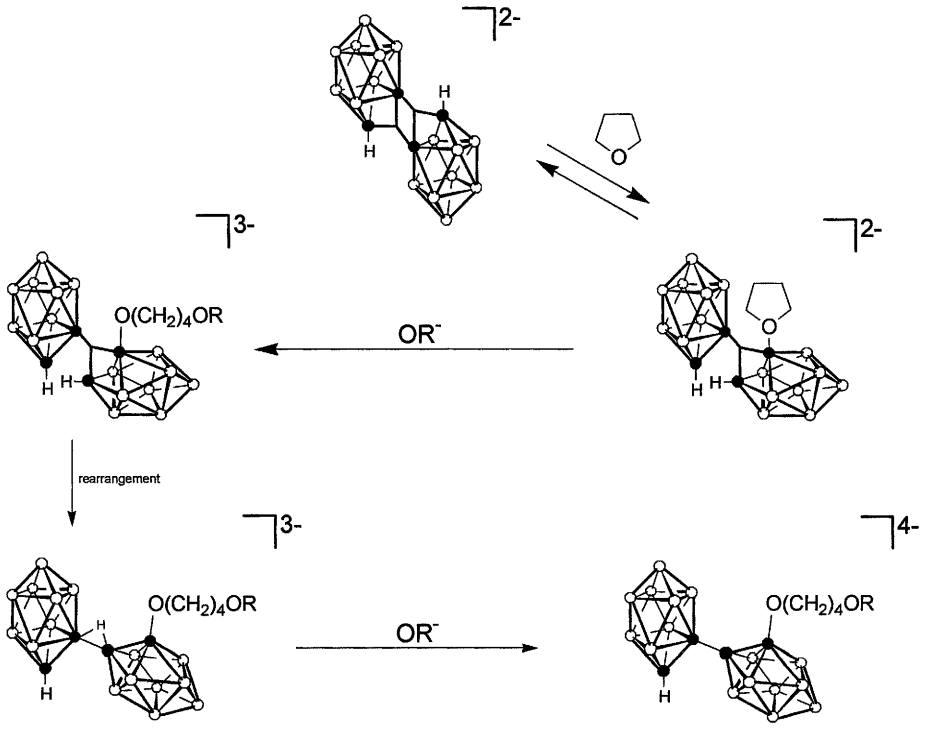


Figure 18: Type 3 mechanism of solvent coordination to the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion. ● = B; ○ = BH.

Understanding the relationships of both the nucleophile and the solvent in the reaction with the $[B_{20}H_{18}]^{2-}$ anion has become increasingly important to the synthesis of substituted polyhedral borane anions. The unusual isomeric arrangements of the thiol

carbamate as well as the ability for certain solvents to coordinate to these compounds raises new questions as to the nature of the mechanism of nucleophilic attack of the two center three electron linkage and the nucleophiles role in the substitution pattern on isomers of the $[B_{20}H_{18}]^{2-}$ anion. The complex and unusual chemistry of this anion may one day lead to the development of new mechanistic models leading to the synthesis of new derivatives the $[B_{20}H_{18}]^{2-}$ anion with potential applications to developments in medicinal chemistry.

2.0 STATEMENT OF PROBLEM

Although two mechanisms of nucleophilic attack on the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion have been proposed,[4,17] neither of the mechanisms adequately describe the formation of the unexpected isomer in the reaction of $[trans\text{-}B_{20}H_{18}]^{2-}$ and the Bender's salt, $KSC(O)OC(CH_3)_3$. The product of the reaction, $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ is an apical-apical isomer and the substituent is located on the equatorial belt adjacent to the terminal boron apex. The isomer is formed directly, with no spectroscopic evidence of the formation of what has traditionally been considered the kinetic, apical-equatorial, isomer. No reports of the substituent location have been made for a compound derived from the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion. In an effort to understand the steric and electronic effects controlling the formation of the unusual isomer, an investigation of sterically demanding nucleophiles (Figure 16) was initiated using tetrahydropyran (THP) as the solvent. In three of the cases, reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion and the nucleophile in THP produced the THP adduct, $[B_{20}H_{17}O(CH_2)_5]^{3-}$. There was no reaction observed when the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion was reacted with t-butylcarbamate in THP. Based on the current mechanisms, the role of the nucleophile remains undefined. Additionally, the preparation of the desired compounds, resulting from the reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion and the sterically demanding nucleophiles, has not been accomplished.

Therefore, the specific goals of the thesis research are:

1) Develop a synthetic route to evaluate the reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion with the selected nucleophiles,
2) Evaluate the role of the nucleophile in the formation of the THP-coordinated product, and
3) Evaluate the potential chemistry of the THP-coordinated product.

Information regarding the potential electronic and steric effects which control the formation of specific compounds will enhance the understanding of the mechanism of nucleophilic attack on the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion and, potentially, aid in the development of a more comprehensive mechanism. The results of this project should also provide a means of preparing boron-containing compounds for specific applications.

3.0 EXPERIMENTAL

3.1 Materials

Sublimed decaborane, $B_{10}H_{14}$, was obtained from Professor Lee J. Todd at Indiana University (Bloomington, IN). ***Caution: decaborane is a highly toxic, impact sensitive compound that forms explosive mixtures especially when in contact with halogenated materials. A careful examination of the MSDS is recommended.*** The *t*-butylcarbamate was purchased from Lancaster (Pelham, NH) and used without further purification. The *n*-butyl alcohol was purchased from EMD (Gibbstown, NJ) and the *t*-butyl alcohol was purchased from Mallinckrodt (Paris, KY). Both of the alcohols were dried over molecular sieves. All other reagents were purchased from Sigma Aldrich Chemical Company (St. Louis, MO). All solid reagents were used without further purification. Liquid reagents were dried over molecular sieves unless otherwise specified. The following solvents: tetrahydropyran, diethyl ether, tetrahydrofuran and acetonitrile, were all reagent grade and were distilled in the presence of the appropriate drying agent unless otherwise specified in the synthesis. All synthetic reactions were performed under argon in anhydrous conditions using Schlenk techniques.

3.2 Physical Measurements

One-dimensional ^{1}H, ^{13}C, and ^{11}B Fourier transform nuclear magnetic resonance (NMR) spectra were obtained with a Varian INOVA spectrometer, equipped with a

boron-free probe, operating at 400 MHz, 100 MHz, and 128 MHz respectively. Boron-11 NMR spectra were obtained using quartz tubes. Proton chemical shifts were referenced to residual solvent protons. Carbon shifts were referenced to $CDCl_3$, when appropriate, or to either CD_3CN or d_6-DMSO, added as an internal standard to aqueous samples. Boron chemical shifts were externally referenced to $BF_3{\cdot}Et_2O$ in C_6D_6; peaks upfield of the reference are designated as negative. All Fourier transform infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum One instrument and were obtained either as neat samples or as nujol mulls.

3.3 Synthetic Procedures

Preparation of $(Et_3NH)_2[B_{10}H_{10}]$. The $(Et_3NH)_2[B_{10}H_{10}]$ preparation was based on the technique developed by Hawthorne and coworkers.[8] Sublimed decaborane (30.0g, 0.246 mol) was added to a 1-Liter three neck flask that had been equipped with an argon inlet, a 250 mL pressure equalizing dropping funnel (PED), and an overhead stirrer. The flask was flushed with argon gas and placed into an oil bath. Xylene (300 mL) was added to the reaction flask and triethylamine (90.0 mL, 0.616 mol) was placed into the PED and added dropwise to the stirred decaborane solution. As the triethylamine was added, a yellow precipitate of the $B_{10}H_{12}(NEt_3)_2$ intermediate was produced. After all of the triethylamine had been added, the PED was replaced with a thermometer adapter and thermometer. The temperature of the reaction mixture was raised to 100 °C and the mixture was allowed to react for 3 hours. After 3 hours the thermometer adapter was replaced with a condenser and the reaction was allowed to reflux for an additional 12 hours.

The reaction mixture was cooled in an ice bath and filtered. The light yellow solid was washed with isopropyl alcohol (7 x 50 mL), removing a majority of the yellow color. The white solid was washed with diethyl ether (2 x 100 mL) and transferred to a 1 L round-bottom flask and dried *in vacuo*. The resulting white product was dissolved in approximately 70 mL of boiling water and quickly filtered through a hot sintered glass filter, removing any insoluble residue. The yellow filtrate was brought to a rolling boil and 50 mL portions of ethanol were added to the filtrate until the solution just began to appear cloudy. Filtration of the solution resulted in 59 grams of $(Et_3NH)_2[B_{10}H_{10}]$ in 74 % yield. ^{11}B NMR (ppm, acetonitrile) δ -1.8, -16.2,($[B_{12}H_{12}]^-$) -30.9.

Preparation of $(Et_3NH)_2$[trans-$B_{20}H_{18}$]. The $(Et_3NH)_2[B_{20}H_{18}]$ preparation was based on the technique developed by Hawthorne and coworkers.[12] $(Et_3NH)_2[B_{10}H_{10}]$ (30.0 g, 0.093 mol) was placed in a 1 L three-neck flask that that been equipped with a condenser, a pressure equalized dropper (PED), and a stir bar. Distilled water (300 mL) was added to the reaction flask to dissolve the $(Et_3NH)_2[B_{10}H_{10}]$ and the mixture was refluxed. A solution of $FeCl_3 \cdot 6H_2O$ (57.2 g, 0.212 mol) dissolved in a minimum amount of distilled water was prepared. The $FeCl_3 \cdot 6H_2O$ solution was transferred to the PED and added dropwise to the refluxing solution of $(Et_3NH)_2[B_{10}H_{10}]$. After addition was complete, the reaction was allowed to reflux an additional 3 hours. The reaction mixture was cooled and the solid was filtered. The residue was recrystallized from boiling water, cooled and filtered, resulting in the isolation of 15.4 g of pale yellow crystals of $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] in 75% yield. ^{11}B NMR (ppm, acetonitrile) 28.2, 13.7, -8.9, -14.1, -17.9, -21.3, -27.0.

Preparation of $KSC(O)O(CH_2)_3CH_3$. The Bender's salt derivative was prepared using the method reported by Daly and coworkers.[24] A clean, dry 500 mL three-neck flask was equipped with an argon inlet and a stir bar and flushed with argon gas. The reaction flask was placed in an ice bath. Dry *n*-butanol (125 mL, 1.36 mol) was added to the reaction vessel via syringe. Potassium metal (7.6 g, 0.19 mol), which had been thoroughly cleaned with hexane to remove all residual mineral oil, was added to the vessel in small pieces under an atmosphere of flowing argon. After all of the potassium had reacted, dry dimethylformamide (75 mL) and freshly distilled THF (25 mL) was added to the reaction flask via syringe. Carbonyl sulfide (20 g, 0.33 mol) was bubbled into the reaction mixture, forming a white precipitate. The reaction was allowed to stir under an argon atmosphere overnight at room temperature. The entire reaction mixture was poured into diethyl ether (250 mL) and filtered through a sintered glass frit. The white solid was rinsed with diethyl ether and dried *in vacuo* to yield 28.2 g of the white product in 84.5% yield. ^{1}H NMR (ppm, D_2O) 3.83 (t), 1.14 (p), 1.04 (m), 0.71 (t); ^{13}C (ppm, D_2O; d_6-DMSO) 186.7, 55.4, 32.1, 20.3, 15.0; IR (cm^{-1}, nujol) 1573 (C=O).

Preparation of $K_4[B_{20}H_{17}SC(O)O(CH_2)_3CH_3]$. A clean, dry 100 mL Schlenk flask was equipped with a stir bar and flushed with argon gas. $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] (0.500g, 1.13×10^{-3} mol) was added to the flask and the flask stoppered and evacuated. A solution containing THF, dried over molecular sieves, and 1% (w/v) BHT, was prepared and 20 mL of the solution was syringed into the reaction vessel. The flask was filled with argon and the stopper removed. The Bender's salt, $KSC(O)O(CH_2)_3CH_3$ (1.20 g, 6.97×10^{-3} mol), was added to the flask and the flask was restoppered. The reaction was allowed to stir under an argon atmosphere at room temperature and was monitored periodically

using ^{11}B NMR spectroscopy. After a two week period, the reaction was complete. The reaction mixture was filtered and the solid, containing both the product and the excess Bender's salt, was retained. The crude product was recystallized from water:ethanol, and the solid was isolated and dried *in vacuo* to yield 0.794 grams of white product in 57.8% yield. ^{1}H NMR (ppm, D_2O) 3.34 (t), 2.60 (t), 1.47-1.40 (m); ^{13}C (ppm, D_2O;d_6-DMSO) 32.0, 31.0, 30.9, 27.2; ^{11}B NMR (ppm, D_2O) -5.4, -9.4, -23.4, -27.6, -29.4, -34.7.
IR (cm^{-1}, nujol) 2431 (BH), 1607 (C=O).

Preparation of $Rb_4[B_{20}H_{17}O(CH_2)_3CH_3]$. A clean, dry 100 mL Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Freshly distilled diethyl ether (5.0 mL) and *n*-butanol (0.60 mL, 6.6×10^{-3} mol) were added to the flask via syringe. The stopper was removed and a 60% dispersion of NaH in mineral oil was added (0.286 g, 6.90×10^{-3} mol). The stopper was replaced and the mixture was allowed to stir until the evolution of hydrogen gas was no longer evident. The polyhedral borane starting material, $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$], was added (0.500 g, 1.13×10^{-3} mol) after increasing the flow of argon gas and removing the stopper. The flask was restoppered and the reaction was allowed to stir under an argon atmosphere overnight at room temperature. Complete reaction was confirmed by ^{11}B NMR spectroscopy. The reaction mixture was dried *in vacuo* and the residue dissolved in a minimum amount of room temperature water. The solution was extracted with $CHCl_3$ (4 x 50 mL). The aqueous layer was retained and the solvent removed under vacuum to yield the crude product, $Na_4[B_{20}H_{17}O(CH_2)_3CH_3]$. The white solid residue was dissolved in a minimum amount of room temperature methanol; water was added to dissolve any solid which remained undissolved. Precipitation of the rubidium salt of the desired anion was achieved by

adding the solution of the sodium salt to a solution of rubidium acetate, $RbC_2H_3O_2$, in methanol (10 mL, 0.5 M). The salt was isolated by filtration of the mixture through a sintered glass frit. The rubidium salt of the product was recrystallized from water:methanol. The solid was filtered and dried *in vacuo* to yield 0.734 g of white product, $Rb_4[B_{20}H_{17}O(CH_2)_3CH_3]$, in 82.2% yield. ^{1}H NMR (ppm, D_2O) 3.03(t), 1.11(m), 0.95(m), 0.59(t); ^{13}C (ppm, D_2O;d_6-DMSO) 72.7, 35.2, 20.4, 15.1; ^{11}B NMR 7.0, 2.1, 0.9, -3.3, -10.2, -25.3, -26.6, -28.7, -30.1, -34.4; IR (cm^{-1}, nujol) 2450 (BH).

Preparation of $Rb_4[B_{20}H_{17}OC(CH_3)_3]$. A clean, dry 100 mL Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Freshly distilled diethyl ether (5 mL) and *t*-butanol (0.60 mL, 6.6×10^{-3}mole) were added to the flask via syringe. The argon flow was increased and a 60% dispersion of NaH in mineral oil was added (0.778 g, 1.87×10^{-2} mol). The stopper was replaced and the mixture was allowed to stir until the evolution of gas was no longer evident. Additional freshly distilled diethyl ether (15 mL) was added to the reaction mixture via syringe. The flow of argon was again increased and the stopper was removed to add $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] (0.501g, 1.14×10^{-3} mol). The flask was stoppered and allowed to stir under argon overnight at room temperature. Complete reaction was confirmed by ^{11}B NMR spectroscopy. The reaction mixture was dried *in vacuo* and the residue of $Na_4[B_{20}H_{17}OC(CH_3)_3]$ was dissolved in 50 mL of room temperature water and extracted with $CHCl_3$ (4 x 50 mL). The aqueous layer was retained and the solvent removed under vacuum. The white solid residue was dissolved in a minimum amount of room temperature methanol; water was added to dissolve any solid which remained undissolved. The desired anion was precipitated as a rubidium salt by adding the solution of $Na_4[B_{20}H_{17}OC(CH_3)_3]$ to a solution of rubidium

acetate, $RbC_2H_3O_2$, in methanol (10 mL, 0.5 M). The solid was isolated by filtration through a sintered glass frit. The rubidium salt of the product was recrystallized from water:methanol. The solid was filtered and dried *in vacuo* to yield the product (0.261 g) in 34.8% yield. ^{1}H NMR (ppm, D_2O) 0.92 (s); ^{13}C (ppm, D_2O;d_6-DMSO) 31.3. ^{11}B NMR (ppm, D_2O) 5.1, 2.4, -3.5, -9.6, -24.9, -30.4,-47.9; IR (cm^{-1}, nujol) 2452 (BH).

Preparation of $Rb_4[B_{20}H_{17}NHC(O)O(CH_2)_3CH_3]$. A clean, dry 100 mL Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Freshly distilled diethyl ether (5 mL) was added to the flask via syringe. The stopper was removed under an atmosphere of flowing argon and *n*-butylcarbamate (0.669 g, 5.70 x 10^{-3}mol) and a dispersion of NaH in mineral oil (0.550 g, 3.68 x 10^{-3} mol) was added to the flask. The reaction mixture was stirred at room temperature until the evolution of hydrogen ceased. After increasing the flow of argon, the stopper was removed and (Et_3NH_2)[*trans*-$B_{20}H_{18}$] (0.500g, 1.13 x 10^{-3}mol) was added. The flask was restoppered and allowed to stir under argon overnight. Reaction completion was confirmed by ^{11}B NMR spectroscopy. The solvent was removed under vacuum, resulting in a white solid which was dissolved in a 50 mL of room temperature water and extracted with $CHCl_3$ (4 x 50mL). The aqueous layer was retained and dried under vacuum. The white solid was dissolved in a minimum amount of room temperature methanol and the resulting solution was added to a solution of rubidium acetate, $RbC_2H_3O_2$ (10 mL, 0.5 M), in methanol to yield a white precipitate. The mixture was filtered through a sintered glass frit to isolate the solid rubidium salt which was recrystallized from water:methanol. The solid was filtered and dried *in vacuo*, resulting in 0.521 grams of the product, 66% yield. ^{1}H NMR (ppm, D_2O) 4.05 (m), 3.28 (m), 1.72(s) ($RbC_2H_3O_2$), 1.15 (m), 1.01 (t), 0.92 (m), 0.73 (m). ^{13}C (ppm, D_2O;

d_6-DMSO) 181.9, 80.2 (ethyl contaminant), 55.3, 50.3 (acetate), 32.2, 25.0 (ethyl contaminant), 20.1, 14.5; ^{11}B NMR(ppm, D_2O) 2.6, -3.0,-8.6,-29.5; IR (cm^{-1}, nujol) 3434 (NH), 2444 (BH), 1550 (C=O).

Preparation of $Rb_4[B_{20}H_{17}NHC(O)OC(CH_3)_3]$. A clean, dry 100 mL Schlenk flask was equipped with a stir bar and flushed with argon gas. The *t*-butylcarbamate (0.539 g, 0.460 mol) was added to the flask and the flask was stoppered. Freshly distilled diethyl ether (5 mL) was added to dissolve the *t*-butylcarbamate. The argon flow was increased, the stopper removed, and a 60% dispersion of NaH in mineral oil was added (0.214 g, 5.16×10^{-3} mol). The stopper was replaced and the mixture was allowed to stir under argon until no gas evolution was evident. The flow of argon was increased, the stopper was removed, and the starting material (Et_3NH_2)[*trans*-$B_{20}H_{18}$] (0.497 g, 1.13×10^{-3} mol) was added. The flask was restoppered and allowed to stir under an argon atmosphere overnight. The reaction was monitored for completion using ^{11}B NMR spectroscopy. The solvent was removed under vacuum, resulting in a white solid. The solid was dissolved in 50 mL of room temperature water and extracted with $CHCl_3$ (4 x 50mL). The aqueous layer was retained and dried under vacuum. The white solid was dissolved in a minimum amount of room temperature methanol and the solution was added to a solution of rubidium acetate, $RbC_2H_3O_2$ (10 mL, 0.5 M), in methanol, yielding a precipitate of the rubidium salt of the product. The mixture was filtered through a sintered glass frit and the solid recrystallized from water:methanol. The solid was filtered and dried *in vacuo* resulting in 0.186 g of the product in 23.7% yield. ^{1}H NMR (ppm, D_2O) 1.17(s); ^{13}C (ppm, D_2O;d_6-DMSO) 55.3, 29.6; ^{11}B NMR (ppm, D_2O)9.1, 2.2, -4.0, -

7.0, -8.6, -15.5, -25.2, -29.4, -30.2, -33.3; IR (cm^{-1}, nujol) 3575 (NH), 2418 (BH), 1677 (C=O).

Preparation of $Rb_4[B_{20}H_{17}S(CH_2)_3CH_3]$. A clean, dry 100 mL three-neck flask was equipped with a stir bar, an argon inlet, and a stopper, and flushed with argon gas. Freshly distilled diethyl ether (5 mL) and *n*-butanethiol (0.70 mL, 7.60×10^{-3}mol) were added via syringe. The argon flow was increased and a 60% dispersion of NaH (0.245 g, 5.90×10^{-3} mol) in mineral oil was added. The stopper was replaced and the mixture was allowed to react until the evolution of gas was no longer observed. Additional freshly distilled diethyl ether (15 mL) was added to the reaction mixture via syringe. The starting material $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] (0.500 g, 1.14×10^{-3} mol) was added after increasing the flow of argon and removing the stopper. The flask was fitted with a water jacketed condenser and placed into an oil bath. The reaction was brought to reflux and allowed to react overnight. The reaction mixture was dried *in vacuo* and the residue dissolved in a minimum amount of room temperature water. The solution was extracted with $CHCl_3$ (4 x 50 mL). The aqueous layer was retained and the solvent removed under vacuum to yield the crude product, $Na_4[B_{20}H_{17}S(CH_2)_3CH_3]$. The white solid residue was dissolved in a minimum amount of room temperature methanol; water was added to dissolve any solid which remained undissolved. The rubidium salt of the desired anion was precipitated by adding the solution of the sodium salt to a solution of rubidium acetate, $RbC_2H_3O_2$ (10 mL, 0.5 M), in methanol. The salt was isolated by filtration through a sintered glass frit. The rubidium salt of the product was recrystallized from water:methanol. The product was isolated by filtration and dried *in vacuo* to yield 0.382 g of white product in 50.5% yield. ^{1}H NMR (ppm, D_2O) 3.33 (m), 3.17 (s), 3.16 (m),

0.90-0.75(m); ^{13}C (ppm, D_2O;d_6-DMSO) 76.0, 63.4, 6.53, 1.60; ^{11}B NMR (ppm, D^2O) 7.0, -3.2, -5.9, -8.0, -10.0, -24.7, -29.8 ;IR (cm^{-1}, nujol) 2414 (BH).

Preparation of $Rb_3[B_{20}H_{17}O(CH_2)_5]$. A clean, dry 100 mL Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Freshly distilled THP (5 mL) and *n*-butanol (0.60 mL, 6.6 $x10^{-3}$ mol) were added to the flask via syringe. The flow of argon was increased, the stopper removed, and a 60% dispersion of NaH in mineral oil was added (0.24g, 5.8 x 10^{-3} mol) to the mixture. The stopper was replaced and the reaction was allowed to stir until gas evolution was no longer evident. An additional 15 mL of THP was added to the flask via syringe. The flow of argon was increased and the starting material, $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] (0.501 g, 1.14 x 10^{-3} mol) was added to the flask. The flask was restoppered and the mixture was allowed to react overnight at room temperature. The solvent was removed from the reaction under vacuum. The resulting white solid was dissolved in a minimum amount of room temperature methanol; water was added to dissolve any remaining solid. The solution containing the reaction product was added to a solution of $RbC_2H_3O_2$ (10 mL, 0.5M) in methanol, resulting in precipitation of a white solid. The solution was filtered and the solid was retained. The solid was recrystallized using water:methanol, filtered through a sintered glass frit, and dried *in vacuo*, resulting in 0.411 grams of the product in 61.8 % yield. ^1H NMR (ppm, D_2O) 3.97 (t) 1.50 (m) 1.35 (m); ^{13}C (ppm, D_2O;d_6-DMSO) 82.1, 25.1, 20.2; ^{11}B NMR (ppm, D_2O) 2.6, -3.2, -9.7, -25.4, -26.6, -28.4, -29.8, -31.7; IR (cm^{-1}, nujol) 2425(BH).

Preparation of $Rb_4[B_{20}H_{17}O(CH_2)_5OCH_2CH_3]$. A clean, dry Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Freshly distilled THP (25 mL) and ethanol (0.400 mL, 6.80 x 10^{-3} mol) was added to the flask. The flow of

argon was increased, the stopper removed, and a 60% dispersion of NaH (0.302 g, 7.27 x 10^{-3} mol) in mineral oil was added. The flask was restoppered and the mixture was allowed to react until gas evolution was no longer evident. The flow of argon was increased, the stopper was removed, and $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] (0.496 g, 1.13 x 10^{-3} mol) was added to the reaction vessel. A condenser was attached and the reaction mixture was brought to reflux and allowed to react for 72 hours. The reaction was monitored for completion using ^{11}B NMR spectroscopy. The solvent was removed from the reaction under vacuum. The resulting white solid was dissolved in a minimum amount of room temperature methanol; water was added to dissolve any remaining solid. The solution containing the reaction product was added to a solution of $RbC_2H_3O_2$ (10 mL, 0.5M), resulting in the formation of white solid. The mixture was filtered and the solid was retained. The solid was recrystallzed using water:methanol. The product was isolated by filtration and dried *in vacuo*, resulting in the isolation of 0.589 grams of the product (59.9% yield). ^{1}H NMR (ppm, D_2O) 3.52 (m), 3.50 (m), 3.31 (s), 3.12 (m), 1.50 (m), 1.30 (m), 1.14 (t); ^{11}B NMR (ppm, D_2O) 2.6, -3.2, -9.7, -25.7, -26.8, -30.0, -32.0, -34.0;IR (cm^{-1}, nujol) 2425 (BH).

Preparation of $K_4[B_{20}H_{17}O(CH_2)_5S(CH_2)_3CH_3]$. A clean, dry Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Freshly distilled THP (5 mL) and *n*-butane thiol (0.70 mL, 6.50x10^{-3} mol) was added to the flask via syringe. The flow of argon was increased and the flask was unstoppered to add a 60% dispersion of NaH (0.302 g, 7.3x10^{-3} mol) in mineral oil. The flask was restoppered and the mixture was allowed to react until gas was no longer evolved. An additional 15 mL of THP was added to the flask. The flow of argon was again increased, the stopper removed, and the

starting material, $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ (0.500 g, $1.13x10^{-3}$ mol) was added to the reaction mixture. The stopper was replaced and the reaction mixture was allowed to stir at room temperature overnight. The reaction was monitored for completion using ^{11}B NMR spectroscopy. The solvent was removed from the reaction under vacuum and the resulting white solid was dissolved in a minimum amount of room temperature methanol. The solution was added to a solution of potassium acetate, $KC_2H_3O_2$ (25 mL, 0.5M) in methanol causing the precipitation of a white solid. The solution was filtered using gravity filtration and the solid was retained. The solid was washed with methanol (3 x 50 mL) and allowed to dry under argon, yielding 0.229 g of the product, 26.3 % yield. ^1H NMR (ppm, D_2O) 3.35 (t), 3.10 (t), 2.35 (m),1.73 (s) ($KC_2H_3O_2$) 1.34 (m) , 1.17 (m), 0.67(t);^{13}C (ppm, D_2O;d_6-DMSO) 182.4, 72.8, 32.7, 32.6, 32.5, 32.3, 31.7, 30.3, 30.2, 26.2, 24.9, 22.8, 14.5; ^{11}B NMR (ppm, D_2O) 11.9, 6.2, 2.4, -10.3, -15.5, -19.3, -30.1, 34.3; IR (cm^{-1}, nujol) 2457 (BH).

Preparation of $K_4[B_{20}H_{17}O(CH_2)_4S(CH_2)_3CH_3]$. A clean, dry Schlenk flask that was equipped with a stir bar, stoppered, and flushed with argon gas. THF containing 1 (w/v) % BHT was added to the flask (5 mL) along with *n*-butanethiol (0.70 mL, 6.5×10^{-3} mol). The flow of argon was increased and the stopper removed. A 60% dispersion of NaH in mineral oil (0.307 g, 7.40×10^{-3} mol) was added. The flask was restoppered and the mixture was allowed to react until gas was no longer evolved. Additional THF-BHT solution (15 mL) was added to the flask. The flow of argon was again increased and the stopper was removed. The starting material, $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$, was added to the reaction mixture and the stopper was replaced. The reaction mixture was allowed to stir at room temperature overnight. The reaction was monitored for completion using ^{11}B

NMR spectroscopy. The solvent was removed from the reaction under vacuum and the resulting white solid was dissolved in a minimum amount of room temperature methanol. The solution containing the reaction product was added to a solution of potassium acetate, $KC_2H_3O_2$ (25 mL, 0.5M) in methanol, resulting in the precipitation of a white solid. The solution was filtered using gravity filtration. The solid was washed with methanol (3 x 50 mL) and allowed to dry under argon. The product was isolated in 44.4 % yield. ^{1}H NMR (ppm, D_2O) 3.17 (m), 2.36 (m), 1.17 (s) ($KC_2H_3O_2$) 1.40-1.10 (m), 0.69 (t); ^{13}C (ppm, D_2O;d_6-DMSO) 70.1, 31.5, 31.3, 31.2, 31.0; ^{11}B NMR (ppm, D_2O) 6.9, 2.5, -3.5, -6.1, -10.2, -25.3, -30.0, -34.1, -57.2; IR (cm^{-1}, nujol) 2430 (BH).

4.0 RESULTS and DISCUSSION

4.1 Reactions with Nucleophiles

Six nucleophiles were selected for investigation. The *n*-butyl derivative of the Bender's salt was selected for comparison to the *t*-butyl derivative investigated and reported earlier.[24] Both Bender's salts have a sulfur atom as the nucleophilic atom. Two alkoxides, *t*-butoxide and *n*-butoxide, were selected because of the known ability of oxygen derivatives to react with the electron-deficient bonding region in the [*trans*-$B_{20}H_{18}]^{2-}$ anion.[4,16,17] The varying steric bulk of the substituents enables an investigation of the steric effects of the alkoxide nucleophiles. Two carbamates, the *n*-butylcarbamate anion and the *t*-butylcarbamate anion, were selected because of the structural similarities between the carbamates and the Bender's salt derivatives. As a result, the direct comparison between the effect of varying the sulfur and nitrogen nucleophilic atom can be investigated. Although four of the selected nucleophiles had been investigated earlier, three of the reactions produced the THP-coordinated compound rather than the desired substituted, reduced species of general form $[B_{20}H_{17}X]^{4-}$, where X is the nucleophilic substituent. The reaction of *t*-butylcarbamate and the [*trans*-$B_{20}H_{18}]^{2-}$ ion resulted in no reaction.

The *n*-butyl derivative of the Bender's salt, $KSCOO(CH_2)_3CH_3$, was prepared from the reaction of potassium *n*-butoxide and carbonyl sulfide in a mixed solvent system, using the method reported by Daly and coworkers for the *t*-butoxy derivative,

$KSC(O)OC(CH_3)_3$.[24] The ^1H NMR, ^{13}C NMR, and IR were consistent with the formation of the desired product. The ^1H NMR exhibits four sets of peaks with shifts and splitting patterns consistent with the *n*-butyl group. The IR spectrum exhibits a carbonyl absorption at 1607 cm^{-1}.

Formation of the $[B_{20}H_{17}SC(O)O(CH_2)_3CH_3]^{4-}$ ion was achieved by the reaction of $KSC(O)O(CH_2)_3CH_3$ and $(Et_3NH)_2[B_{20}H_{18}]$ in a solution of THF containing 1% butylated hydroxytoluene (BHT) at room temperature. BHT was added to the reaction mixture to inhibit the THF ring-opening reaction which was observed in the formation of the *t*-butyl derivative, $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$, reported earlier.[4,23] Elimination of the BHT in the reaction mixture, through the use of distilled THF, results in the formation of significant amounts, approaching 50%, of the ring-opened product, $[B_{20}H_{17}O(CH_2)_3CH_3]^{4-}$. The boron-containing starting material, $[trans\text{-}B_{20}H_{18}]^{2-}$, is soluble in THF whereas the product of the reaction, $K_4[B_{20}H_{17}SC(O)O(CH_2)_3CH_3]$, is not. Therefore, the reaction was monitored by the disappearance of the seven peaks corresponding to the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion starting material located at 28.2 ppm, 13.7 ppm, -8.9 ppm, -14.1 ppm, -17.9 ppm, -21.3 ppm, and -27.0 ppm in the ^{11}B NMR spectrum of the solvent. The reaction required two weeks to obtain complete reaction. Refluxing the reaction mixture decreases the required time significantly, but increases the relative amount of ring-opened product. The product was isolated, recrystallized, and characterized. The ^{11}B NMR spectrum of the product is characterized by the presence of two sharp apical boron atom signals, at -5.4 ppm and -9.4 ppm, which are singlets in the proton-decoupled spectrum. Therefore, the product of the reaction (Figure 19) is the apical-apical isomer, consistent with the results obtained in the reaction of the *t*-butyl

Bender's salt derivative. Formation of the apical-equatorial isomer would result in the presence of three sharp apical boron atom signals in the ^{11}B NMR spectrum. The signal centered just above 10 ppm is assigned to the boron atoms in the boron-boron intercage linkage and appears to have two broad peaks as opposed to one single broad peak. The two broad peaks are indicative of substitution on the equatorial belt adjacent to the terminal boron apex. The IR spectrum confirms the presence of the B-H functionality, at 2431 cm^{-1}, and the presence of the carbonyl functionality, at 1607 cm^{-1}. Both values are similar to those observed for the *t*-butyl derivative, $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$, which exhibited a B-H stretch at 2457 cm^{-1} and a C=O stretch at 1590 cm^{-1}.[20] Four distinct sets of peaks are observed in the ^1H NMR spectrum, with the anticipated splitting patterns, which are consistent with the formation of the product. The peaks associated with the CH_2 moiety alpha to the carbonyl group are expected to exhibit the greatest shift. The ^1H NMR spectrum of the starting material exhibits a triplet at 3.83 ppm whereas the ^1H NMR spectrum of the product exhibits a triplet at 3.34 ppm. Similarly, the ^{13}C NMR of spectrum the starting material exhibits a peak at 55.4 ppm whereas the ^{13}C NMR spectrum of the product exhibits a peat at 32.0 ppm.

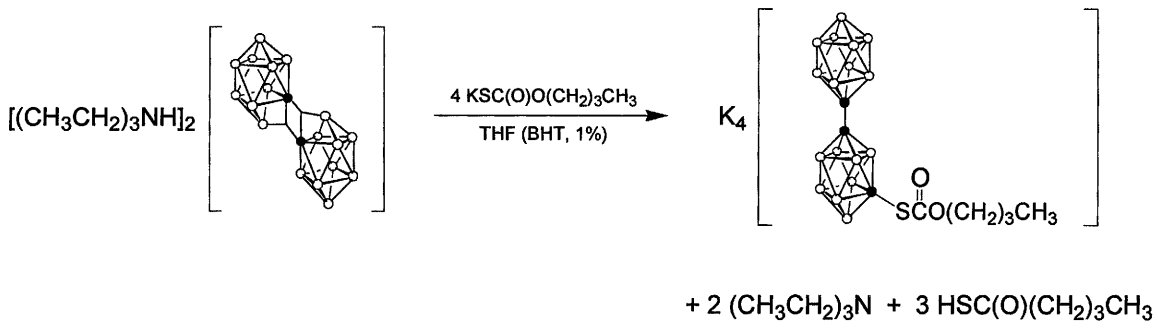


Figure 19: Balanced chemical reaction for the formation of $K_4[B_{20}H_{17}SC(O)O(CH_2)_3CH_3$ from $(CH_3CH_2)_3NH)_2[$*trans*-$B_{20}H_{18}]$ and $KSC(O)O(CH_2)_3CH_3$. ● = B; ○ = BH.

Alkoxide nucleophiles were selected for investigation because of the known reactivity of the [*trans*-$B_{20}H_{18}]^{2-}$ anion with alkoxides[4,16,17] and the availability of alkoxides with varying steric bulk. In order to maintain the similarity between functional groups in the selected nucleophiles, both *n*-butoxide and *t*-butoxide were selected for investigation.

The *n*-butoxide nucleophile was generated *in situ* by the reaction of *n*-butanol with NaH in diethyl ether and the polyhedral borane starting material, $(Et_3NH)_2[$*trans*-$B_{20}H_{18}]$, was added to the mixture. Completion of the reaction was confirmed by the absence of the seven peaks in the ^{11}B NMR spectrum corresponding to the starting material. The reaction was complete within 12 hours. The product, $Rb_4[B_{20}H_{17}O(CH_2)_3CH_3]$, was isolated and characterized. The ^{11}B NMR spectrum is characterized by the presence of three sharp apical boron atom signals, located at 2.6 ppm, -3.0 ppm and -8.6 ppm. The presence of three apical boron atom signals indicates the formation of an apical-equatorial isomer (Figure 20). A single broad signal associated with the B-B intercage linkage indicates that the substituent is located on the equatorial belt adjacent to the intercage linkage. Infrared analysis indicates a peak at 2450 cm^{-1}

associated with the B-H stretch. The –OH absorption associated with the starting material is absent in the product. The ^{1}H NMR spectrum yielded four distinct sets of peaks, with the appropriate splitting pattern, corresponding to the four unique chemical shift environments expected for the *n*-butoxide derivative. The triplet associated with the protons nearest the oxygen atom is shifted upfield from 3.39 ppm in the *n*-butanol starting material to 3.02 ppm in the product. The ^{13}C NMR spectrum exhibits four peaks. The peak observed at 72.7 ppm in the ^{13}C NMR spectrum of the product represents a downfield shift from the analogous peak in the ^{13}C NMR spectrum of the starting material observed at 63.1 ppm.

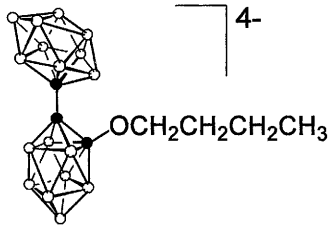


Figure 20: Product of the reaction of the [*trans*-$B_{20}H_{18}]^{2-}$ anion and sodium *n*-butoxide. ● = B; ○ = BH.

NaH was added to a solution of *t*-butanol and diethyl ether, producing the *t*-butoxide nucleophile *in situ*. Reaction between the *t*-butoxide ion and the [*trans*-$B_{20}H_{18}]^{2-}$ anion was monitored by the disappearance of the peaks associated with the polyhedral borane anion starting material. Reaction was complete after 12 hours. The product, $[B_{20}H_{17}OC(CH_3)_3]^{4-}$, was isolated and characterized. The ^{11}B NMR spectrum of the product afforded three sharp peaks at 2.4 ppm, -3.5 ppm and -9.6 ppm which represent three distinct apical boron atom signals and which are characteristic of an

apical-equatorial isomer (Figure 21). A single broad signal associated with the B-B intercage linkage predicts that the substituent is located on the equatorial belt adjacent to the intercage linkage. The IR spectrum of the product exhibits a strong B-H absorption at 2452 cm^{-1} as well as the loss of the broad -OH stretch observed in the IR spectrum of the starting material. The ^{1}H NMR spectrum of the product exhibits a singlet located at 0.923 ppm. No significant shift was observed from the corresponding signal in the ^{1}H NMR spectrum of the starting material, *t*-butanol. There is also a small impurity observed just above 1.00 ppm. The ^{13}C NMR spectrum of the product contains a single peak located at 31.3 ppm, corresponding to the methyl carbons attached to the tertiary carbon of the *t*-butyl substituent. Like the ^{1}H NMR spectrum, no significant shift was observed in the location of the methyl signals associated with the *t*-butyl group of the product as compared to the starting material, *t*-butanol (30.9 ppm). The absence of a significant peak shift is not unexpected since the carbon atoms are further from the polyhedral borane cages and are less likely to be subject to the electronic effects of the cage. The signal associated with the tertiary carbon of the product could not be resolved.

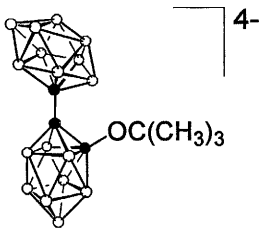


Figure 21: Product of the reaction of the [*trans*-$B_{20}H_{18}]^{2-}$ anion and sodium *t*-butoxide. ● = B; ○ = BH.

The *n*-butyl and *t*-butyl carbamates are available commercially and provide a means to evaluate the properties of the nitrogen analogues of the Bender's salts, $KSC(O)OC(CH_3)_3$ and $KSC(O)O(CH_2)_3CH_3$, in terms of both electronic and steric effects. Since the substituent groups are identical in the two sets of compounds, the reactivity of the nitrogen atom can be assessed compared to the sulfur atom. If the compounds behave the same as the sulfur analogues, the unusual isomer formed in the sulfur reactions may be a result of the carbamate functionality whereas, if the compounds behave differently than the sulfur analogues, the unusual isomer formed in the sulfur reactions may be a result of the nucleophilic behavior of the sulfur atom.

The *n*-butyl carbamate nucleophile was produced from the reaction of *n*-butyl carbamate and NaH in diethyl ether. Reaction between the *n*-butyl carbamate anion and the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion was monitored by the disappearance of the peaks associated with the polyhedral borane anion starting material. Reaction was complete after 12 hours. Two broad signals associated with the B-B intercage linkage indicate that the substituent is located on the equatorial belt adjacent to the terminal apex. The IR spectrum exhibits a B-H absorption at 2444 cm^{-1}, a carbonyl absorption at 1550 cm^{-1}, and a N-H absorption at 3434 cm^{-1}. The N-H absorption and C=O absorption of the starting material appear at 3418 cm^{-1} and 1682 cm^{-1}, respectively. Characterization of this product by NMR resulted in seven sets of peaks in the ^{1}H NMR spectrum three of the sets are impurities. There are eight peaks in the ^{13}C NMR spectrum located at 181.9 ppm, 80.2 ppm, 55.3 ppm, 50.3 ppm, 32.2 ppm, 25.0 ppm, 20.1 ppm, and 14.5 ppm. Three of the peaks are impurities.

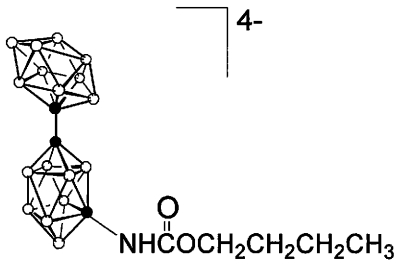


Figure 22: Product of the reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion and the sodium salt of *n*-butylcarbamate. ● = B; ○ = BH.

The *t*-butylcarbamate anion was obtained by deprotonating *t*-butylcarbamate with NaH in diethyl ether. The reaction between the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion and the *t*-butylcarbamate anion was monitored by the disappearance of the peaks associated with the polyhedral borane anion starting material, $[trans\text{-}B_{20}H_{18}]^{2-}$, in the ^{11}B NMR spectrum. After 12 hours, the reaction was complete and the product was isolated. Three sharp peaks in the apical or substituted boron atom region of the ^{11}B NMR spectrum confirm the formation of an apical-equatorial isomer (Figure 23). Two broad signals associated with the B-B intercage linkage predict that the substituent is located on the equatorial belt adjacent to the terminal B-H apex. The IR spectrum displays a B-H absorption at 2418 cm^{-1}, a carbonyl absorption at 1677 cm^{-1}, and a N-H absorption at 3575 cm^{-1}. The N-H absorption and C=O absorption of the starting material appear at 3418 cm^{-1} and 1682 cm^{-1}, respectively. Characterization of the product by NMR resulted in a singlet located at 1.17 ppm in the ^{1}H NMR spectrum and two peaks in the ^{13}C NMR spectrum located at 55.3 ppm and 29.5 ppm, respectively. The peak located at 55.3 ppm is thought to be an artifact of the NMR while the actual signal corresponding to the quaternary carbon of the

t-butyl group and the quaternary carbon of the carbonyl group are most likely too small to be observed in the noise of the spectrum.

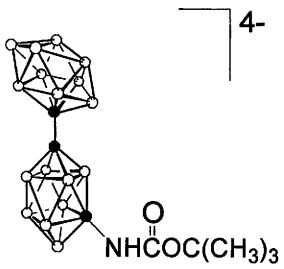


Figure 23: Product of the reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion and the sodium salt of *t*-butylcarbamate. ● = B; ○ = BH.

Based on the experimental data obtained with the two alkoxy nucleophiles and the two carbamate nucleophiles, the *n*-butanethiol anion was added for investigation. The *n*-butanethiol nucleophile is a sulfur analogue of the *n*-butoxide derivative and provides a basis of comparison between the sulfur nucleophiles and the oxygen nucleophiles. The *n*-butanethiol was deprotonated using NaH in diethyl ether and the anion was allowed to react with the polyhedral borane anion starting material, [*trans*-$B_{20}H_{18}$]$^{2-}$. The reaction was monitored by the disappearance of the peaks in the ^{11}B NMR spectrum associated with the starting material. The reaction did not occur in room temperature diethyl ether; however, the reaction occurred overnight in refluxing diethyl ether, probably due to the increased solubility of the sodium salt of *n*-butanethiol in the refluxing diethyl ether. The ^{11}B NMR spectrum of the product exhibits a preponderance of two peaks, at -5.8 ppm and -7.8 ppm, in the apical or substituted boron atom region of the spectrum, indicating the formation of an apical-apical isomer (Figure 24). Although the two apical signals are clearly present, additional signals indicate the possible presence of an apical-equatorial isomer. As a result, the identity of the original isomer remains unknown since the apical-

apical isomer may be a result of thermodynamic conversion of the apical-equatorial isomer. The ^{1}H NMR spectrum exhibits five sets of peaks although only four are expected.

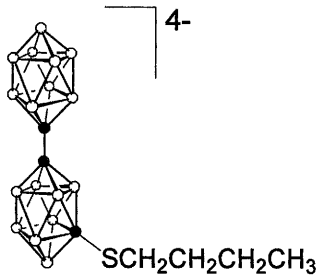


Figure 24: Product of the reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion and the sodium salt of *n*-butanethiol. ● = B; ○ = BH.

4.2 Coordination of THF and THP Molecules

Preliminary investigations of the nucleophile reactions were completed by Mr. Brian Newell using THP as the solvent. The reaction of $[(Et)_3NH]_2[trans\text{-}B_{20}H_{18}]$ and approximately 4.5 equivalents of the *n*-butoxide anion, the *t*-butoxide anion, or the *n*-butylcarbamate anion, THP as the solvent all indicated the formation of an apical-equatorial isomer using ^{11}B NMR spectroscopy. As noted earlier (Figure 17), the ^{1}H, ^{13}C, and ^{11}B NMR spectra were identical to each other. The ^{1}H NMR exhibits three distinct peaks corresponding to the three chemical environments observed in the THP molecule. The chemical shifts are clearly different from the ^{1}H NMR spectrum of the starting material, which exhibits a downfield triplet, at 3.64 ppm, assigned to the protons on the carbon adjacent to the oxygen atom and overlapping pentets, between 1.65 ppm and 1.53 ppm, associated with the remaining hydrogen atoms. The integration of the ^{1}H NMR signals in the product spectrum resulted in an integration ratio of 2:2:1. The THP-

coordinated anion, $[B_{20}H_{17}O(CH_2)_5]^{3-}$, is analogous to the THF-coordinated intermediate proposed, but never isolated, by Hawthorne.[4,23]

When the polyhedral borane anion starting material, $[trans\text{-}B_{20}H_{18}]^{2-}$, is dissolved in THP, no reaction occurs based on the ^{11}B NMR spectrum of the reaction mixture. In the standard reaction procedure, a total of approximately 4.5 equivalents of the nucleophile are added: two equivalents of the nucleophile are required to deprotonate the triethylammonium cation and the remaining two equivalents are added to complete the reductive substitution reaction. Since the triethylammonium salt of the anion is less soluble in THP, both $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ and $Na_2[trans\text{-}B_{20}H_{18}]$ were evaluated to determine if the function of the nucleophile was only to deprotonate the starting material and increase the solubility. The sodium salt of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion also did not react in the absence of a nucleophile based on the ^{11}B NMR spectrum of the reaction mixture despite the fact that it is highly soluble in THP.

All of the nucleophiles investigated have the potential to act as a Bronsted-Lowry base. Therefore, the possibility of the reaction being a base-mediated reaction, as opposed to a nucleophile-mediated, reaction was evaluated. A series of reactions were developed to address the issue. Sodium hydride, NaH, was added to distilled THP to determine whether the THP could be deprotonated by a strong base. The deprotonation process would release H_2 gas. No gas evolution was observed. The triethylammonium salt of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion and NaH was added to THP to determine if the reaction would occur in the absence of the nucleophile. No change in the ^{11}B NMR spectrum of the starting material was observed, even after a period of two months. The reaction was repeated using the sodium salt of $[trans\text{-}B_{20}H_{18}]^{2-}$ ion. No change in the ^{11}B NMR

spectrum was observed. Although both NaH and *n*-butyllithium are much stronger bases than the nucleophiles used in the investigation, the reaction was repeated using *n*-butylithium. The ^{11}B NMR spectrum of the reaction mixture changed significantly. The product of the reaction was isolated and ^{1}H NMR was obtained. Only one singlet was observed in the ^{1}H spectrum which is not indicative of the THP-coordinated product. The product of the reaction is predicted to be the result of the *n*-butyl carbanion reaction with the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion. The singlet would be consistent with a 1,2 rearrangement of the butyl group producing a tertiary alkyl substituent and forming the $[B_{20}H_{17}C(CH_3)_3]^{4-}$ anion.[25] Although, if accurate, the product would be the first reported product of a carbanion reaction with the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion, the reaction was not within the scope of the current project and the investigation was tabled for future research. The series of reactions completed indicate that the coordination of the THP molecule is not base-mediated and that the nucleophile is required for the reaction, forming the THP-coordinated adduct, to proceed.

The stoichiometry of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion and THP reaction was also investigated for the possibility that the nucleophile is a catalytic species. Two reactions were completed. One reaction was completed with $Na_2[trans\text{-}B_{20}H_{18}]$ and 0.5 mole percent potassium *t*-butoxide in THP and the other reaction was completed with $Na_2[trans\text{-}B_{20}H_{18}]$ and 5 mole percent *t*-butoxide. The reactions were monitored using ^{11}B NMR spectroscopy. After 24 hours, the ^{11}B NMR spectrum of each reaction mixture was obtained. Most of the mixture contained unreacted $[trans\text{-}B_{20}H_{18}]^{2-}$ ion; however, small, yet obvious peaks, were present in the spectra. The reaction was allowed to react over the course of a two week period and the ^{11}B NMR spectra were obtained

periodically. The relative intensity of the small peaks did not increase over the entire reaction period. Therefore, the nucleophile is not a catalyst for the reaction. When the reaction was completed using one equivalent of $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$], one equivalent of THP, and four equivalents of *n*-butoxide in acetonitrile as the solvent, a change in the staring material was observed but the isolated product was not consistent with the THP coordinated product. Coordination of the THP intermediate was only observed when the THP was used as the solvent. Therefore, the coordination of the THP molecule appears to be the result of mass action.

The revised mechanism of nucleophilic attack on the [*trans*-$B_{20}H_{18}$]$^{2-}$ proposed by Hawthorne (Figure 18) was used to describe the nucleophile-induced ring-opening of THF.[4] To determine whether an analogous reaction would produce the ring-opened THP product, a mixture of $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$], ethanol, and NaH was allowed to react in refluxing THP. The reaction was monitored by ^{11}B NMR spectroscopy and was complete after 72 hours. The ^{11}B NMR spectrum exhibited three sharp peaks in the apical or substituted boron atom region of the spectrum, indicating the formation of an apical-equatorial isomer (Figure 25). A single broad signal associated with the B-B intercage linkage indicates that the substituent is located on the equatorial belt adjacent to the intercage linkage. The ^{1}H NMR spectrum contains multiple sets of peaks, several of which are overlapping The ^{1}H NMR peaks characteristic of the THP-coordinated product were not observed. The IR spectrum of the product contained a B-H absorption at 2425 cm^{-1}.

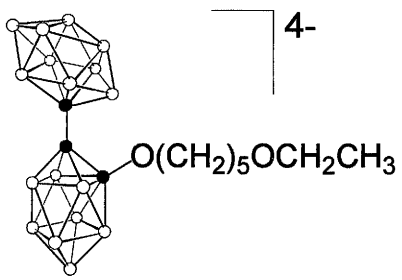


Figure 25: Product of the ring-opening reaction of THP with ethoxide ion. ● = B; ○ = BH.

The reaction of *n*-butanethiol and the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion was of interest because of the analogies that could be drawn to the *n*-butoxide ion in the investigations of the nucleophiles completed earlier. Deprotonation of *n*-butanethiol was achieved using NaH in THP as a solvent. The triethylammonium salt of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion was added and the reaction was monitored for completion by the disappearance of the peaks characteristic of the polyhedral borane starting material. The reaction was complete after a period of 12 hours and the product was isolated. Three sharp peaks in the apical or substituted boron atom region of the ^{11}B NMR spectrum indicate formation of the apical-equatorial isomer (Figure 26). The presence of two signals in the region for the intercage connection indicates the possibility that the substituent is located on the equatorial belt adjacent to the terminal apex. A B-H absorption at 2457 cm^{-1} is observed in the IR spectrum. The ^1H NMR spectrum shows sets of peaks at 3.12 ppm, 2.35 ppm, 1.35ppm 1.21-0.90 ppm and 0.69 ppm. Reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion with both the alkoxides and the carbamates in THP as the solvent produce the THP-coordinated adduct; however, the *n*-butanethiol anion produces the ring-opened product analogous to the THF-coordinated intermediate in Hawthorne's proposed mechanism.[4] Therefore, *n*-

butanethiol acts as a stronger nucleophile then either the alkoxides or the carbamates in the reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion in THP.

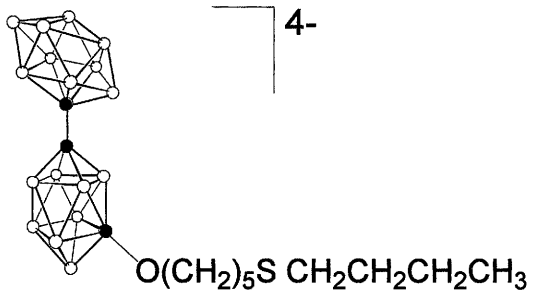


Figure 26: Product of the ring-opening reaction of THP with the *n*-butanethiol anion. ● = B; ○ = BH.

Based on the success obtained with the THP investigation, attempts were made to isolate the THF-coordinated intermediate proposed by Hawthorne.[4] A nucleophile which was sufficiently bulky or sufficiently weak should result in the formation of the THF-coordinated product. Reaction of *t*-butoxide, a sterically demanding nucleophile, and the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion in THF resulted in the formation of an apical-equatorial isomer with a THF substituent that had been ring-opened with *t*-butoxide (Figure 27). Gabel and coworkers reported the unsuccessful ring-opening of a THP-coordinated $[B_{12}H_{11}O(CH_2)_5]^{2-}$ anion with halogens.[26] Therefore, the reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion with tetraethylammonium fluoride and another with tetrabutylammonium bromide, both in THF, was completed. Both reactions were monitored using ^{11}B NMR spectroscopy. No reaction was observed. Clearly, the strength of the nucleophile is critical not only for the formation of the THF-adduct, but also for the ring-opened product. Butylated hydroxy toluene (BHT) is a stabilizer that is added to THF, typically

in the amount of 0.025%. The possibility of isolating a THF-coordinated species by using an increased concentration of the stabilizer in conjunction with a sterically demanding nucleophile was tested. Two reactions were completed using $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] and *t*-butoxide, one reaction containing 1% added BHT and the other containing 5% added BHT. The reactions were monitored using ^{11}B NMR and, upon completion, the products were isolated and characterized. In both cases, the ring-opened product was observed. Ring-opening of the THF molecule occurs at room temperature whereas ring-opening of the THP molecule requires elevated temperatures. The possibility of the ring-opening reaction being thermodynamically controlled was investigated by completing a reaction between the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion and *n*-butoxide in THF at 5 °C. Reaction aliquots were taken and the *n*-butoxide ion was quenched using trifluoroacetic acid. The reaction was monitored for completion using ^{11}B NMR spectroscopy. Once the reaction was complete, the remaining reaction mixture was quenched with trifluoroacetic acid and the product was isolated. Evaluation of the ^{1}H NMR spectrum indicated that the ring-opened product was formed; however, preliminary results also indicate the possible presence of the THF-coordinated product.

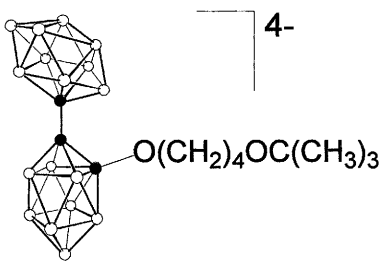


Figure 27: Product of the ring-opening reaction of THP with the *t*-butoxide anion. ● = B; ○ = BH.

The reaction of $(Et_3NH)_2[B_{20}H_{18}]$ and the *n*-butane thiol anion, formed from the deprotonation of *n*-butanethiol using NaH, in THF was completed as a comparison to the results obtained with the THP solvent. The reaction was monitored for completion by observing the disappearance of the peaks characteristic of the polyhedral borane anion starting material. The reaction was complete within 24 hours and the product was isolated. The ^{11}B NMR spectrum is characterized by three sharp peaks in the apical or substituted boron atom region of the spectrum, indicating the formation of an apical-equatorial isomer (Figure 28). The presence of two signals in the region for the intercage connection indicates the possibility that the substituent is located on the equatorial belt adjacent to the terminal apex. The IR spectrum contains a BH absorption at 2430 cm^{-1}. The ^1H NMR spectrum shows sets of peaks at 3.15 ppm, 2.45 ppm, 1.40-1.10 ppm and 0.68 ppm some of the multiples observed overlap each other. The carbon NMR spectrum contains nine distinct peaks. One of the peaks is attributed to a potassium acetate impurity.

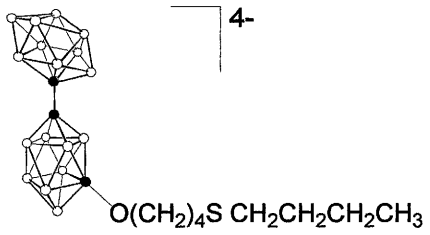


Figure 28: Product of the ring-opening reaction of THF with the *n*-butanethiol anion. ● = B; ○ = BH.

4.3 Coordination of Other Solvent Molecules

Preliminary investigations were completed using solvent molecules which contained nucleophilic heteroatoms in an effort to evaluate the potential of alternative five and six-membered rings to coordinate to the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion. The solvent molecules selected for investigation contain either sulfur or nitrogen in the ring system (Figure 29).

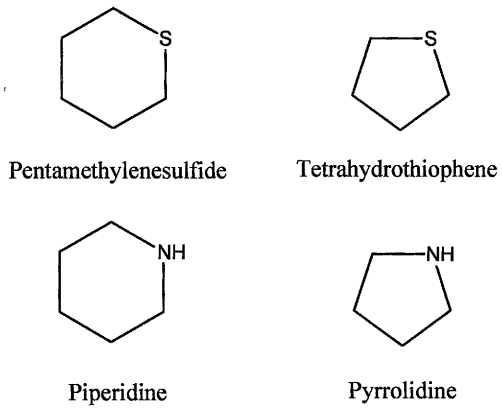


Figure 29: Solvents selected for investigation.

Pentamethylenesulfide and $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] were mixed and an aliquot of the reaction was monitored for a period of one week using ^{11}B NMR spectroscopy. No change was observed in the ^{11}B NMR spectrum of the product when compared to that of the polyhedral borane anion starting material. A solution containing 4.5 mole equivalents of *n*-butoxide was added to the reaction mixture and allowed to react at room temperature overnight. The ^{11}B NMR spectrum of the reaction mixture containing the nucleophile exhibited significant changes from the ^{11}B NMR spectrum of the polyhedral borane anion starting material.

Tetrahydrothiophene and $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] was placed in a reaction vessel and an aliquot of the reaction mixture was removed and monitored using ^{11}B NMR spectroscopy. After 24 hours, no change was observed in the spectrum as compared to the spectrum of the polyhedral borane starting material. A solution containing 4.5 mole equivalents of *n*-butoxide was added to the original reaction mixture and another aliquot was taken for NMR analysis after 24 hours at room temperature. The ^{11}B NMR spectrum of the reaction mixture containing the nucleophile exhibited significant changes from the ^{11}B NMR spectrum of the polyhedral borane anion starting material. The original aliquot, which did not contain the nucleophile, was retained and monitored for reaction over the course of two months. No reaction was observed in the absence of nucleophile.

Pyrrolidine and $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] were combined and an aliquot was removed for ^{11}B NMR analysis after 24 hours at room temperature. No reaction was observed in the ^{11}B NMR spectrum. A solution containing 4.5 equivalents of *n*-butoxide was added to the original reaction mixture and allowed to react overnight. The ^{11}B NMR spectrum of the reaction mixture exhibited complete reaction by the absence of the peaks characteristic of the polyhedral borane anion starting material. The NMR tube of the original reaction mixture was retained and monitored over a period of two months. After 72 hours, the sample exhibited appreciable reaction and by the end of the two month period, no starting material was observed in the ^{11}B NMR spectrum.

Piperidine and $(Et_3NH)_2$[*trans*-$B_{20}H_{18}$] were placed in a reaction vessel and the reaction progress monitored. An aliquot of the reaction mixture was taken after 24 hours and evaluated using ^{11}B NMR spectroscopy. No reaction was observed. A solution of *n*-butoxide was added to the original reaction mixture and the ^{11}B NMR spectrum was

obtained. In the presence of the nucleophile, complete reaction was observed within 24 hours. The aliquot of the original reaction mixture was retained and the reaction monitored for a period of two months. After 72 hours, substantial reaction was evident; after two months, no starting material was observed in the reaction mixture.

No products were isolated in the solvent reactions; however, preliminary reaction results that the nucleophile is either required, in the case of the sulfur rings, or the presence of the nucleophile enhances the rate of reaction, in the case of the nitrogen nucleophiles. Further investigation is recommended.

5.0 CONCLUSIONS

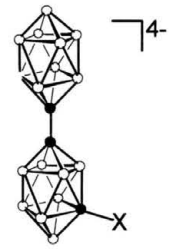
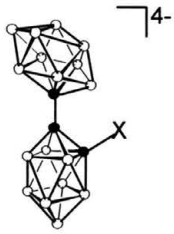
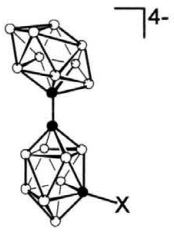
5.1 Reactions with Nucleophiles

The reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion and each of the six different nucleophiles was completed and the products isolated and characterized. Particular emphasis was placed on the identification of the isomeric assignment of the reaction product (*ae* or a^2) and the characteristics of the boron-boron signal associated with the intercage linkage in the ^{11}B NMR spectrum of the products. Comparisons were made based on the identity of the nucleophilic atom as well as the steric demands of the substituent group.

The formation of the apical-apical isomer of [$B_{20}H_{17}SC(O)OC(CH_3)_3$]$^{4-}$ directly from the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion and the location of the substituent on the equatorial belt adjacent to the terminal boron apex was initially attributed to the steric demands of the nucleophile, [$SC(O)OC(CH_3)_3$]$^-$. The results of the current investigation do not support the original hypotheses (Table 1). Both *n*-butoxide and the sterically hindered *t*-butoxide nucleophiles formed the apical-equatorial isomer of the product directly with the substitution predicted to be on the equatorial belt adjacent to the intercage linkage. The formation of the apical-equatorial isomer is also observed when the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion is allowed to react with both of the carbamate derivatives. The substitution of both the *n*-butylcarbamate and the *t*-butylcarbamate derivatives appear to be located on the equatorial belt adjacent to the terminal boron apex. Confirmation could be completed

using two-dimensional ^{11}B NMR spectroscopy, not currently available within the department. Substitution on the equatorial belt adjacent to the terminal boron apex appears to require either the ester moiety present in the Bender's salts and the carbamate derivatives or a sulfur nucleophile.

Table 1: Summary of the products formed from the reaction of the nucleophiles with the [*trans*-$B_{20}H_{18}]^{2-}$ anion. X represents the nucleophile investigated. ● = B; ○ = BH.

 $[a^2\text{-}B_{20}H_{17}X]^{4-}$	 $[ae\text{-}B_{20}H_{17}X]^{4-}$	 $[ae\text{-}B_{20}H_{17}X]^{4-}$
X	X	X
$-SCOO(CH_2)_3CH_3$	$-O(CH_2)_3CH_3$	$\overset{-}{N}HCOO(CH_2)_3CH_3$
$-S(CH_2)_3CH_3$	$-OC(CH)_3$	$\overset{-}{N}HCOOC(CH)_3$

Direct formation of the apical-apical isomer appears to be the result of the electronic characteristics of the sulfur-containing nucleophiles, regardless of the steric demands of the alkyl group. Both of the Bender's salts, $[SC(O)OC(CH_3)_3]^-$ and $[SC(O)O(CH_2)_3CH_3]^-$, clearly produce the apical-apical isomer of the product. The product of the reaction of [*trans*-$B_{20}H_{18}]^{2-}$ ion and the *n*-butanethiol anion appears to be an apical-apical isomer; however, the result can not yet be confirmed since the reaction must be heated to reflux to form the product. Refluxing temperatures may lead to the

thermodynamic conversion of the kinetic apical-equatorial isomer to the more thermodynamically stable apical-apical isomer.

5.2 Coordination of THF and THP Molecules

The solvent-coordinated THP species, $[B_{20}H_{17}O(CH_2)_5]^{3-}$, has been isolated and the reactions forming the anion, as well as the reactivity of the anion, have been investigated. Coordination of the THP to the polyhedral borane anion does not occur in the absence of the nucleophile. The coordination reaction does not occur in the presence of NaH nor *n*-butyllithium and is therefore, not base-mediated. The reaction is incomplete when a catalytic amount, 0.5% or 5%, of the nucleophile is added. The coordination reaction only occurs if THP is used as a solvent. Therefore, the reaction is believed to be a result of mass action.

The product of the nucleophile-induced ring opening of THP was isolated and characterized. Both ethoxide and the anion of *n*-butanethiol lead to the ring-opened product of THP. Likewise, the anion of *n*-butanethiol was able to ring-open THF in similar reaction conditions. Based on the reaction results, the THP-coordinated species exhibits a greater stability that the THF-coordinated species. Despite several efforts, the THF-coordinated species could not be isolated.

5.3 Coordination of Other Solvent Molecules

Preliminary investigations involving the sulfur and nitrogen analogues of THP and THF were completed. Analogous to the THP reactions, both sulfur analogues, tetrahydrothiophene and pentamethylenesulfide, require the presence of a nucleophile for

the reaction to occur. Absence of the nucleophile results in no reaction. In contrast, the nitrogen analogues, piperidine and pyrrolidine, did react with the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion in the absence of the nucleophile; however, complete reaction occurred much more quickly in the presence of the nucleophile. Additional reactions and complete characterization of the product are necessary for complete analysis of the results.

6.0 SUGGESTIONS FOR FUTURE RESEARCH

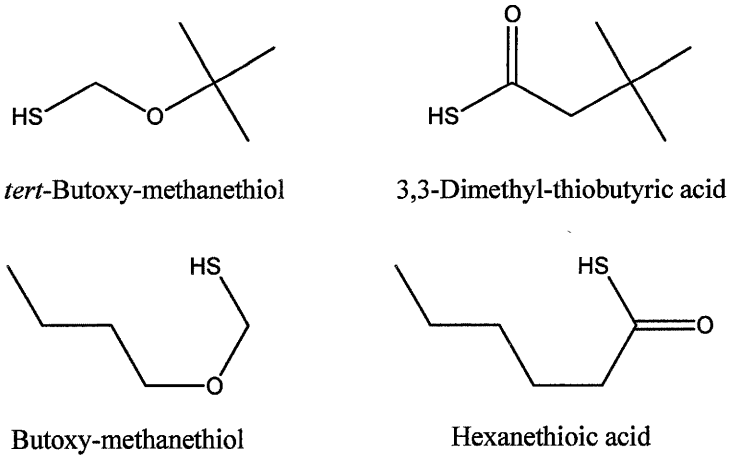
The chemistry of the $[B_{20}H_{18}]^{2-}$ isomers remains relatively unexplored. Results of the current project serve as the basis for additional research which would enhance the understanding of the mechanism of nucleophilic attack and lead to the development of novel target materials. A series of reactions has also been proposed which would investigate the range of reactivity of the $[B_{20}H_{18}]^{2-}$ isomers with a variety of nucleophiles and provide additional compounds available for investigation by chemists specializing in the area of boron chemistry.

6.1 Extension of the Current Project

Reaction of the [*trans*-$B_{20}H_{18}]^{2-}$ anion and *n*-butanethiol yielded ambiguous results since a clear isomeric assignment, a^2 or *ae*, could not be made from the ^{11}B NMR spectrum. The low solubility of the sodium salt of *n*-butanethiol in diethyl ether necessitated heating of the reaction mixture. Therefore, what appears to be a prevalence of the a^2 isomer may be a result of either the electronic characteristics of the sulfur-containing nucleophile or thermodynamic conversion of the *ae* isomer to the a^2 isomer. A reaction performed at ambient temperature would confirm one of these possibilities. In order to complete the reaction at ambient temperature, a change of solvent, and potentially the use of the sodium salt of the [*trans*-$B_{20}H_{18}]^{2-}$ anion, may be required. Suggested dry solvents include: acetone, acetonitrile, and *n*-butanethiol.

If the reaction of the sodium salt of *n*-butanethiol and the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion under ambient conditions produces the a^2 isomer, the formation of the a^2 isomer is likely to be the result of the electronics associated with the sulfur-containing nucleophile. In contrast, if the reaction yields the *ae*-isomer, the formation of the a^2-isomer may be due to either steric effects or be a consequence of the electron- withdrawing groups present in the Bender's salts, $KSC(O)O(CH_2)_3CH_3$ and $KSC(O)OC(CH_3)_3$.

Reaction of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion with a series of thiol-containing compounds (Figure 30) would investigate the effect of a sulfur nucleophile in conjunction with varying steric and electronic characteristics. The nucleophiles of interest are not commercially available; however, analogs similar to the two carbonyl derivatives have been synthesized using methods developed by Sunner and Nilsson.[27] Additionally, the butoxy-methane thiol compounds could, potentially, be formed by the reduction of the appropriate precursors which contain a disulfide bond and which are commercially available. Reduction could be accomplished using either β-mercaptoethanol or sodium sulfite.[28]



tert-Butoxy-methanethiol

3,3-Dimethyl-thiobutyric acid

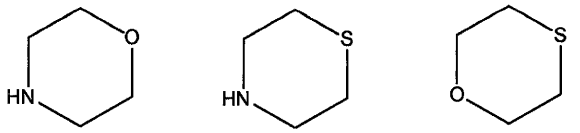
Butoxy-methanethiol

Hexanethioic acid

Figure 30: Compounds proposed for future investigation.

Preliminary reactions between solvents capable of coordination and the [*trans*-$B_{20}H_{18}]^{2-}$ anion were completed using tetrahydrothiophene, pentamethylensulfide, piperidine and pyrolidine (Figure 29). Replacement of the triethylammoniom cation by the sodium cation should enhance the solubility of the [*trans*-$B_{20}H_{18}]^{2-}$ anion in the desired solvents. Additionally, the experiments should be refined to improve the isolation techniques. The ability of the product of a solvent coordination reaction to undergo a nucleophile-induced ring-opening reaction should be investigated in order to provide comparison between the coordination chemistry of five-membered rings compared to that of six-membered rings.

The relative nucleophilicity of the heteroatoms when reacted through solvent coordination to the [*trans*-$B_{20}H_{18}]^{2-}$ ion could be evaluated by investigating the reaction of a solvent species containing two different heteroatoms (Figure 31). The identification of the heteroatom bound to the polyhedral borane anion would require a careful examination of the chemical shifts in the ^{1}H, ^{13}C, and ^{11}B NMR spectra. If the reaction is not selective and both heteroatoms bind, the results could be extraordinarily complicated.



Morpholine Thiomorpholine 1,4-Thioxane

Figure 31: Proposed compounds for competitive reactions

The investigations completed in the thesis research as well as the proposed reactions have been based on the chemistry of the [*trans*-$B_{20}H_{18}]^{2-}$ anion. All of the

reactions could be repeated using both the [*cis*-$B_{20}H_{18}]^{2-}$ isomer and the [*iso*-$B_{20}H_{18}]^{2-}$ isomer. Both the [*cis*-$B_{20}H_{18}]^{2-}$ and the [*iso*-$B_{20}H_{18}]^{2-}$ isomers are characterized by the presence of the three-center two-electron bonding region which is susceptible to nucleophilic attack. The isomers have similar reactivity characteristics to the [*trans*-$B_{20}H_{18}]^{2-}$ anion, but yield different isomeric arrangements in the products. The synthesis of both isomers has been reported in the literature and the [*iso*-$B_{20}H_{18}]^{2-}$ ion has been made in our laboratory.[13,14] A reinvestigation of the nucleophiles with the two different isomers can lead to a better understanding of the relationship between the [*trans*-$B_{20}H_{18}]^{2-}$, [*cis*-$B_{20}H_{18}]^{2-}$and [*iso*-$B_{20}H_{18}]^{2-}$ isomers.

6.2 Potential New Projects

During the course of the base-mediated investigations, the formation of what may be the product formed by the reaction of the [*trans*-$B_{20}H_{18}]^{2-}$ anion and a carbon nucleophile was observed. Reaction of the [*trans*-$B_{20}H_{18}]^{2-}$ ion and *n*-butylithium in THP lead to the formation of a substituted apical-equatorial derivative based on the ^{11}B NMR spectrum. The ^{1}H spectrum for this compound yields a singlet, consistent with the formation of the [*ae*-$B_{20}H_{17}C(CH_3)_3]^{4-}$ anion, possibly the result of methyl shift causing a carbanion rearrangement yielding a tertiary alkyl substituent.[25] The reaction should be repeated and the product completely characterized. The ^{13}C NMR spectrum as well as a NMR DEPT experiment should be performed to confirm the identity of the product. No reports of reaction of [*trans*-$B_{20}H_{18}]^{2-}$ with a carbon nucleophile have been found in the literature. A series of carbon-containing nucleophiles could be investigated, including acetylide and cyanide.

The cyano derivative, $[B_{20}H_{17}CN]^{4-}$, is of great interest to chemists who develop boron-containing compounds for application in boron neutron capture therapy (BNCT). Conversion of the cyano group to an acid or amide group should be possible by reaction with triethyloxonium tetrafluoroborate, followed by either treatment with acid or base.[29-31] Coupling of the acid derivative, in particular, to biologically active molecules should be possible through standard coupling techniques. The preparation of the desired compound has been limited by the lack of suitable solvents for the reaction. Both KCN and NaCN have limited solubility in organic solvents. They are freely soluble in water; however, the resulting solutions are basic and the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion will react with the hydroxide present in solution. Both KCN and NaCN are reasonably soluble in alcohols. The tetramethylammonium salt of $[CN]^-$ anion could potentially be precipitated from a solution of Me_4NBr and methanol and subsequently isolated. The tetramethylammonium salt should have an increased solubility in non-aqueous polar solvents as compared to the sodium or potassium salts. Dry acetonitrile or dry acetone may serve as solvents for the reaction of $[trans\text{-}B_{20}H_{18}]^{2-}$ and the tetramethylammonium salt of the cyanide ion.

Hawthorne and coworkers reported the production of bridged anion, designated $[\mu\text{-}B_{20}H_{16}X]^-$ where the bridging species, X, is an oxygen atom or an amidium moiety, in 1996 and 1998, respectively.[32,32] The oxygen-bridged species was obtained by heating a solution of $[B_{20}H_{17}OH]^{2-}$ in a solution of 1 N HCl, followed by deprotonation in strongly basic solutions. The amidium-bridged species was obtained by oxidation of the $[B_{20}H_{17}NH_3]^{3-}$ anion with an organic oxidant, such as benzoquinone, in acetonitrile.[33] The bridged compounds can only be formed if the substituted starting material exhibits

substitution on the equatorial boron atom adjacent to the intercage linkage. Reports of compounds using a single sulfur or nitrogen as the bridging group in the $[\mu\text{-}B_{20}H_{16}X]^-$ ion have not been found in the literature.

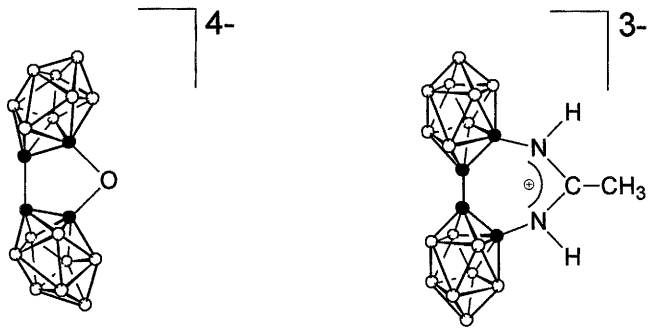


Figure 32: Structure of bridged species reported by Hawthorne. ● = B; ○ = BH.

The $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion can also undergo bis-substitution reactions. Accounts of a bis-substituted carbonyl product as well as a bis-substituted isocyanate product were reported in the literature by Hawthorne and coworkers.[34] New derivatives of the bis-substituted $[a^2\text{-}B_{20}H_{18}]^{4-}$ anion may provide new starting compounds suitable for polymerization reactions. Polymerized chains of the $[B_{20}H_{18}]^{2-}$ anion have not been reported in the literature.

Both phosphorus and arsenic have electronic structures similar to that of nitrogen. As a result, phosphide and arsinide compounds should react in a similar manner with the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion. No literature reports of a reaction between either a phosphorus nucleophile or an arsenic nucleophile and the $[B_{20}H_{18}]^{2-}$ anion have been found. Reactions with the phosphorus and arsenic nucleophiles would provide a basis for comparison of the possible differences observed with nitrogen nucleophiles.

The proposed reactions provide an essential foundation for the thorough investigation of the complex nature and unusual chemistry of the three-center, two-electron bond in the isomers of the $[B_{20}H_{18}]^{2-}$ anion and provide a prelude for the vast array of reactions which can be developed with the $[B_{20}H_{18}]^{2-}$ anion. Investigations of this nature will allow for better description of the potential reactivity of the $[B_{20}H_{18}]^{2-}$ anion.

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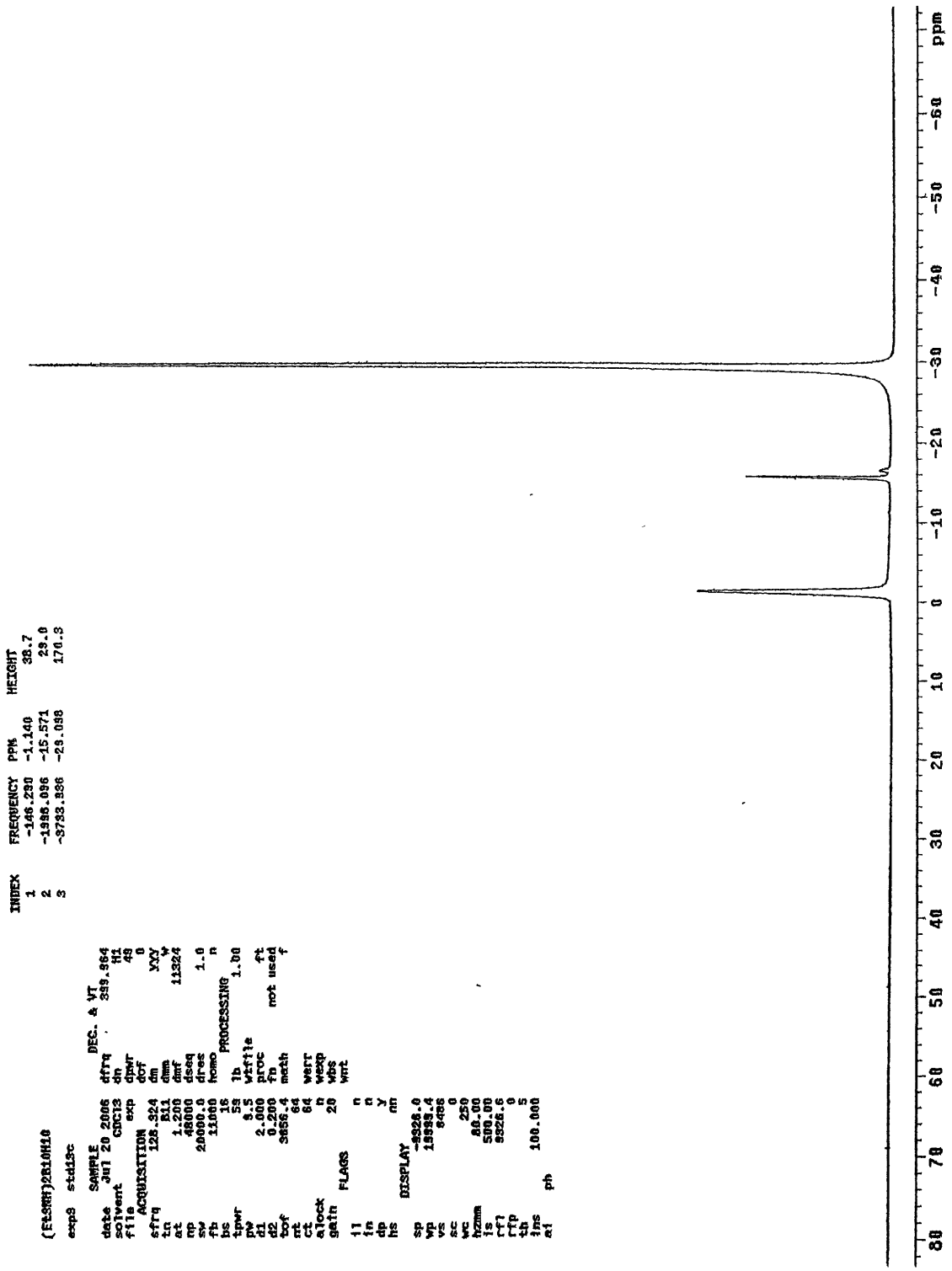
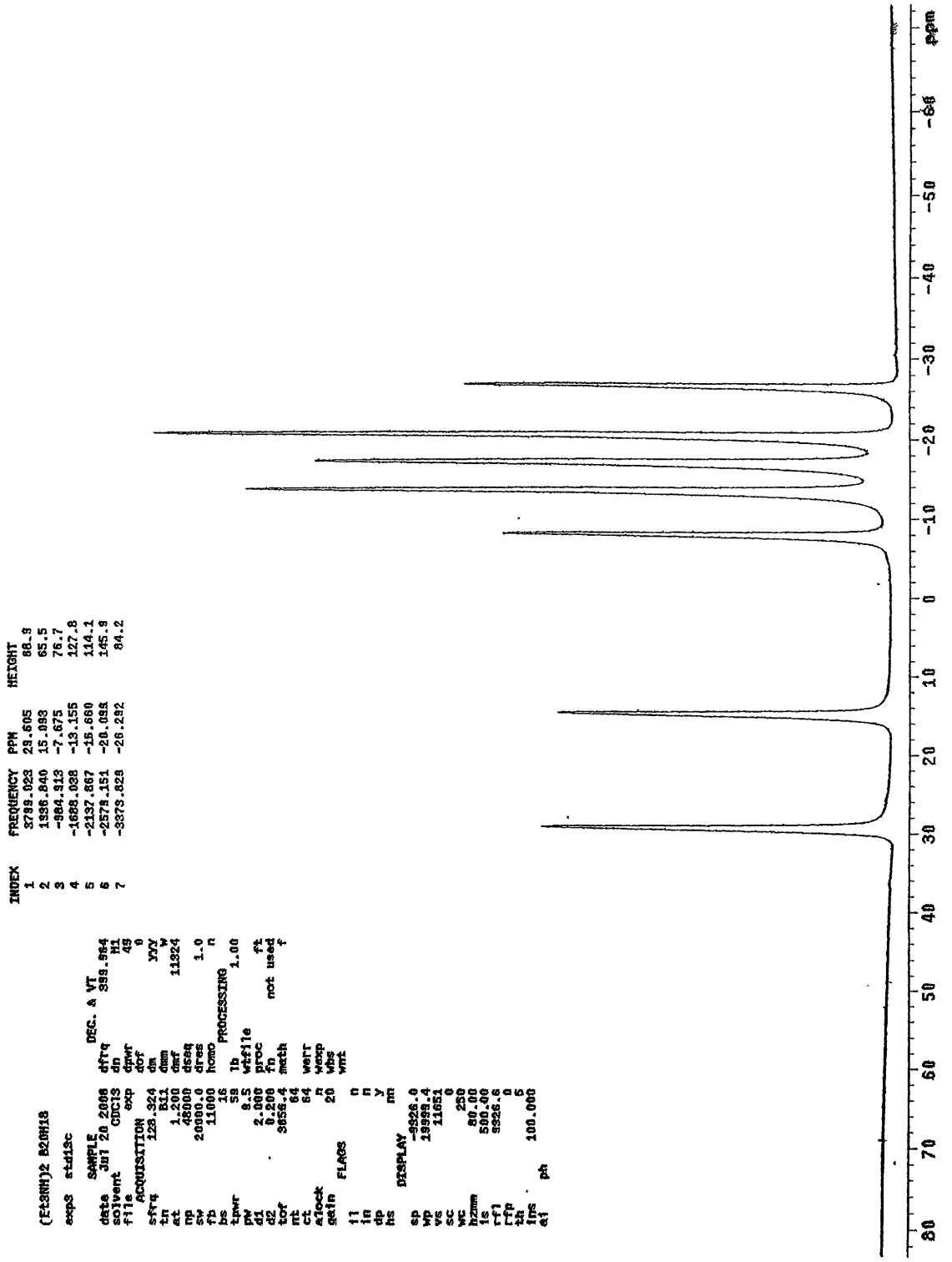
APPENDIX: SPECTRA

^{11}B NMR of $(Et_3NH)_2[B_{10}H_{10}]$



^{11}B NMR of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$



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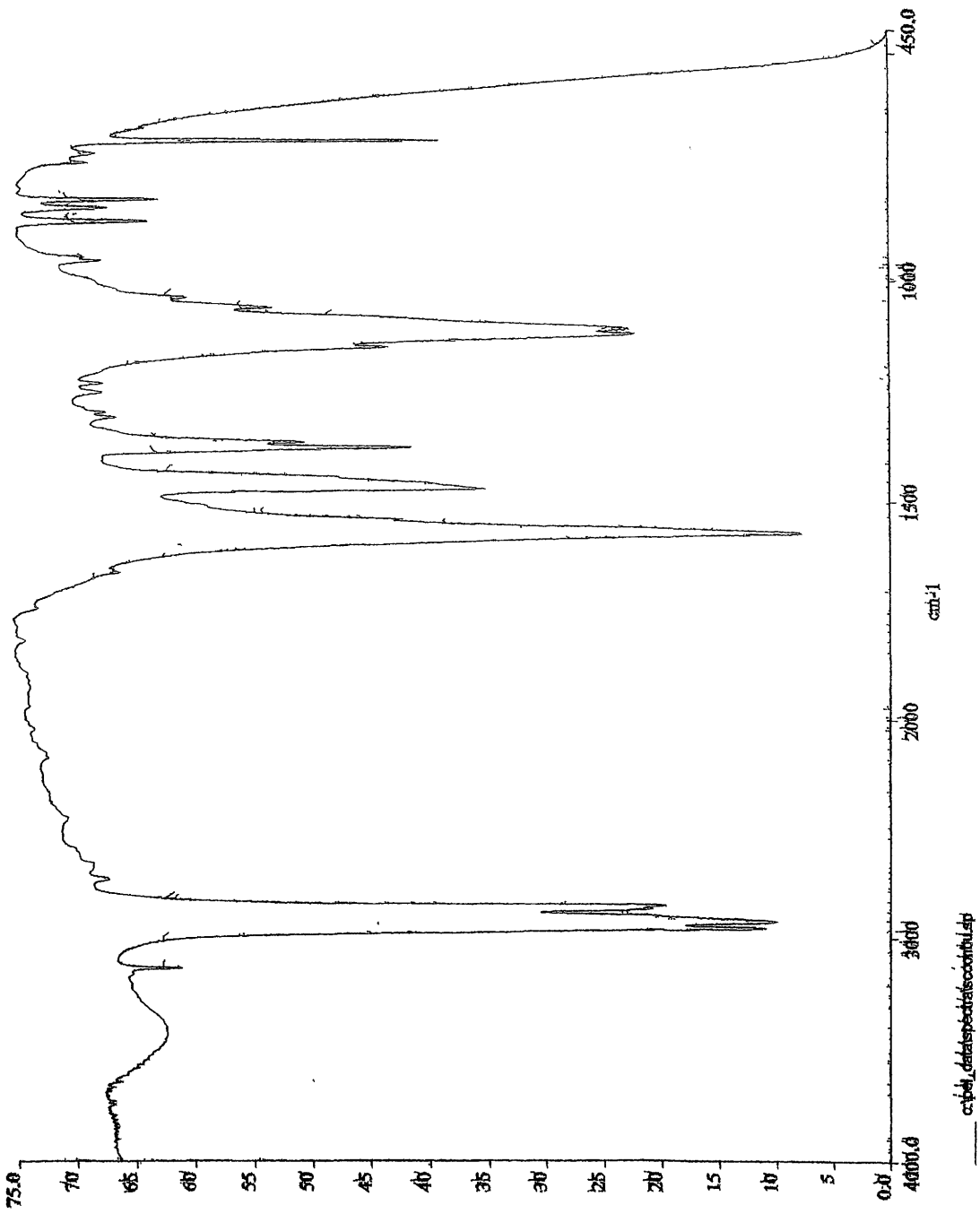

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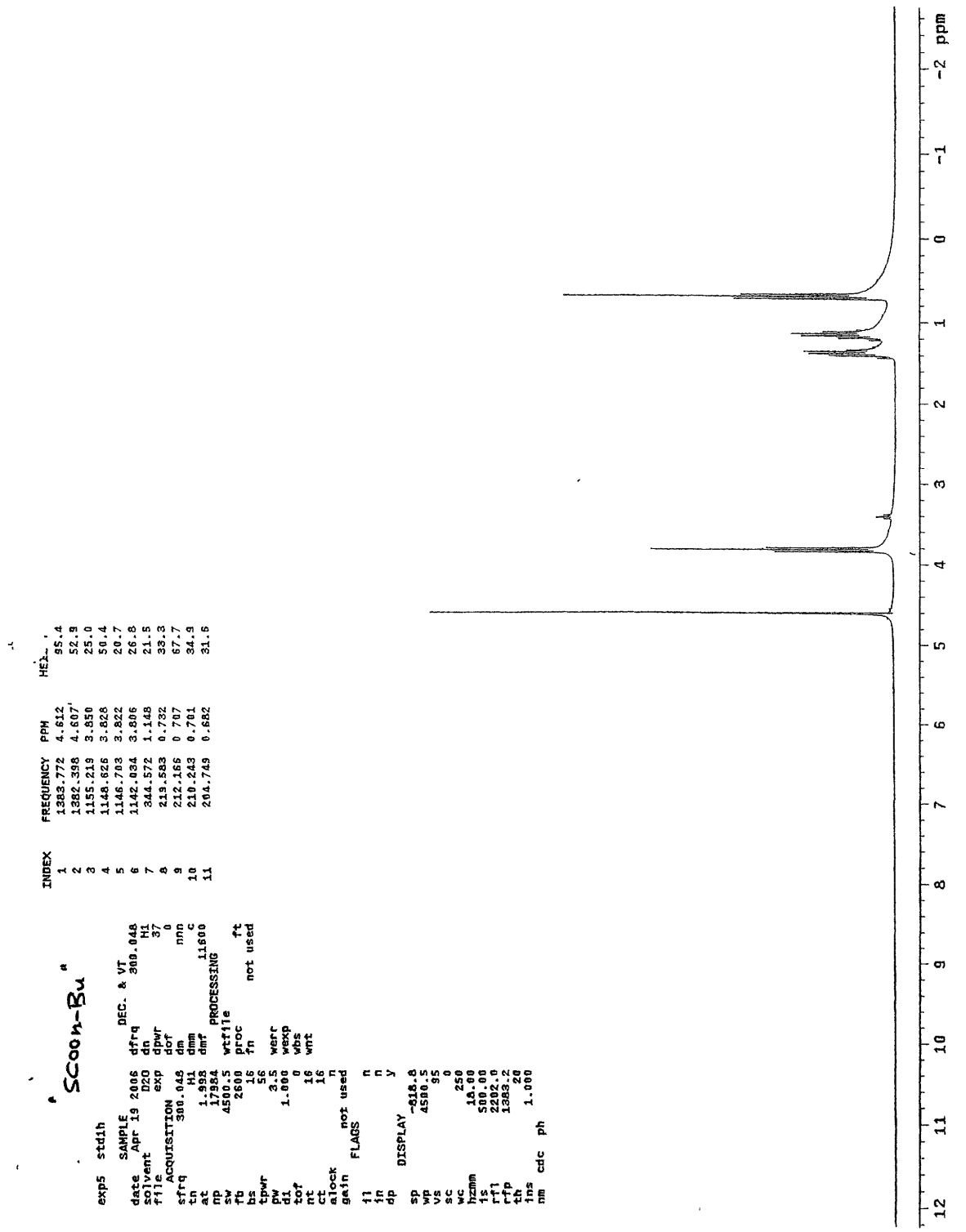

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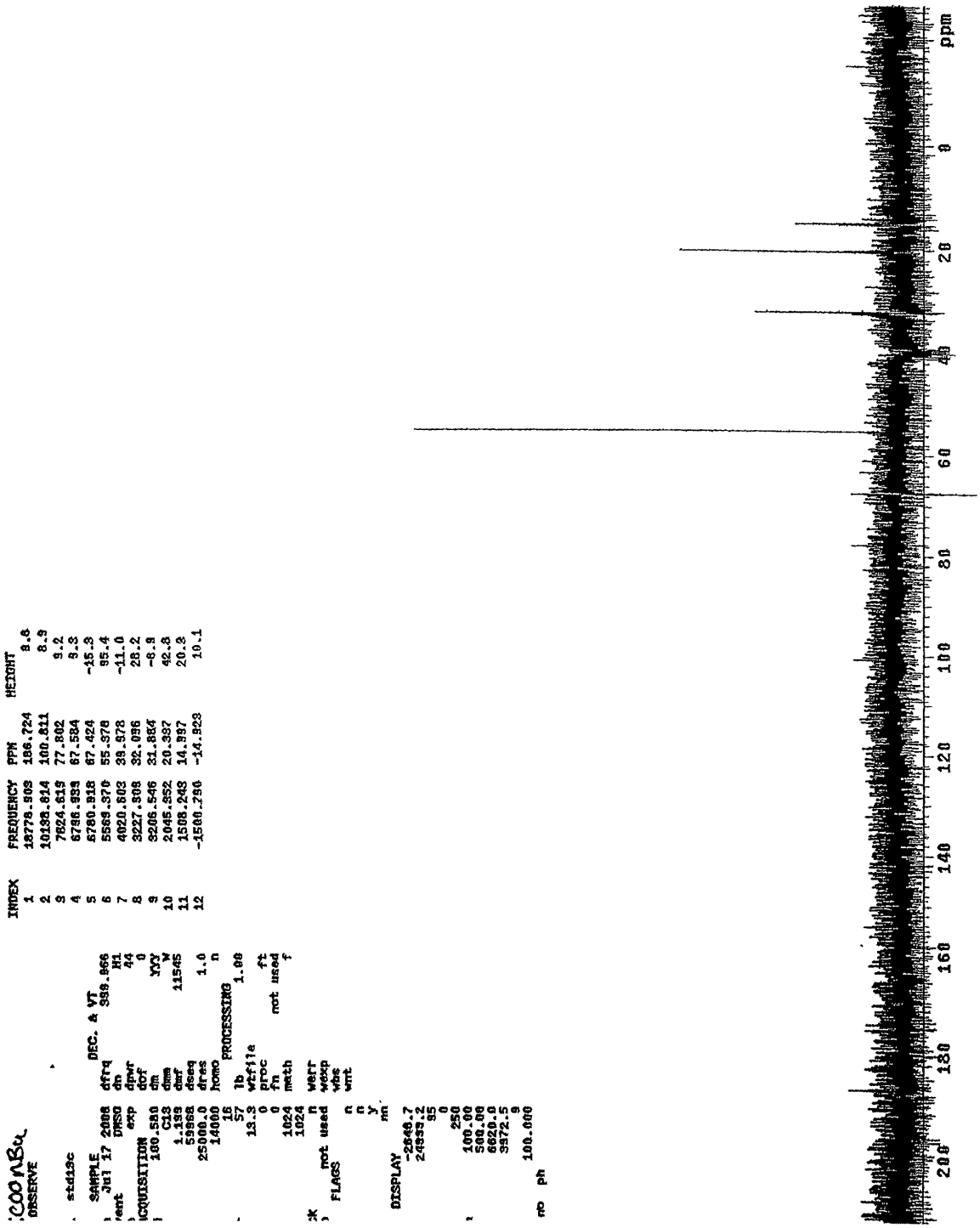

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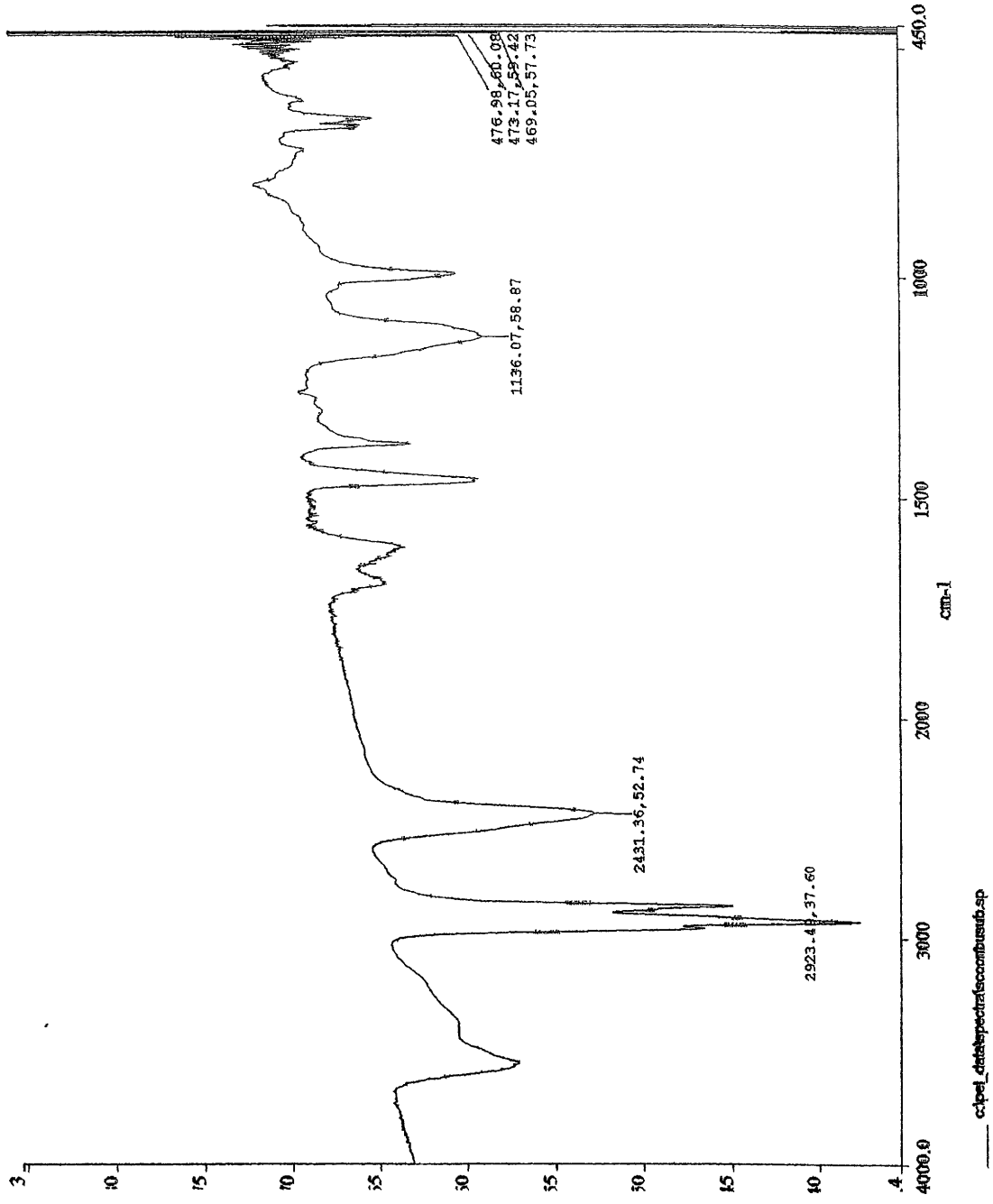

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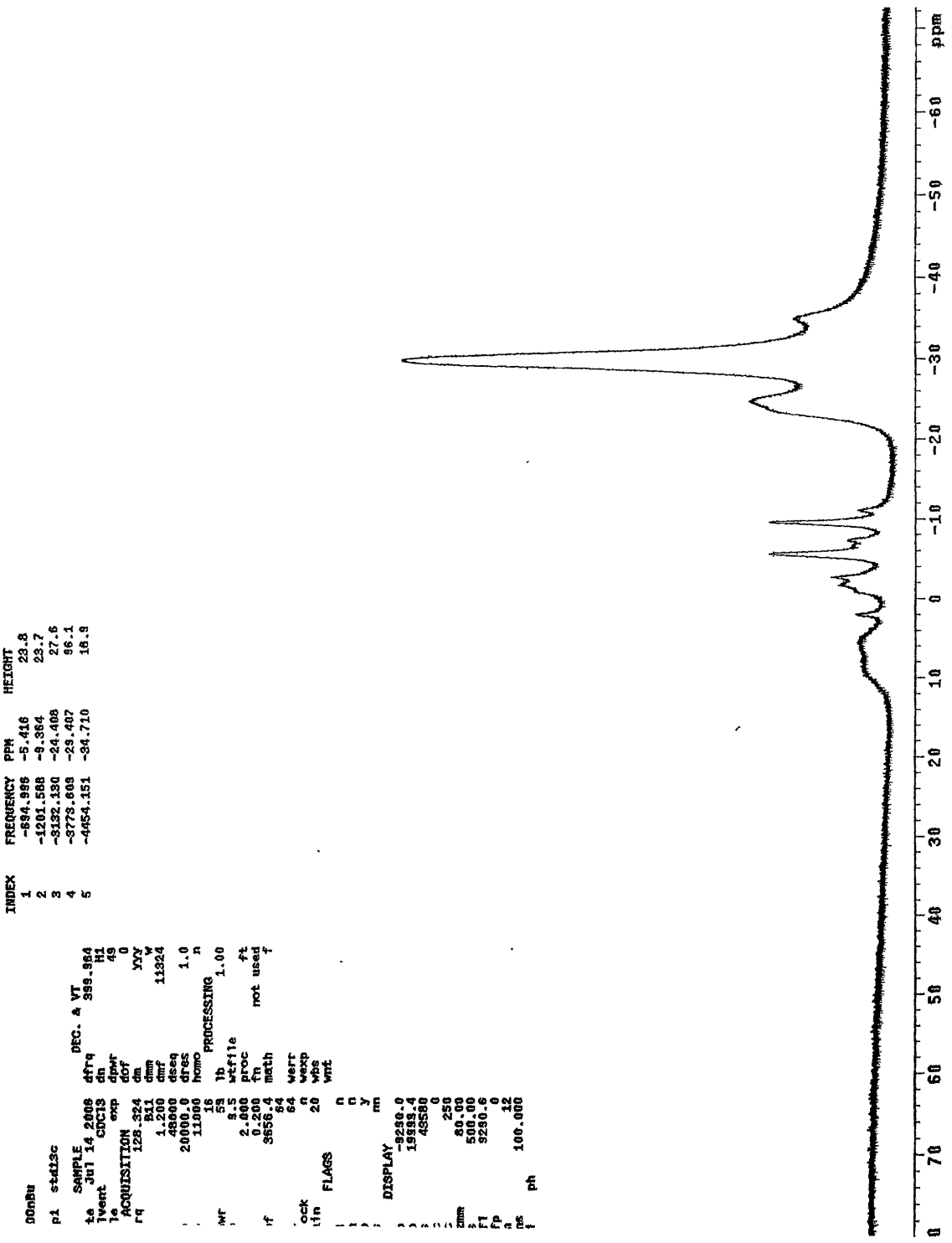

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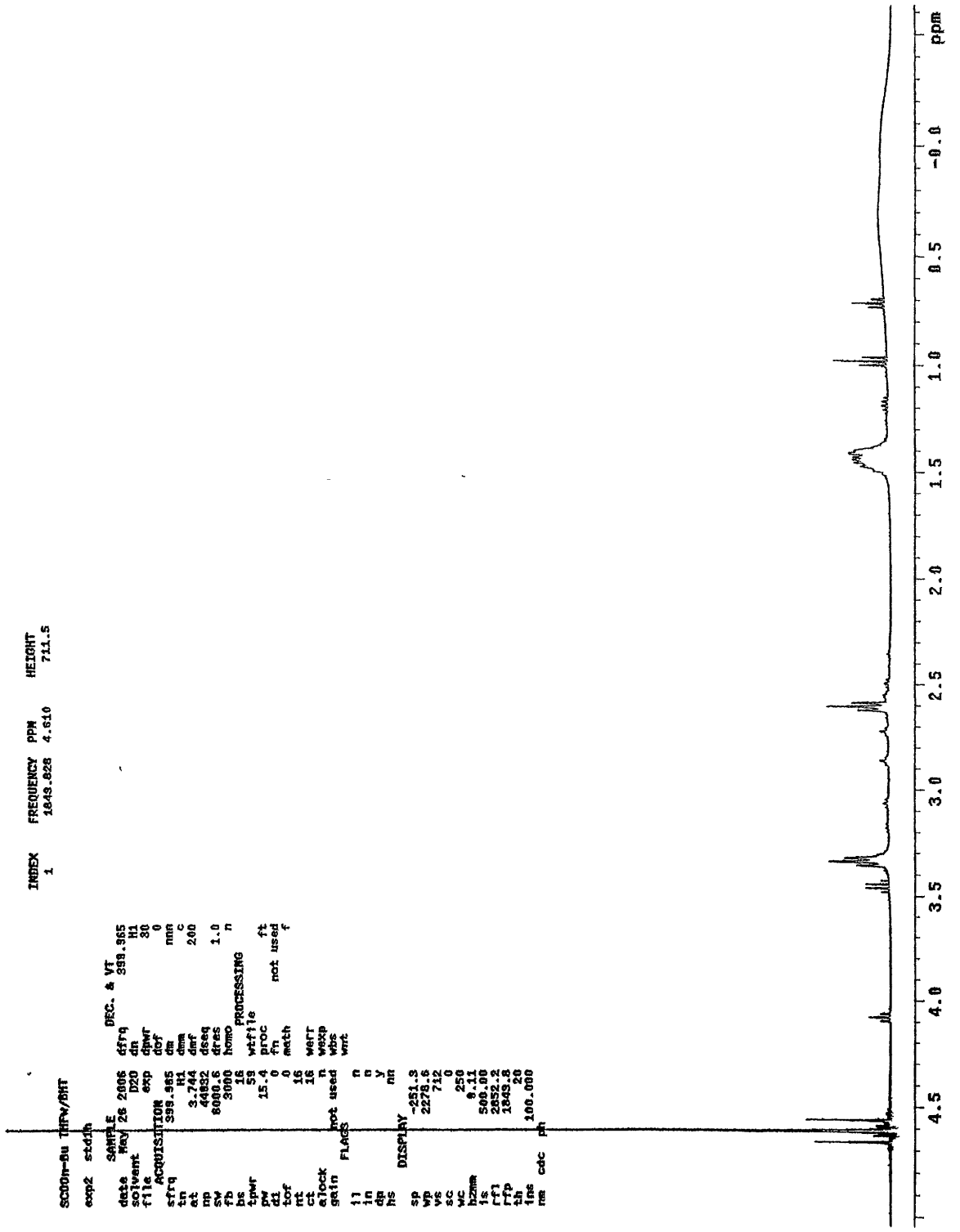

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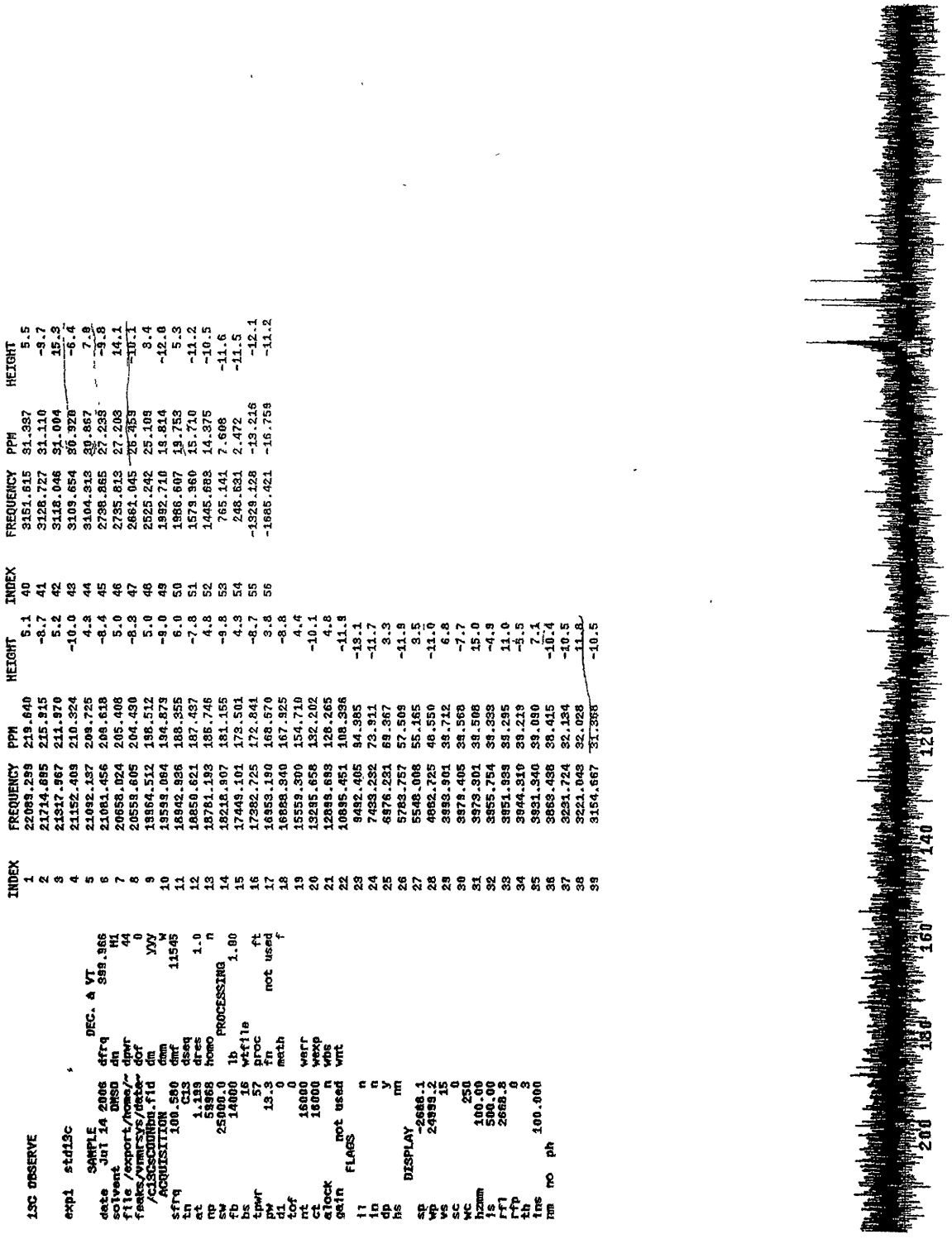

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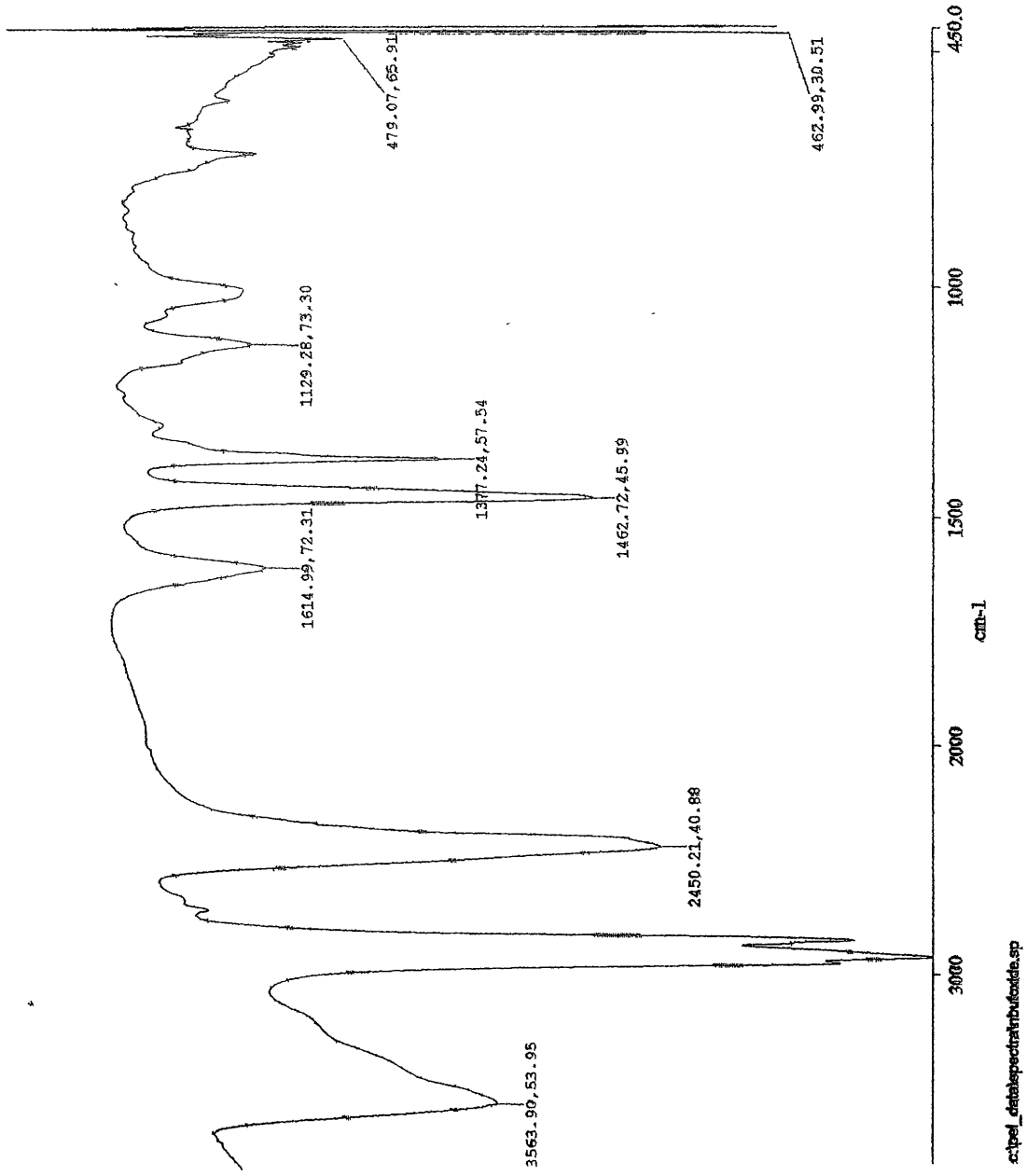

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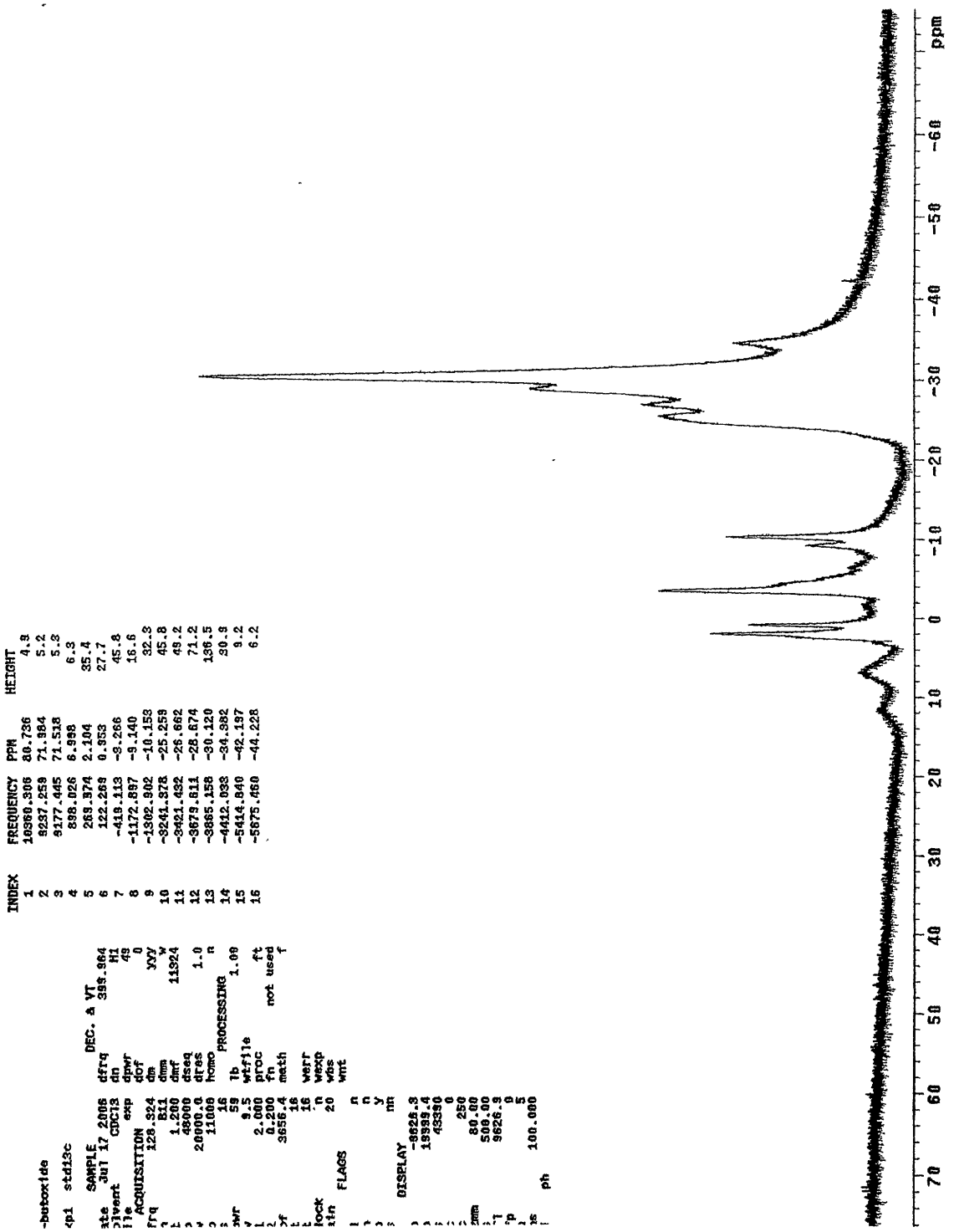

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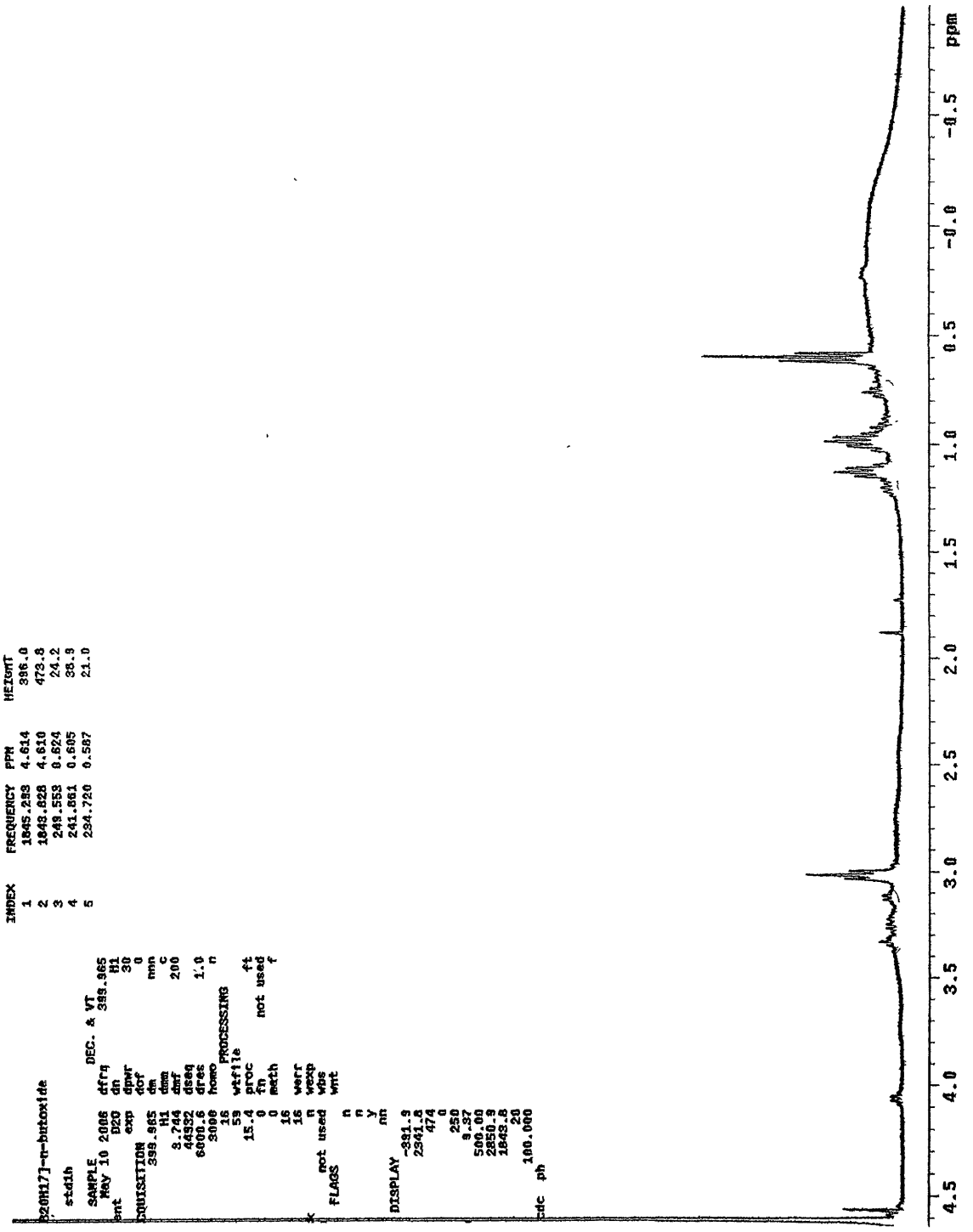

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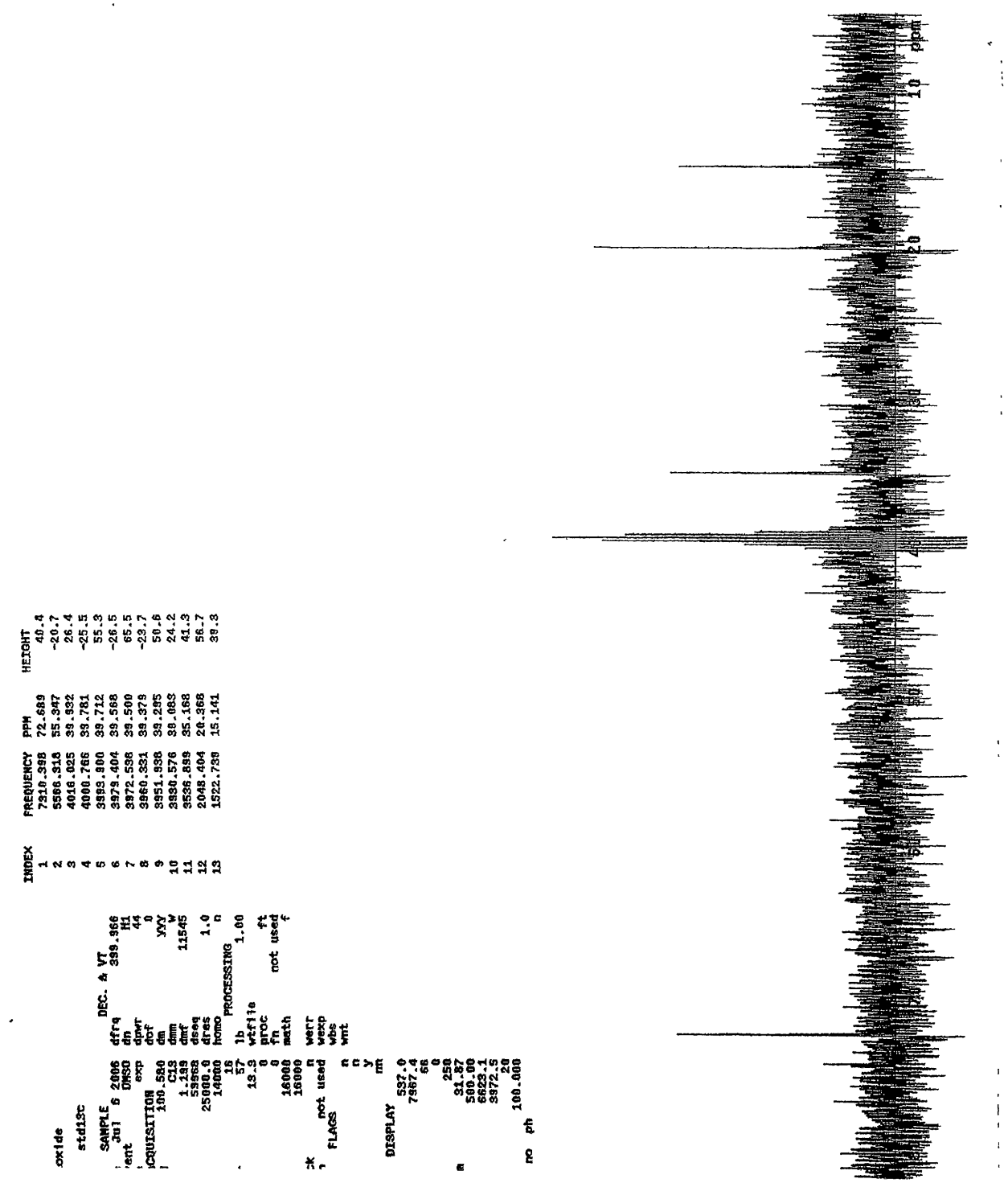

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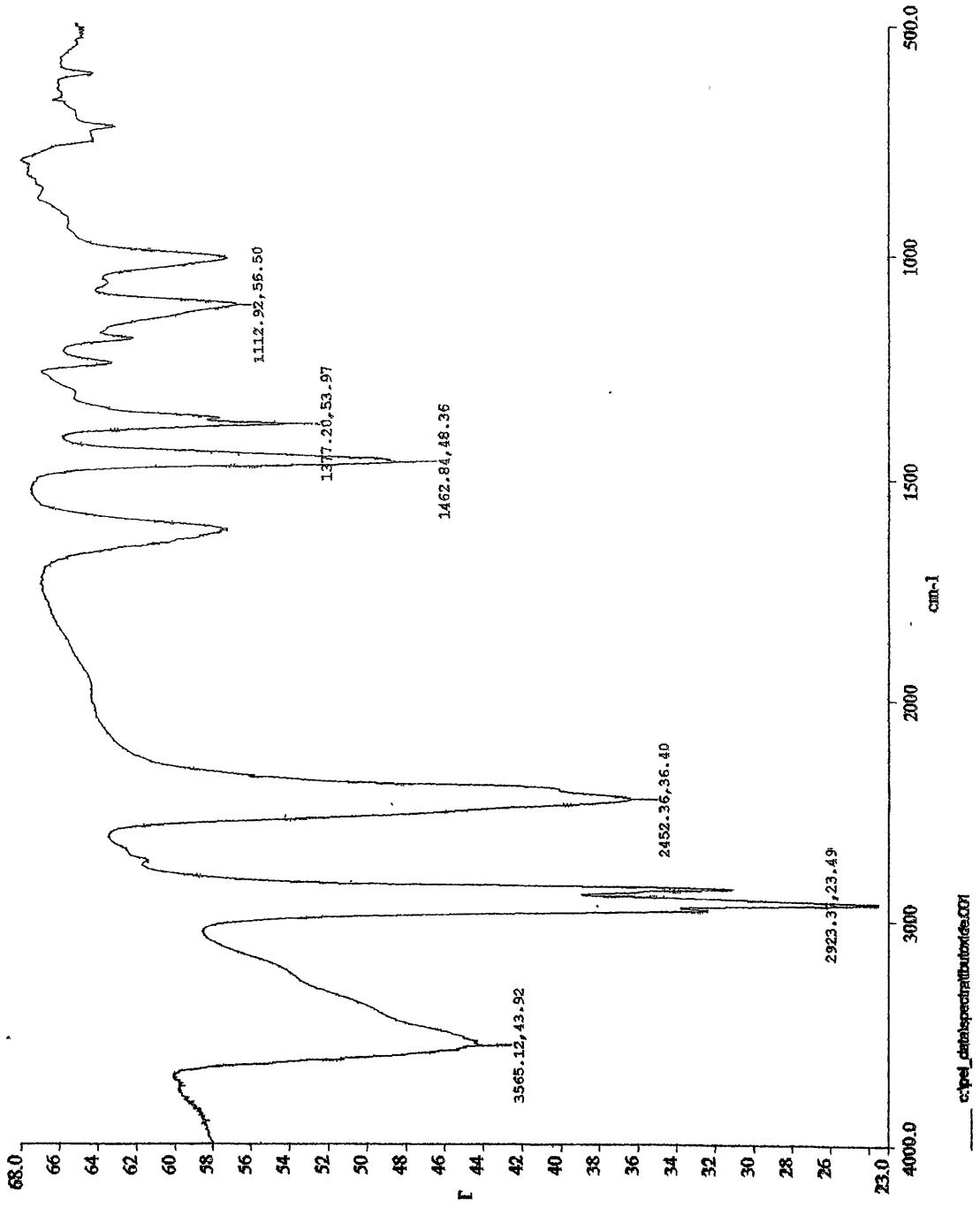

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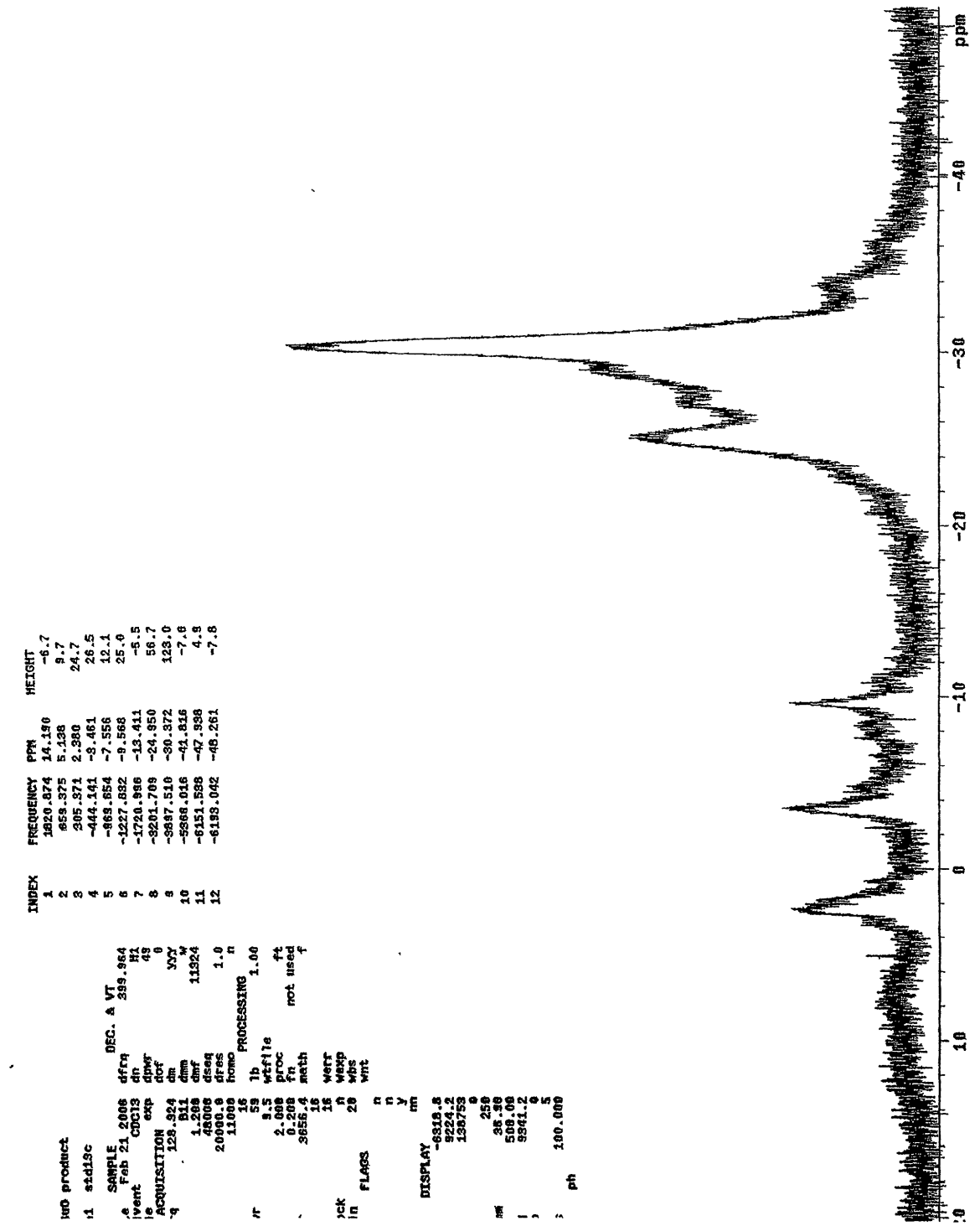

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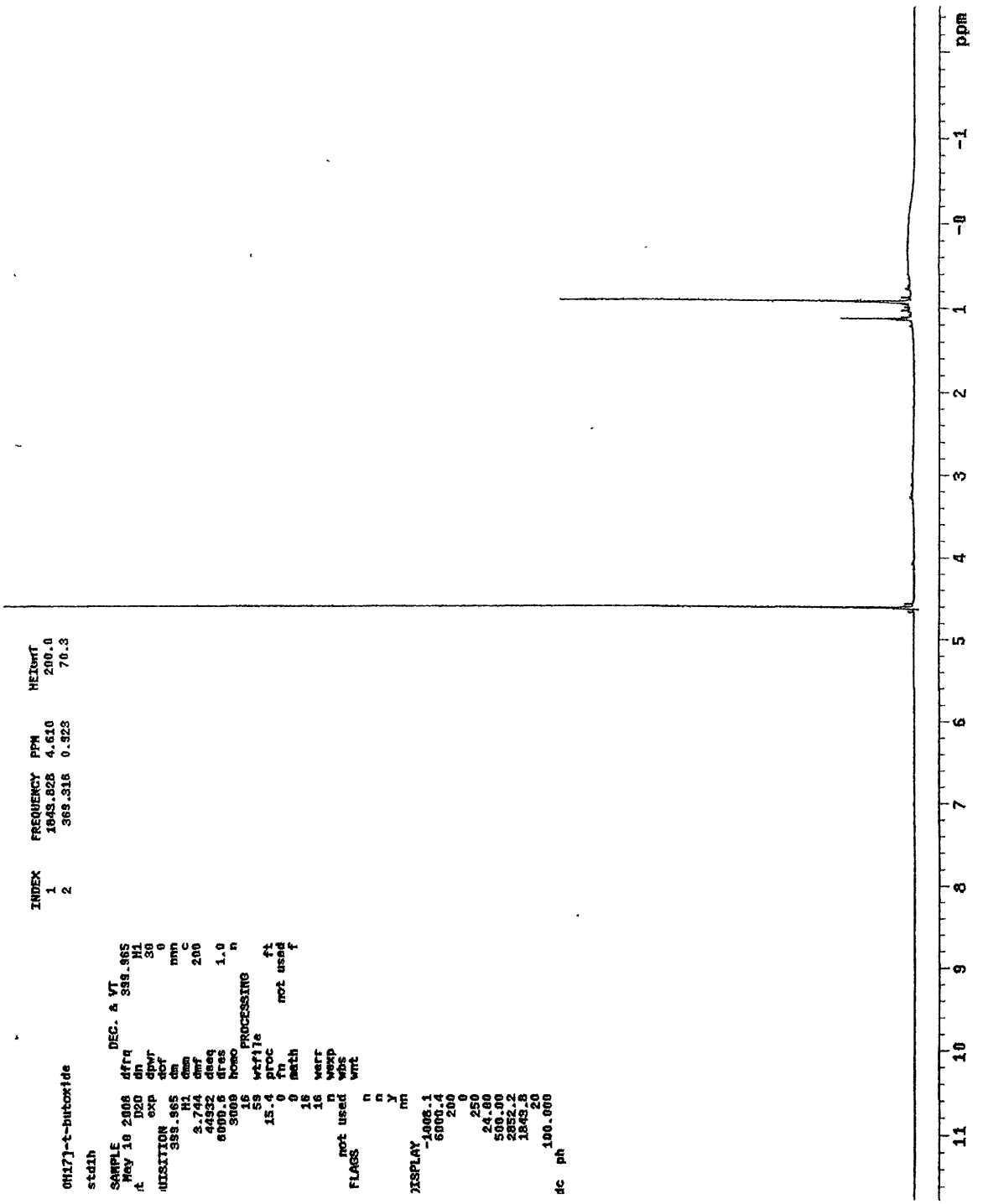

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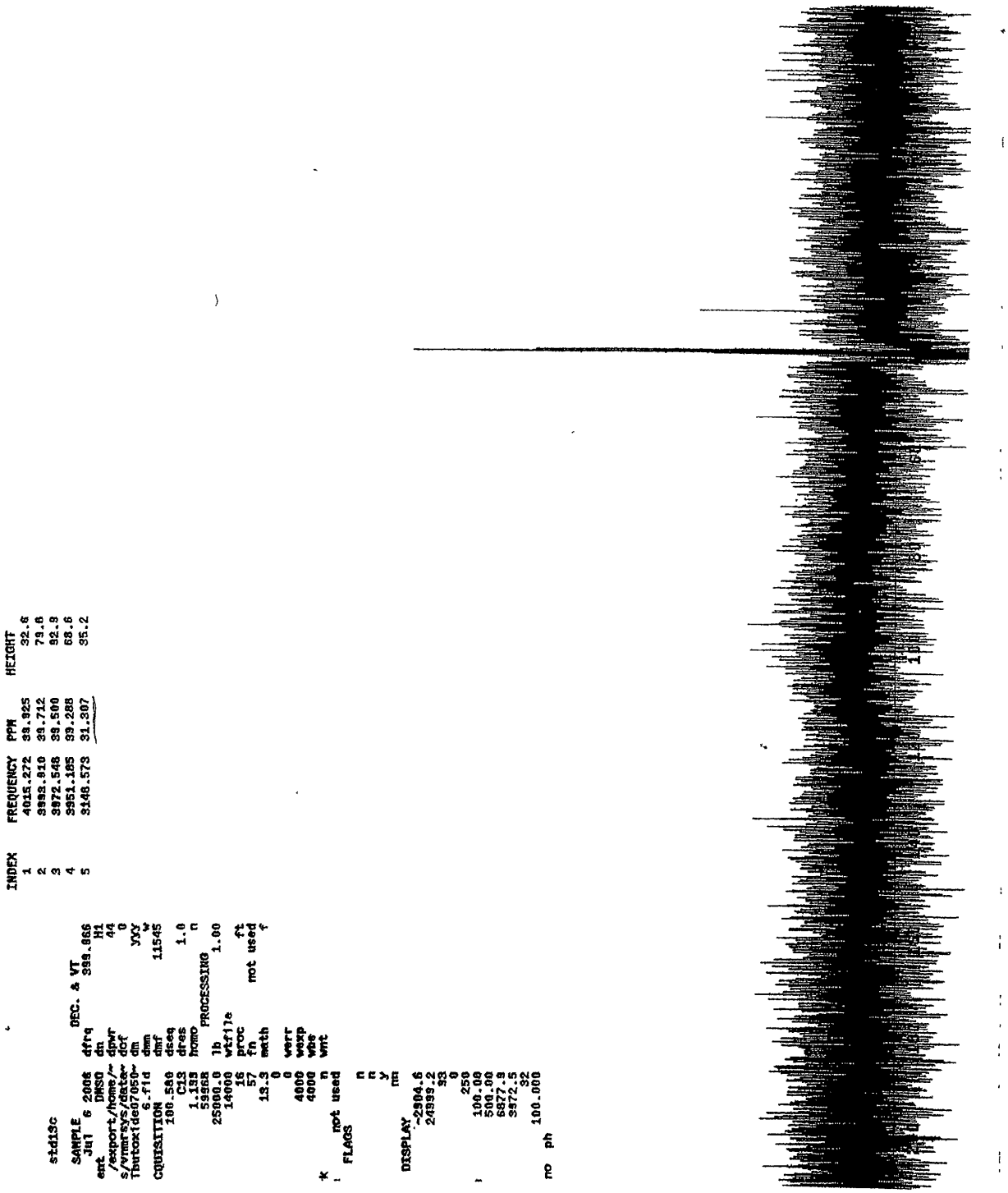

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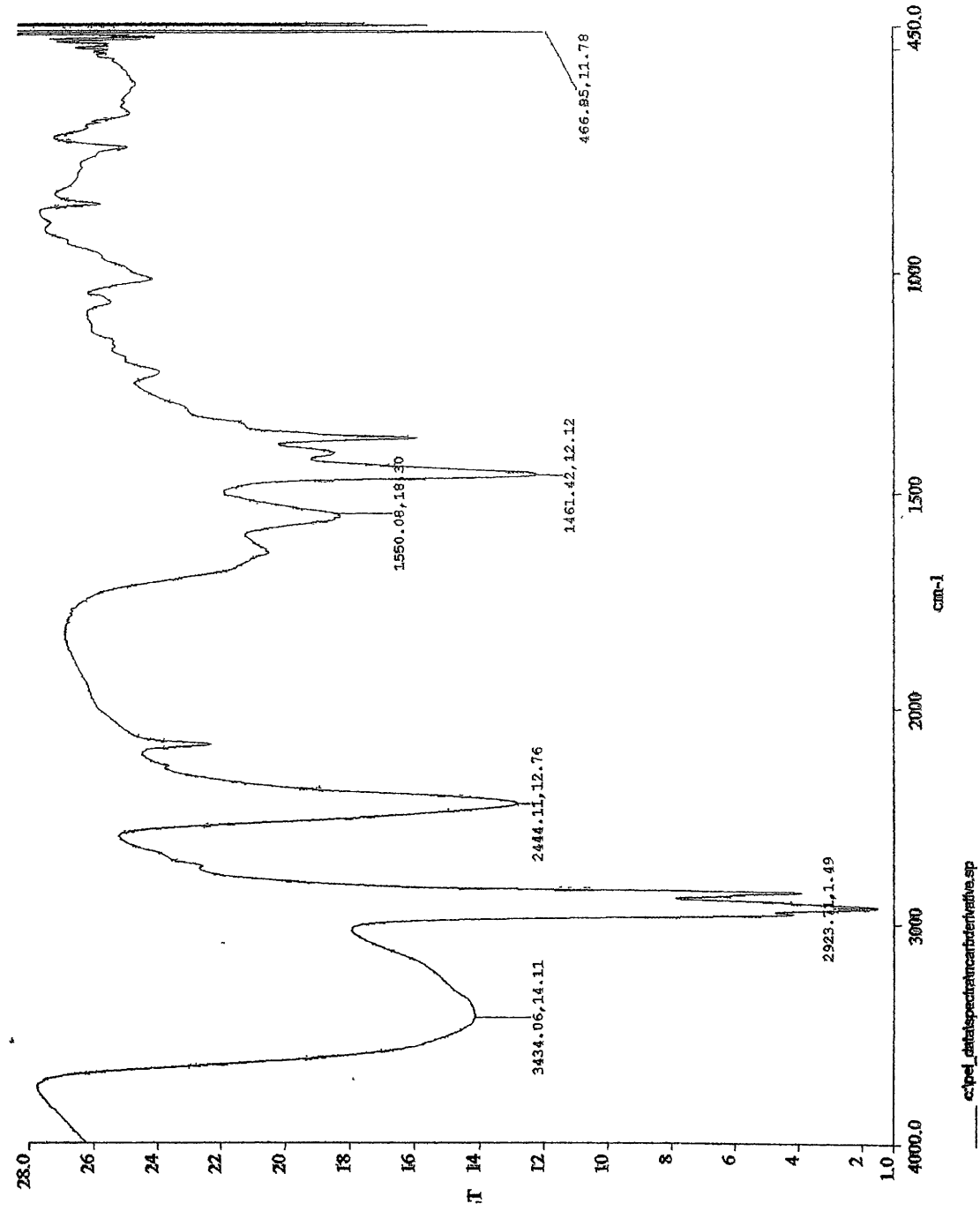

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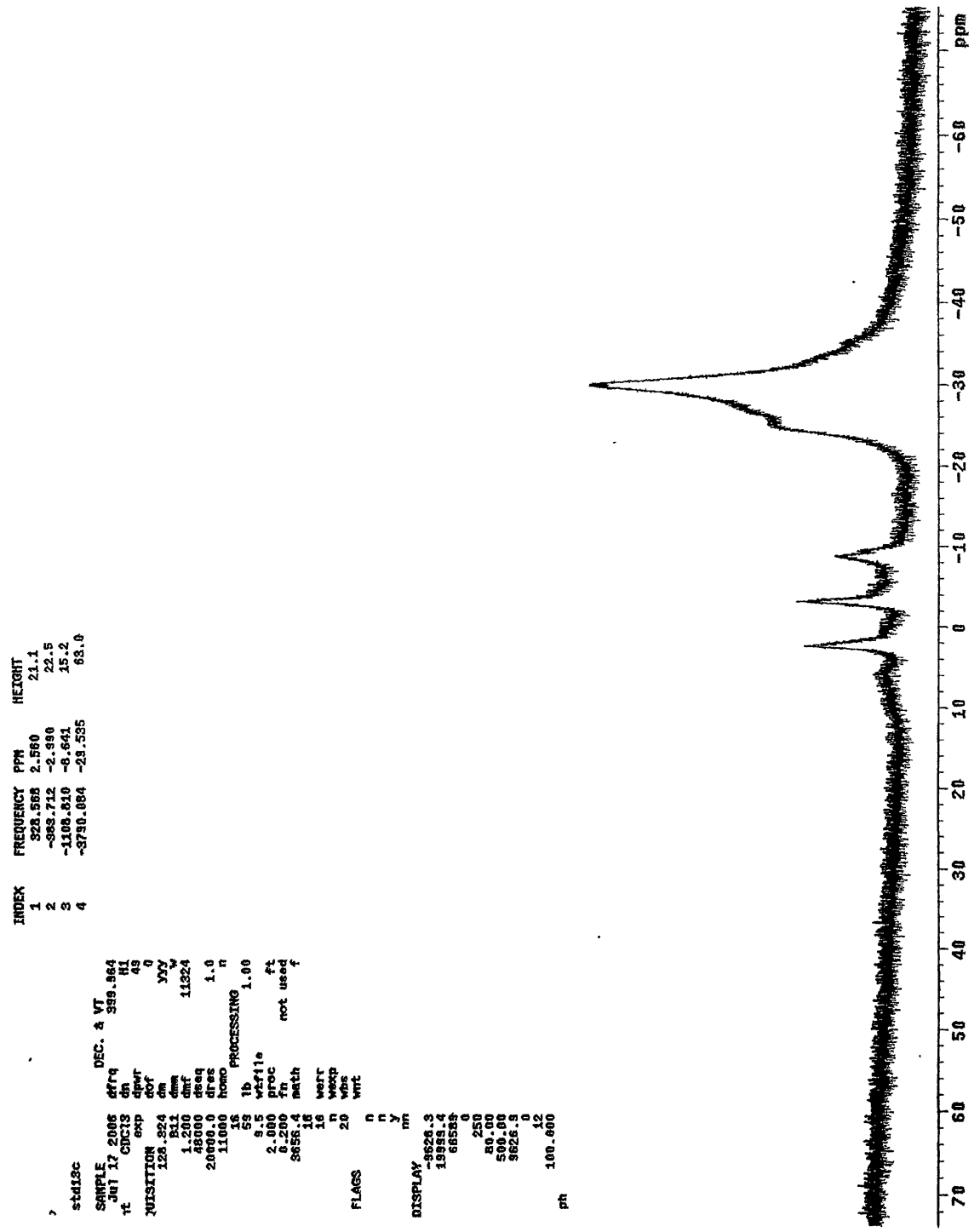

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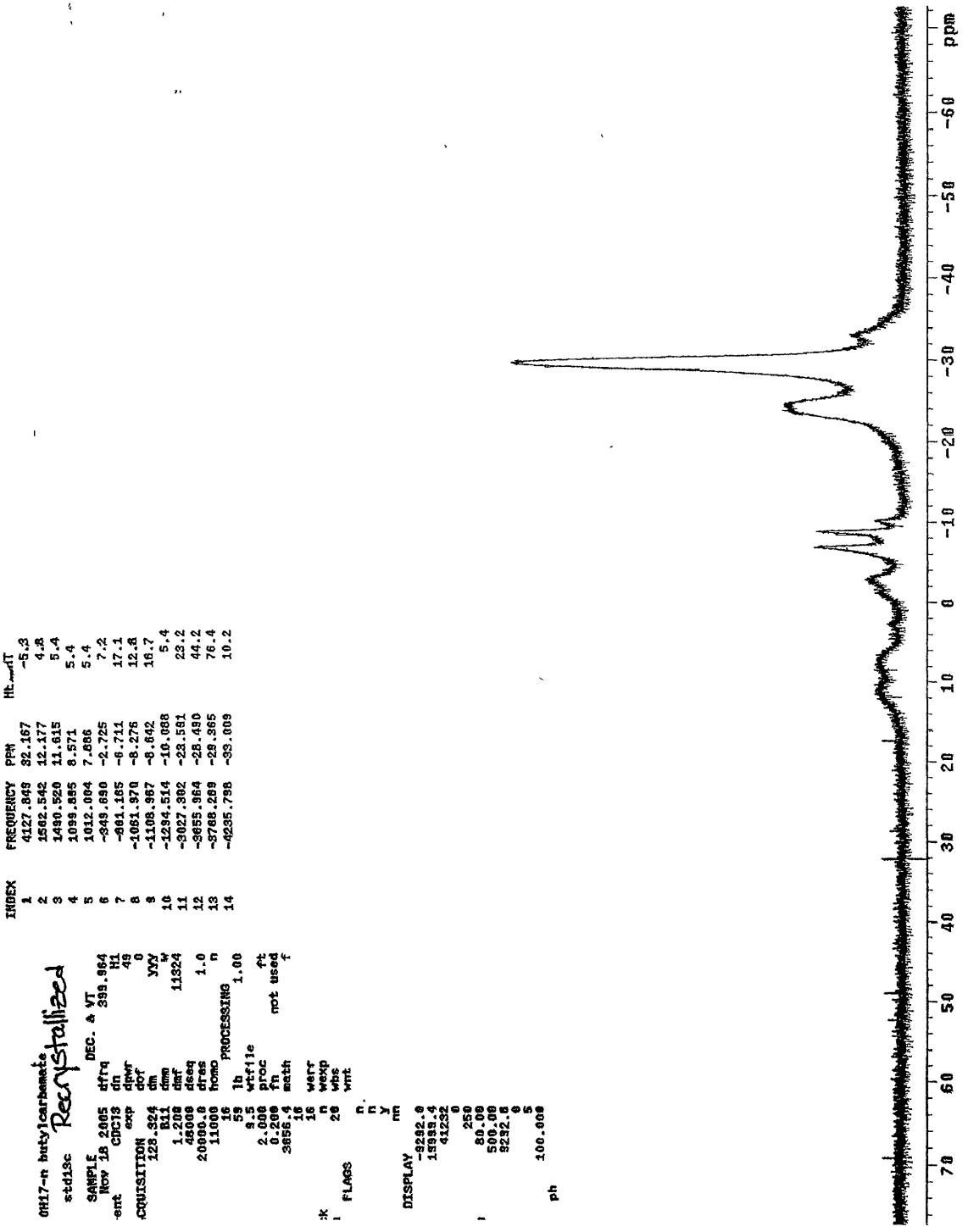

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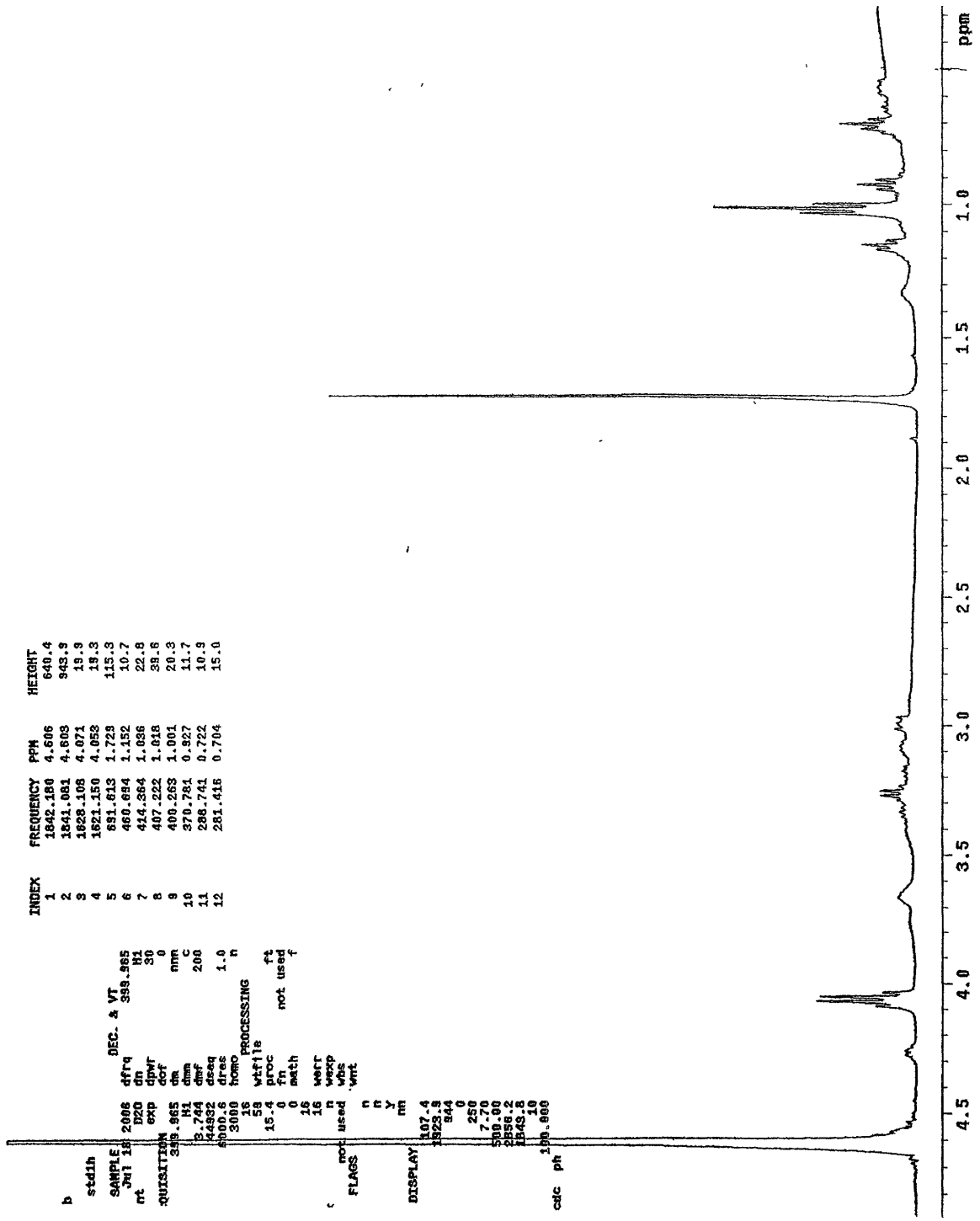

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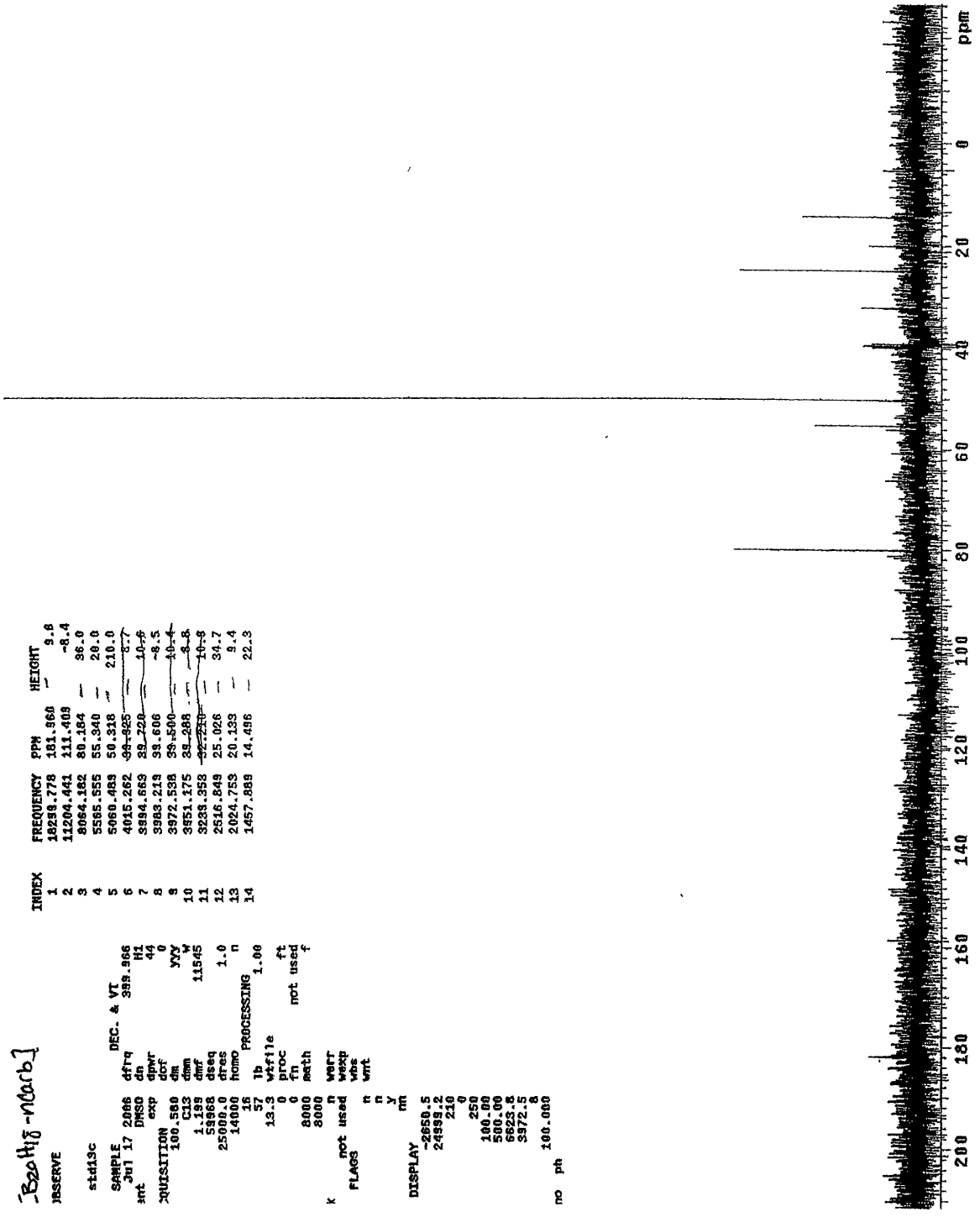
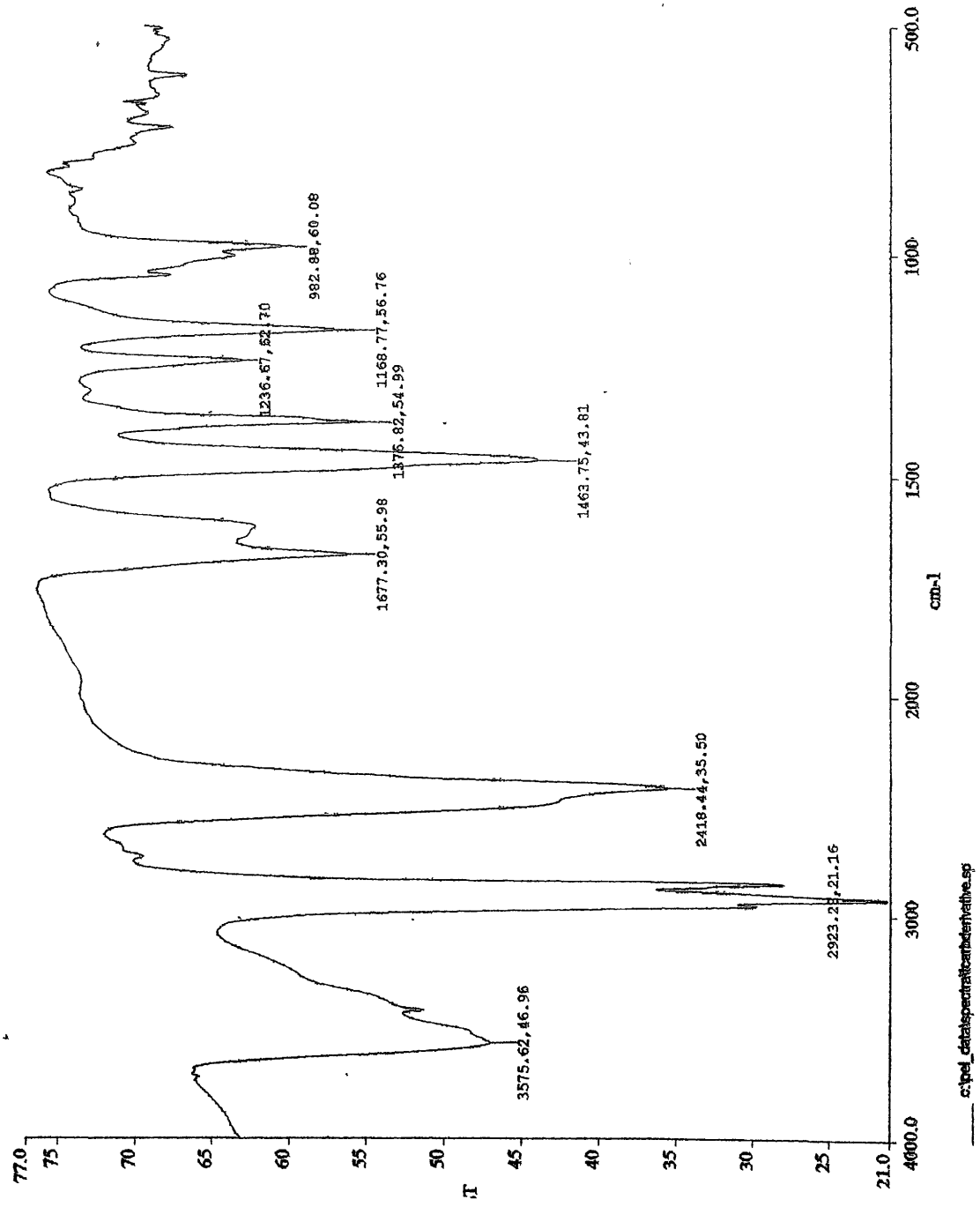
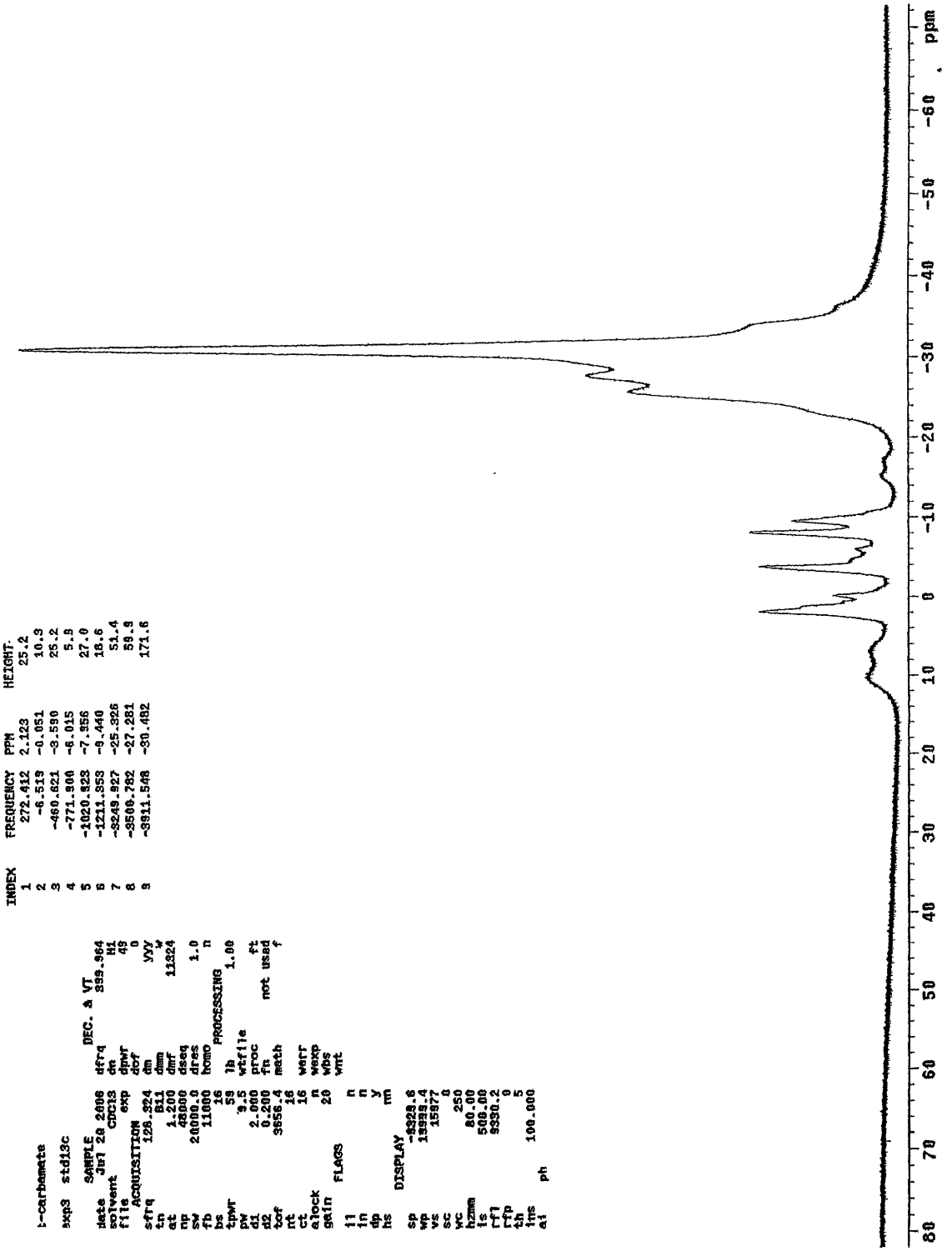


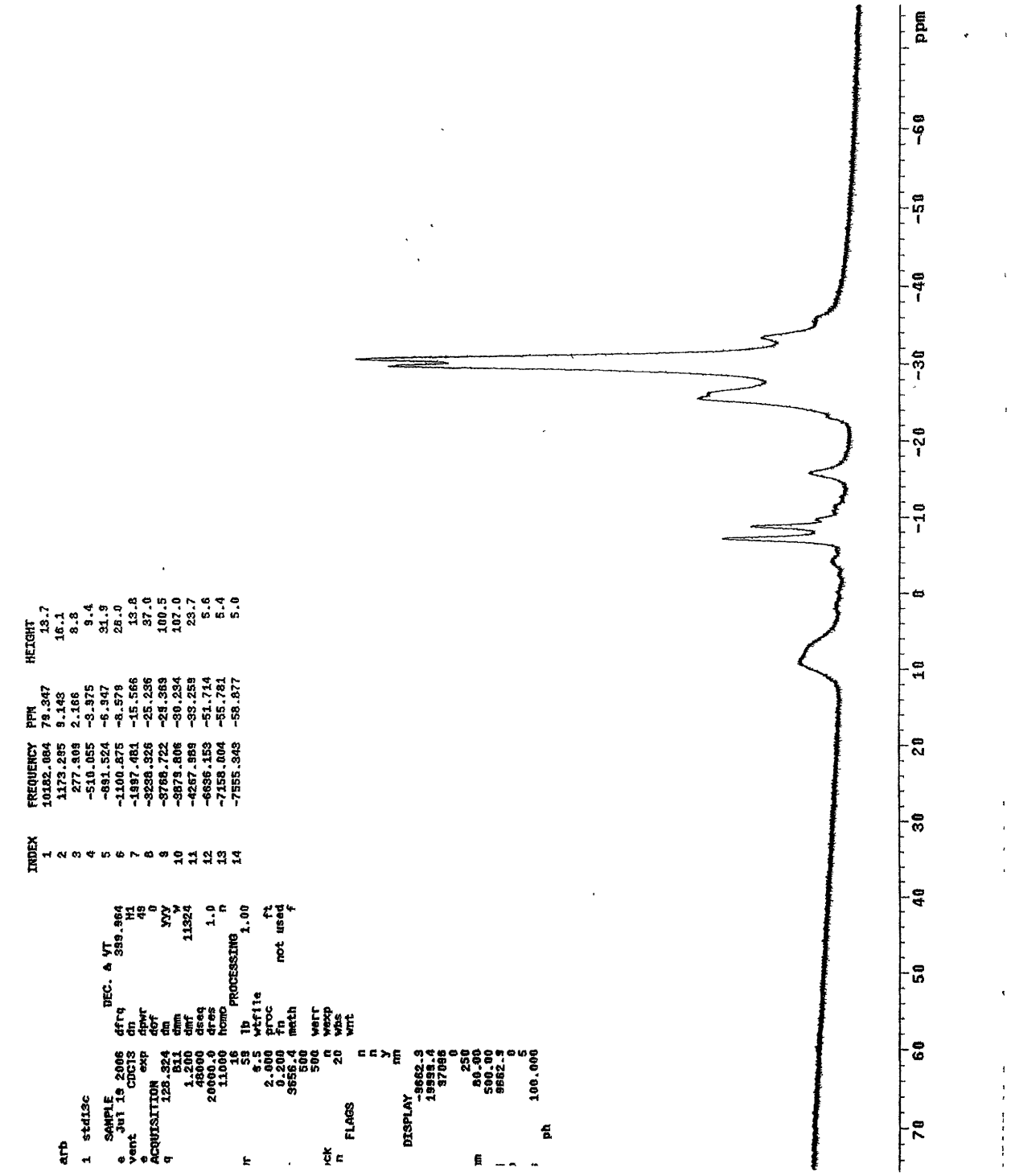
IR of $Rb_4[B_{20}H_{17}NHC(O)OC(CH_3)_3]$



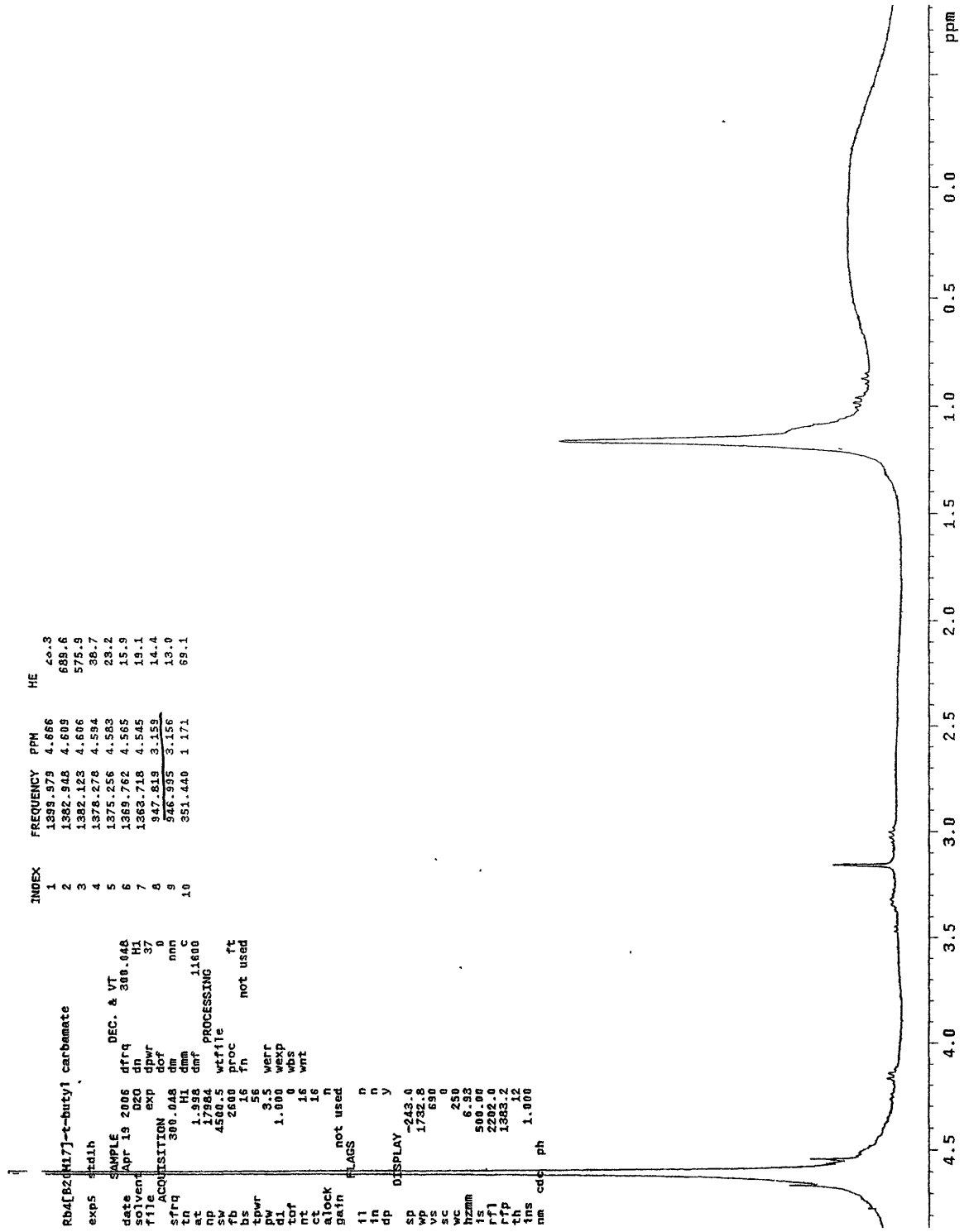
^{11}B NMR of $Rb_4[B_{20}H_{17}NHC(O)OC(CH_3)_3]$



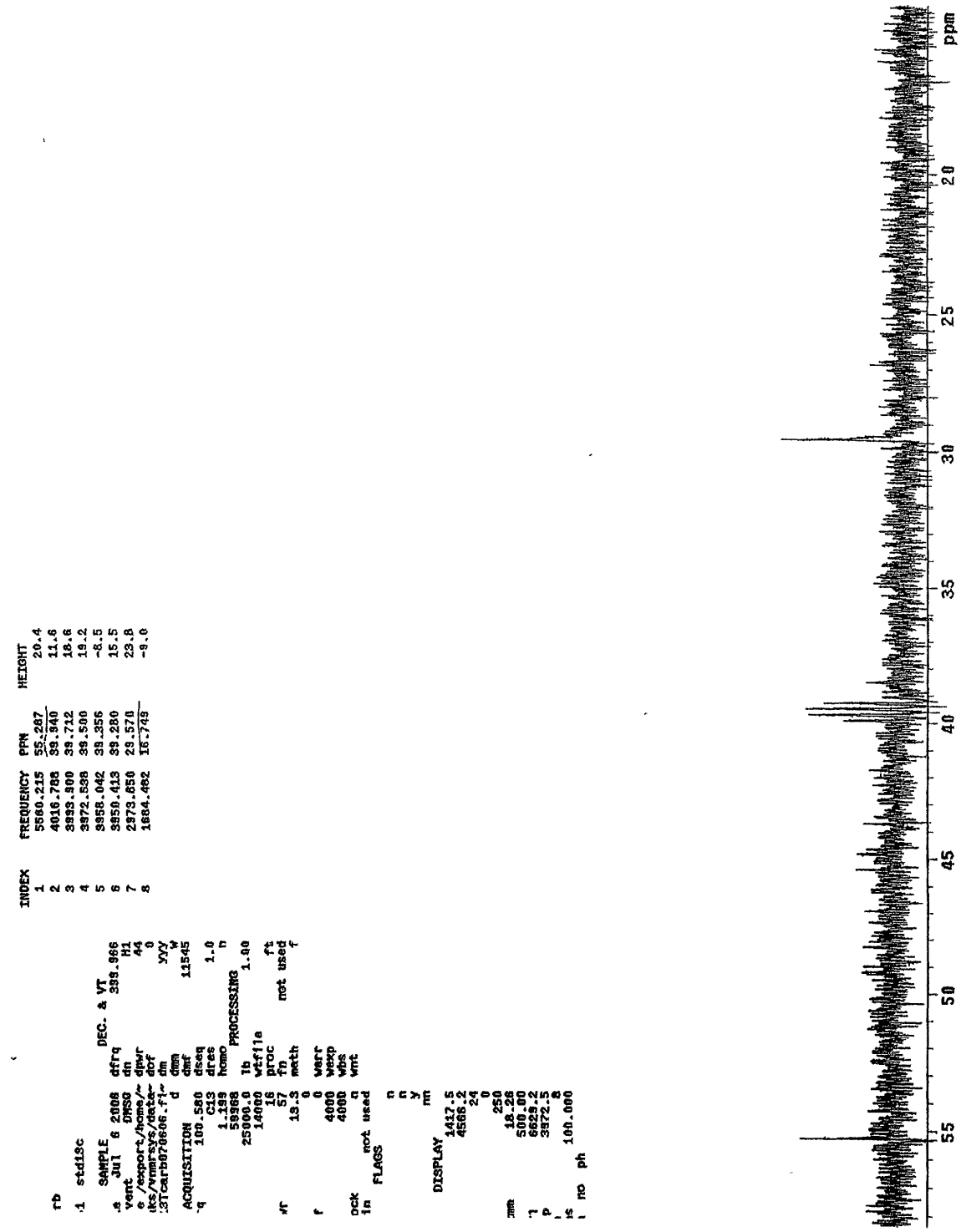
^{11}B NMR of Recrystallized $Rb_4[B_{20}H_{17}NHC(O)OC(CH_3)_3]$



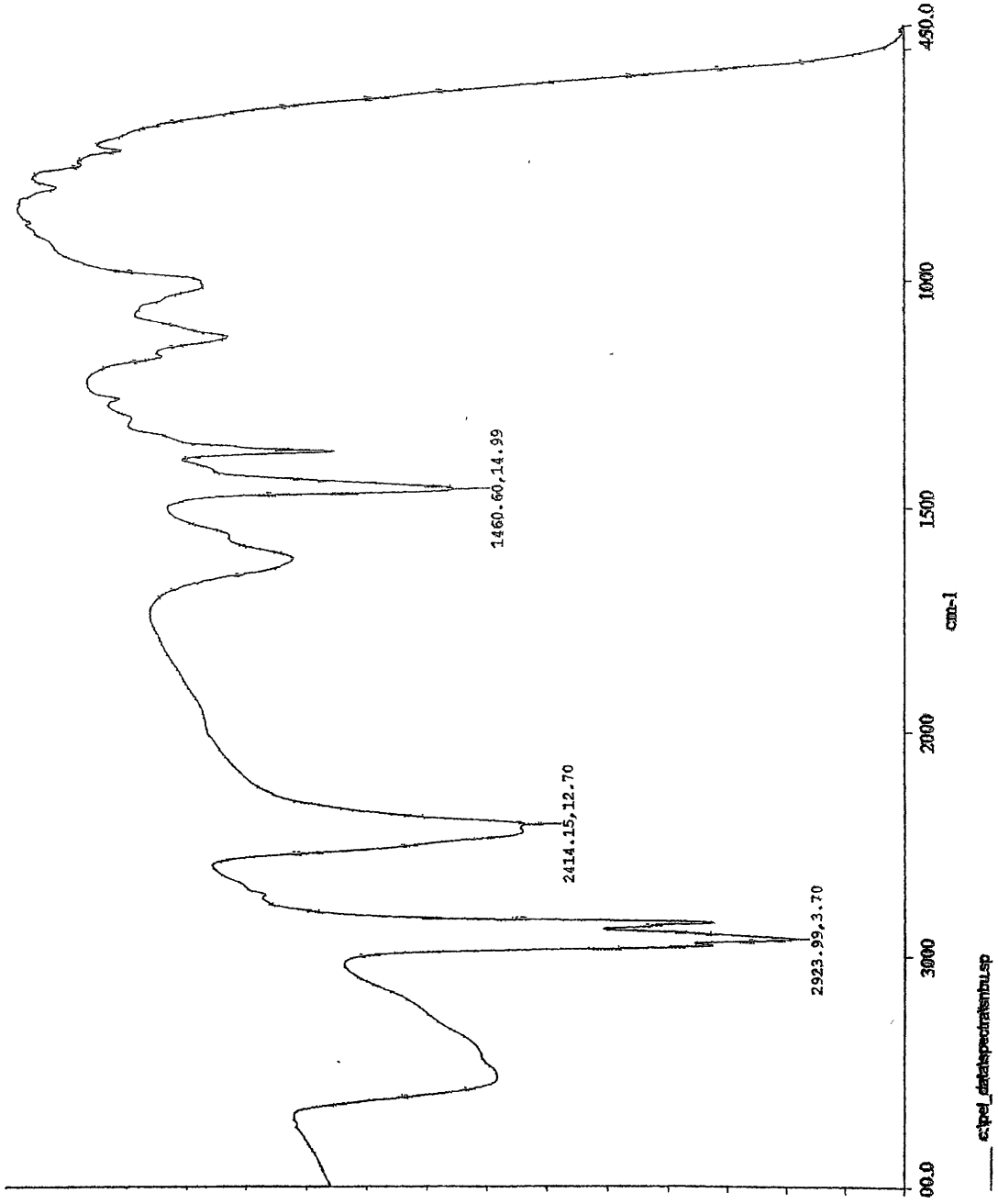
^{1}H NMR of $Rb_4[B_{20}H_{17}NHC(O)OC(CH_3)_3]$



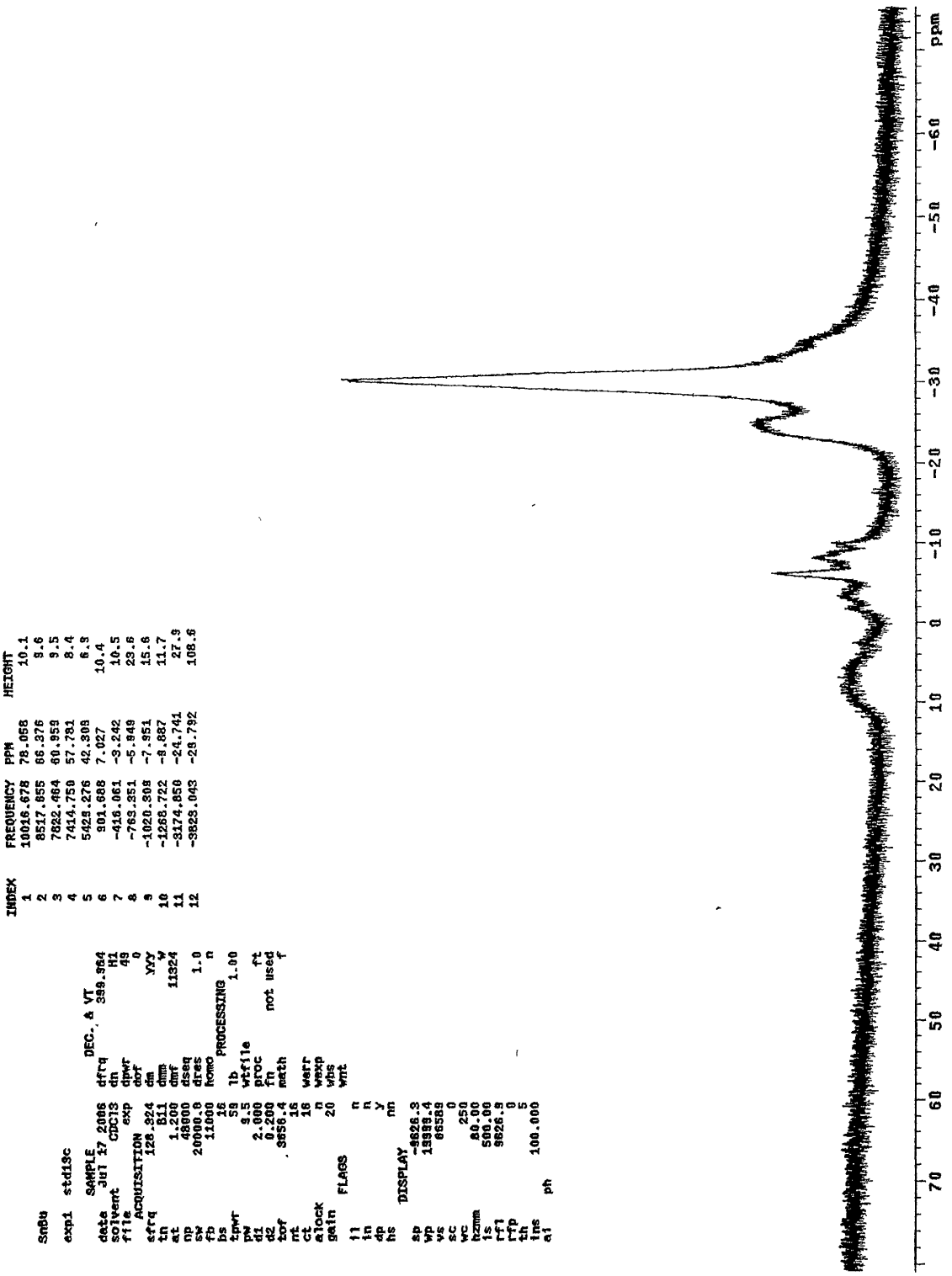
^{13}C NMR of $Rb_4[B_{20}H_{17}NHC(O)OC(CH_3)_3]$



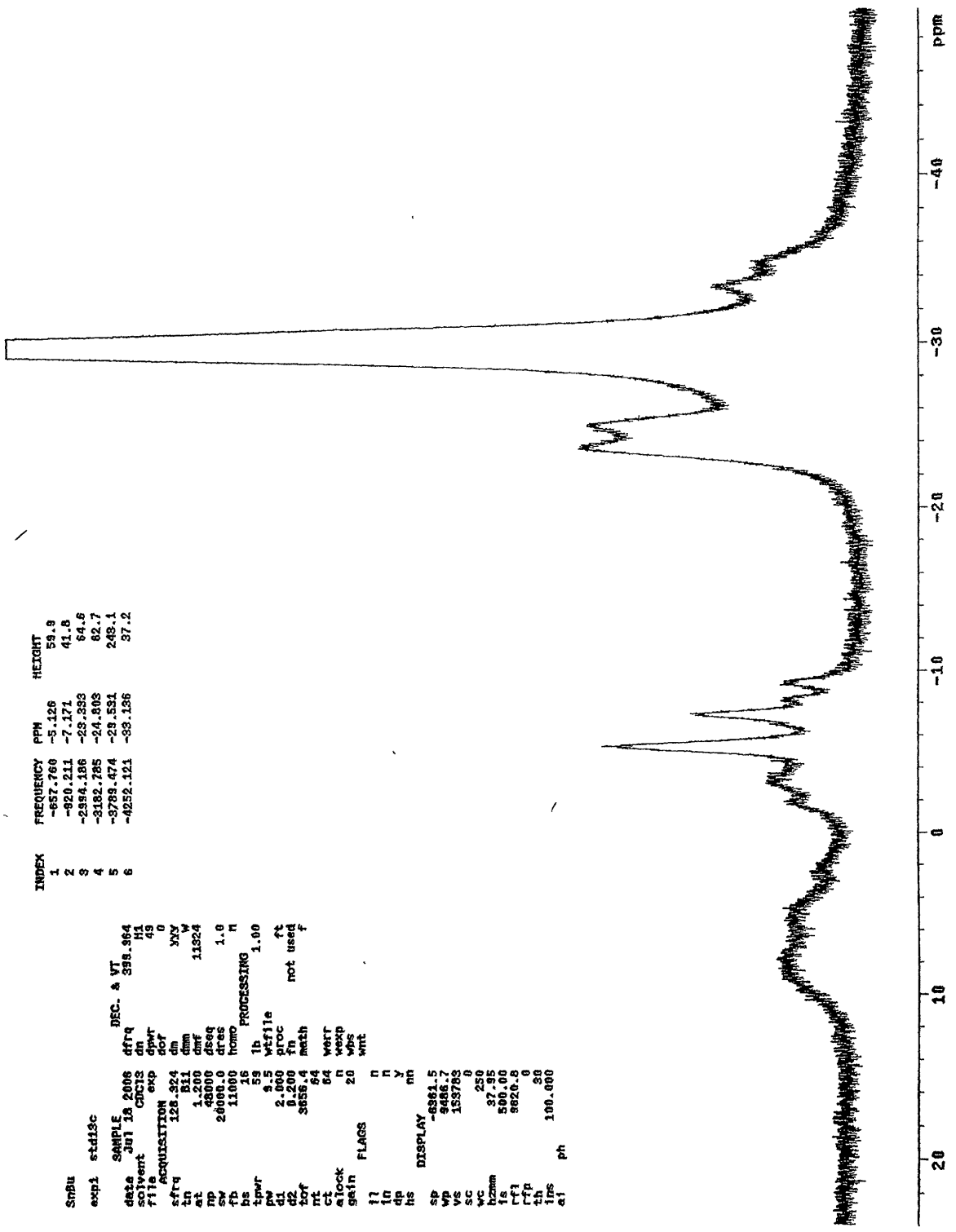
IR of $Rb_4[B_{20}H_{17}S(CH_2)_3CH_3]$



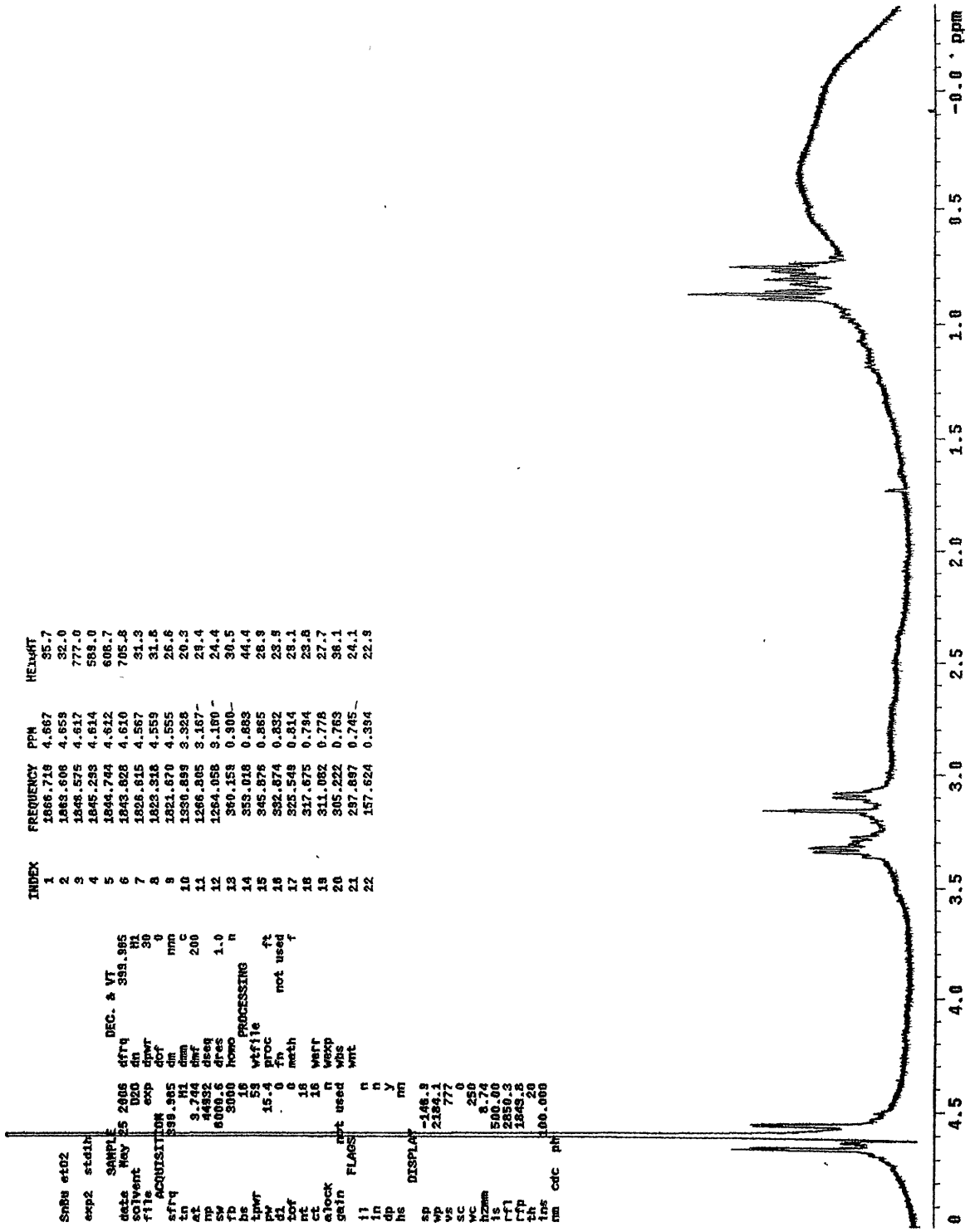
^{11}B NMR of $Rb_4[B_{20}H_{17}S(CH_2)_3CH_3]$



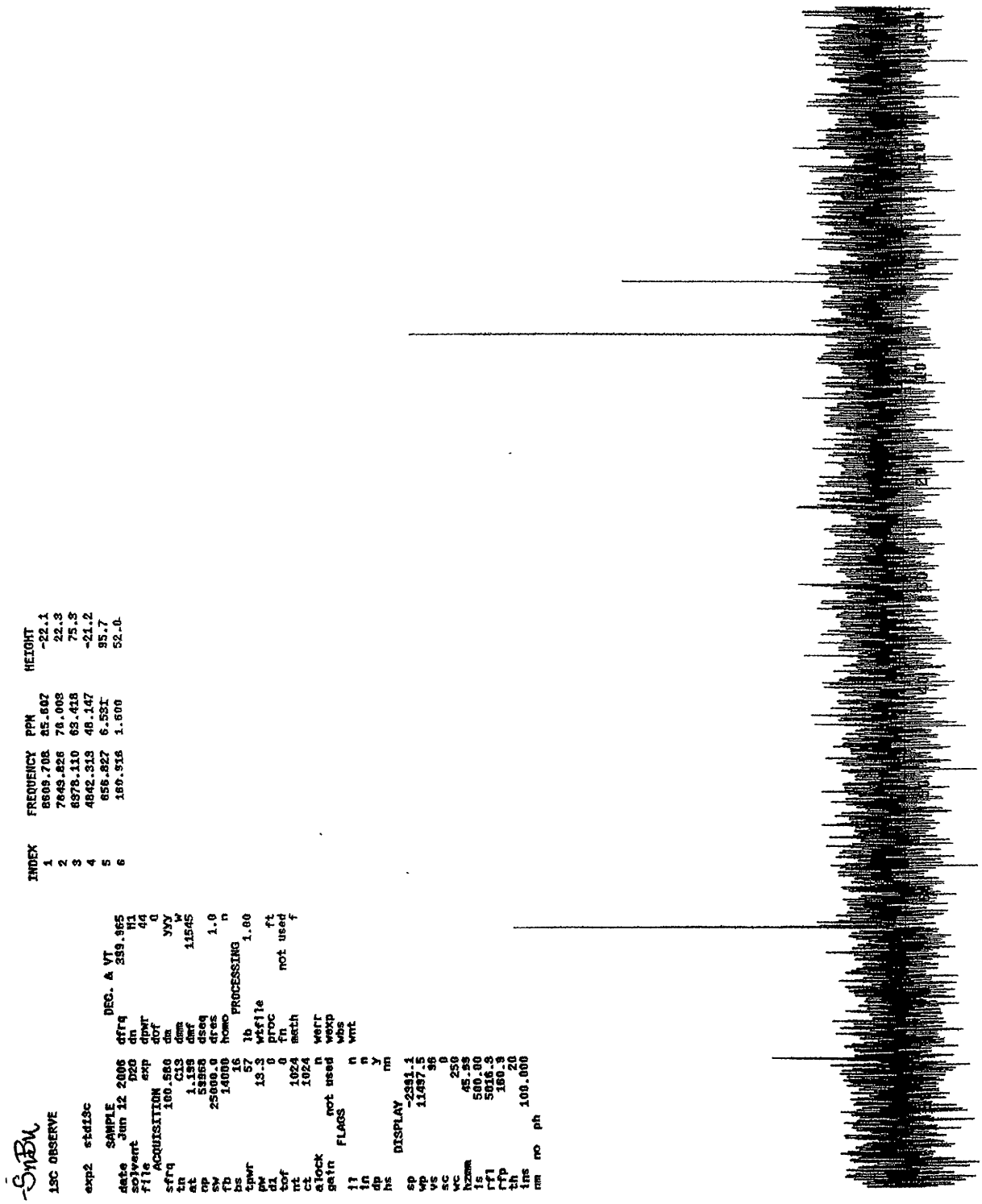
Expanded ^{11}B NMR of $Rb_4[B_{20}H_{17}S(CH_2)_3CH_3]$



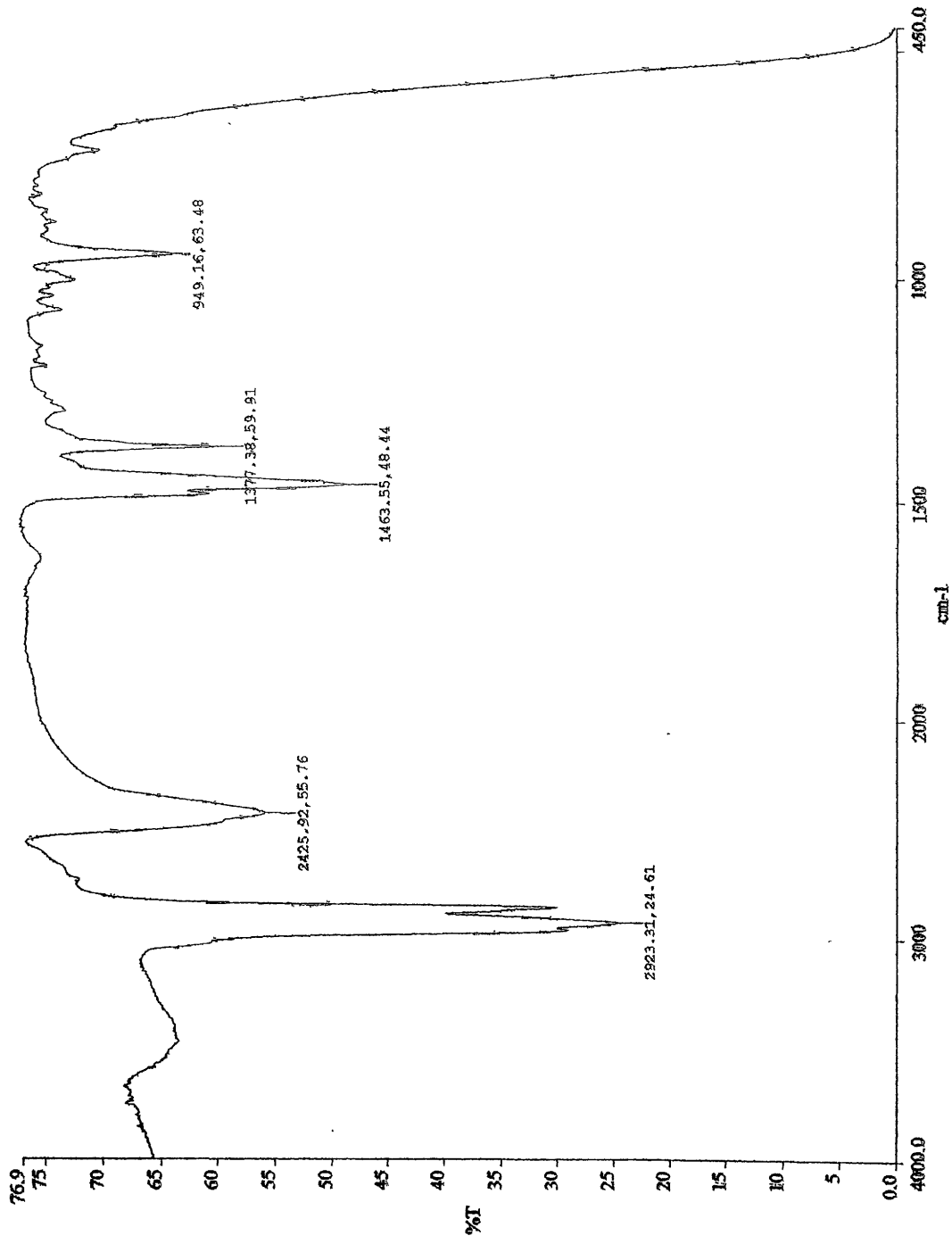
^{1}H NMR of $Rb_4[B_{20}H_{17}S(CH_2)_3CH_3]$



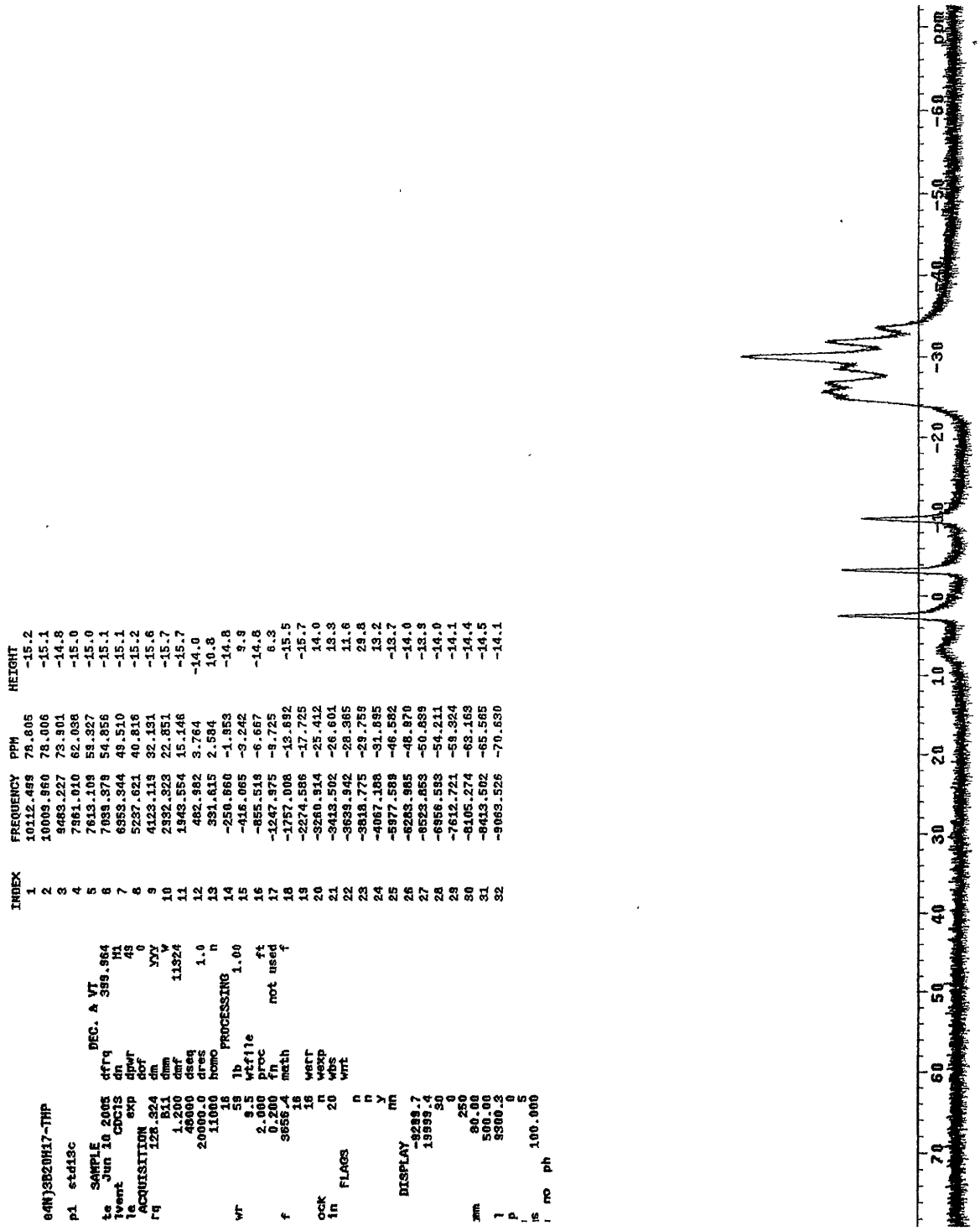
^{13}C NMR of $Rb_4[B_{20}H_{17}S(CH_2)_3CH_3]$



IR of $[(CH_3)_4N]_3[B_{20}H_{17}O(CH_2)_5]$

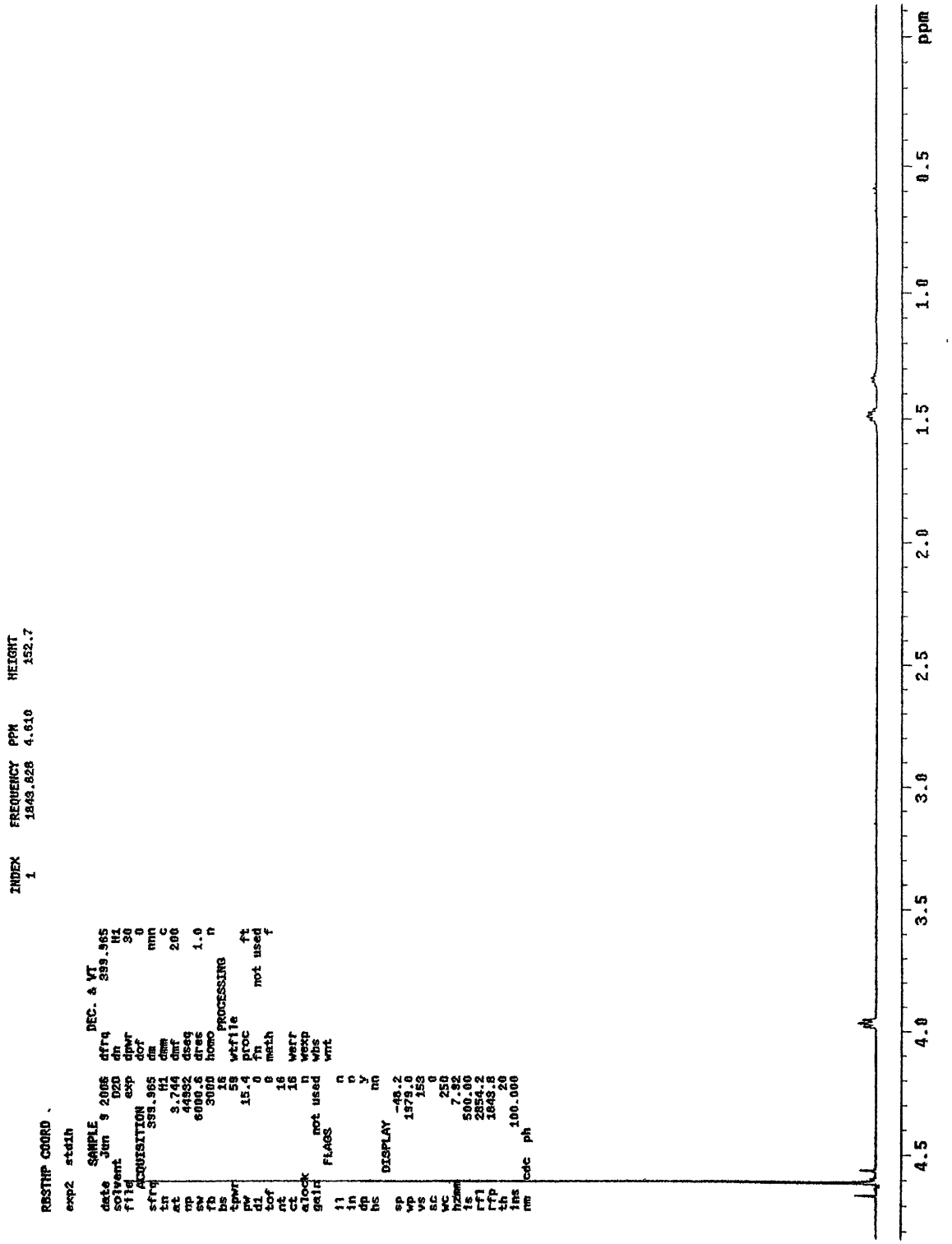


^{11}B NMR of $[(CH_3)_4N]_3[B_{20}H_{17}O(CH_2)_5]$

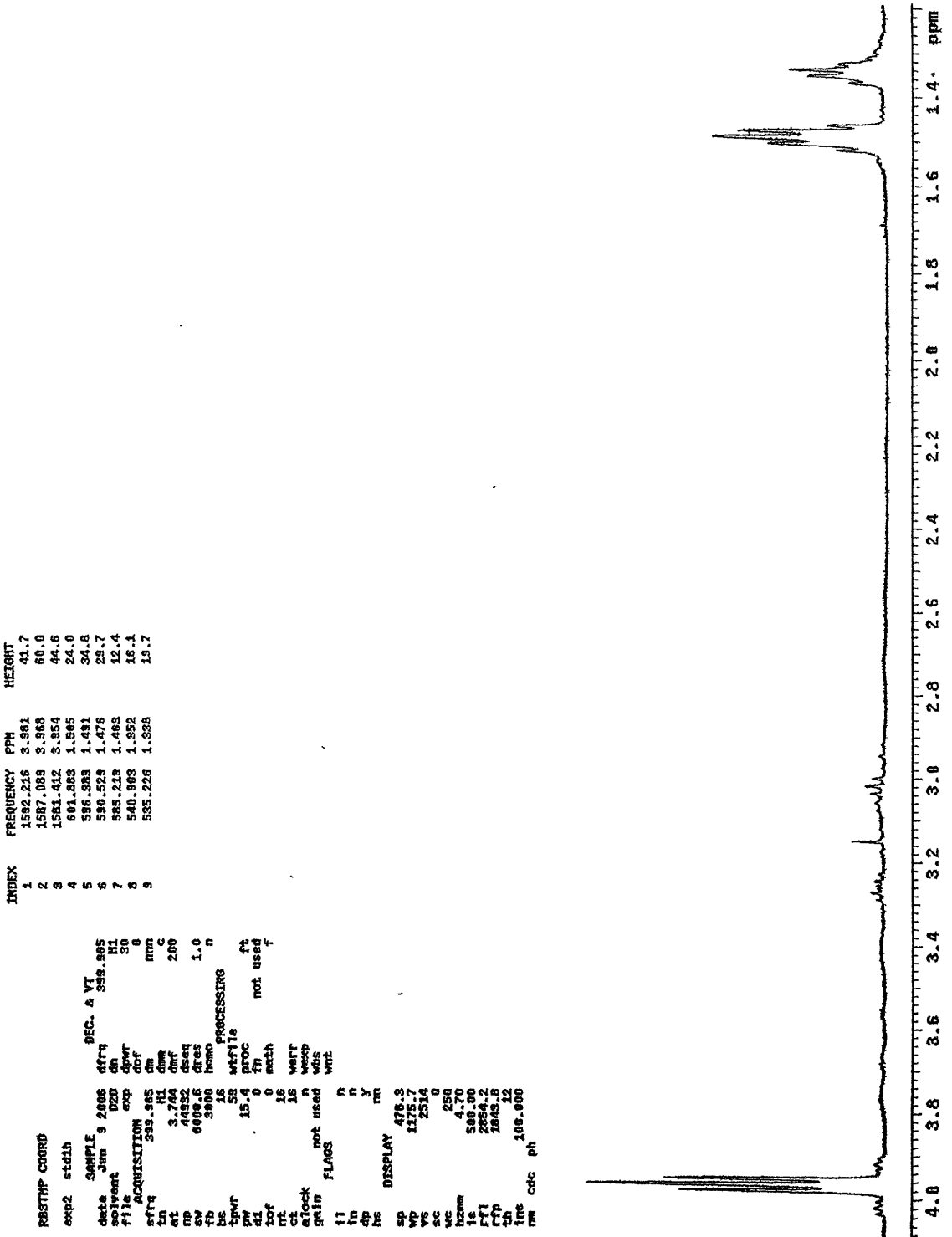


INDEX	FREQUENCY	PPM	HEIGHT
1	10112.499	78.805	-15.2
2	10009.860	78.006	-15.1
3	9483.227	73.901	-14.8
4	7961.010	62.038	-15.0
5	7613.109	53.327	-15.0
6	7039.378	54.856	-15.1
7	6353.344	49.510	-15.1
8	5237.621	40.818	-15.2
9	4123.119	32.131	-15.6
10	2932.323	22.851	-15.7
11	1943.554	15.146	-15.7
12	482.382	3.764	-14.0
13	331.615	2.584	10.8
14	-250.860	-1.953	-14.8
15	-416.065	-3.242	9.9
16	-855.518	-6.667	-14.8
17	-1247.375	-9.725	6.3
18	-1757.008	-13.692	-15.5
19	-2274.586	-17.725	-15.7
20	-3260.314	-25.412	14.0
21	-3413.502	-26.601	13.3
22	-3639.942	-28.365	11.6
23	-3818.775	-29.759	29.8
24	-4067.188	-31.695	13.2
25	-5977.589	-46.582	-13.7
26	-6283.985	-48.870	-14.0
27	-6523.853	-50.839	-13.9
28	-6956.593	-54.211	-14.0
29	-7612.721	-58.324	-14.1
30	-8105.274	-63.163	-14.4
31	-8413.502	-65.565	-14.5
32	-9063.526	-70.630	-14.1

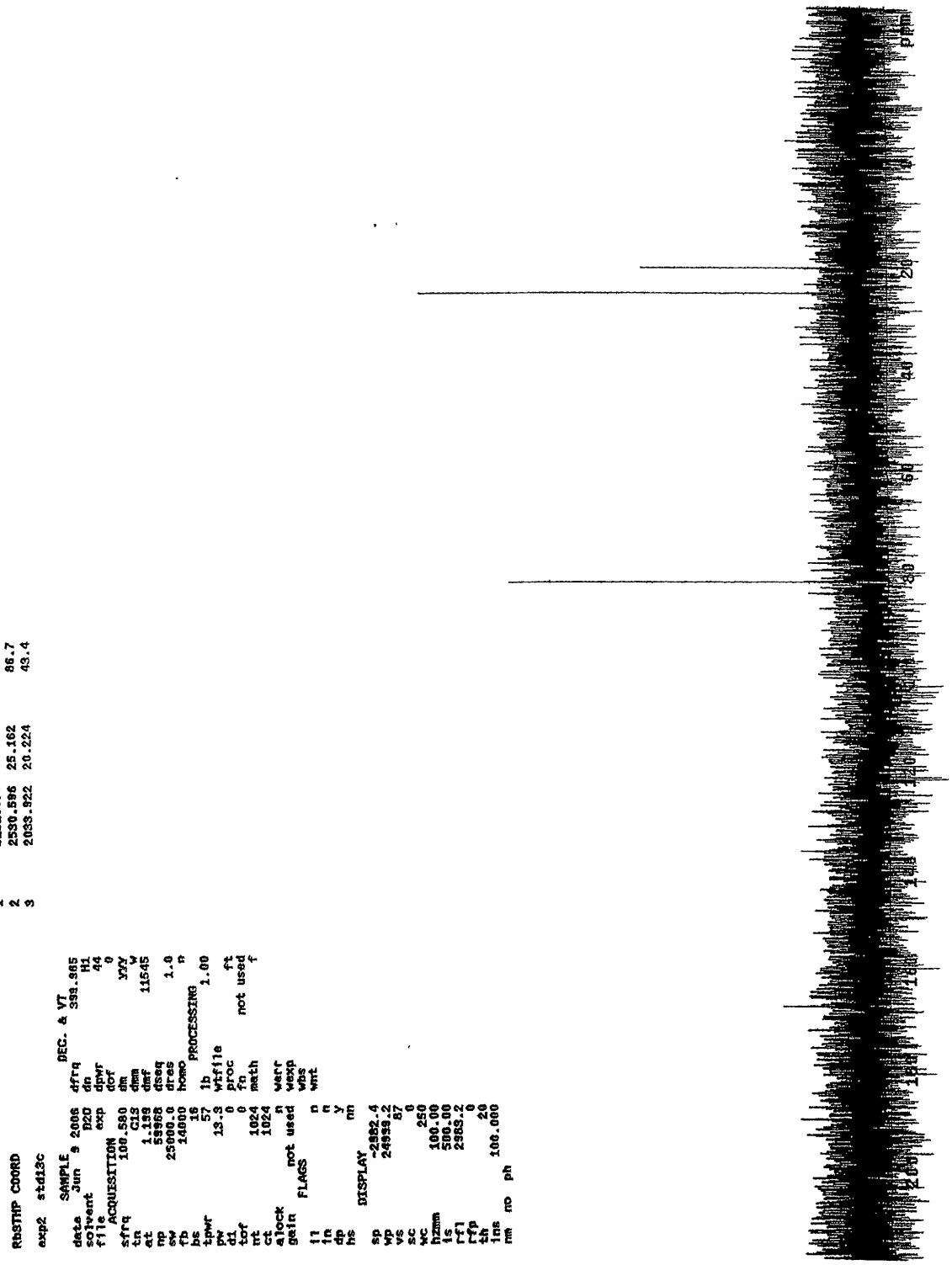
^{1}H NMR of $Rb_3[B_{20}H_{17}O(CH_2)_5]$



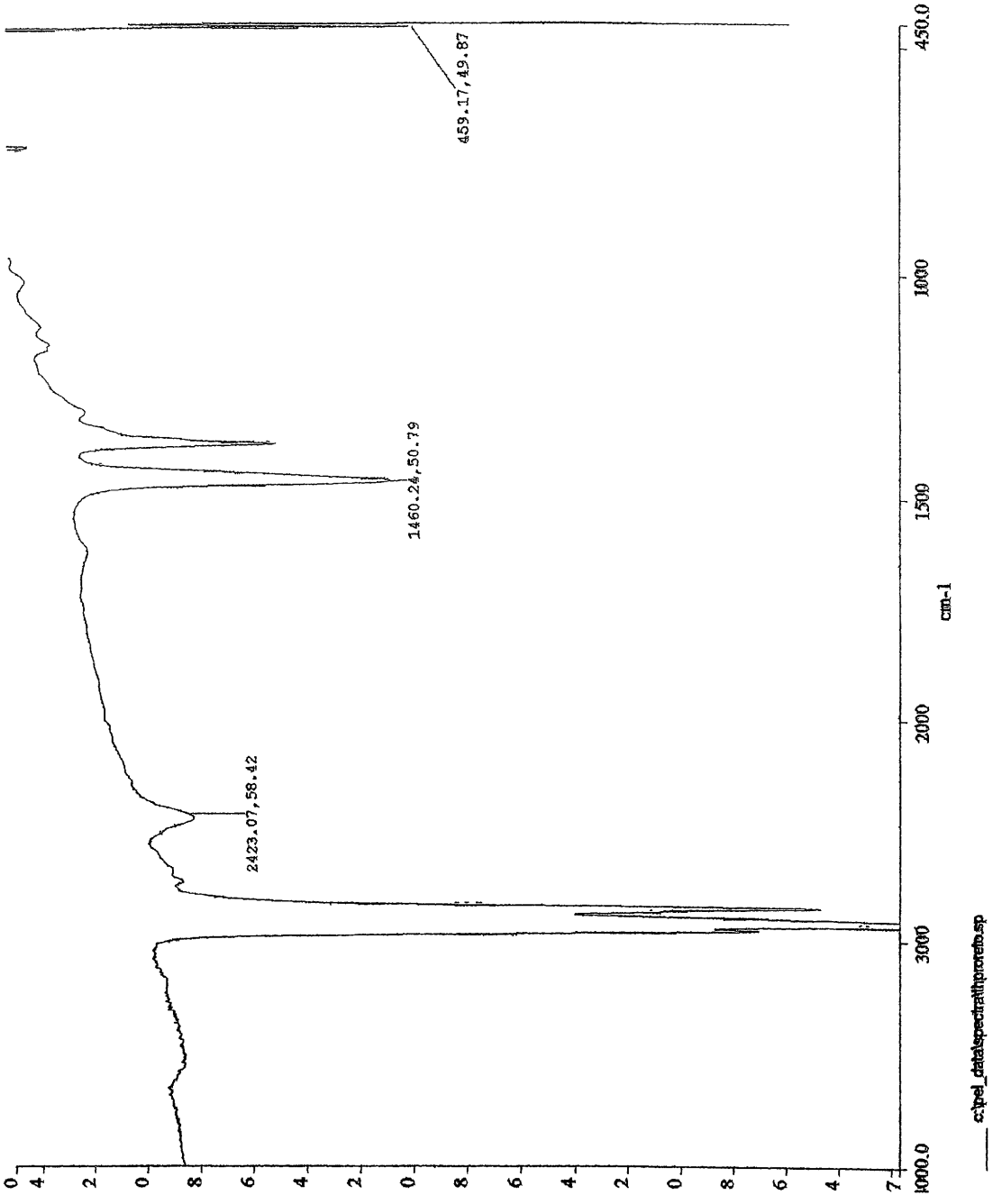
Expanded ^{1}H NMR of $Rb_3[B_{20}H_{17}O(CH_2)_5]$



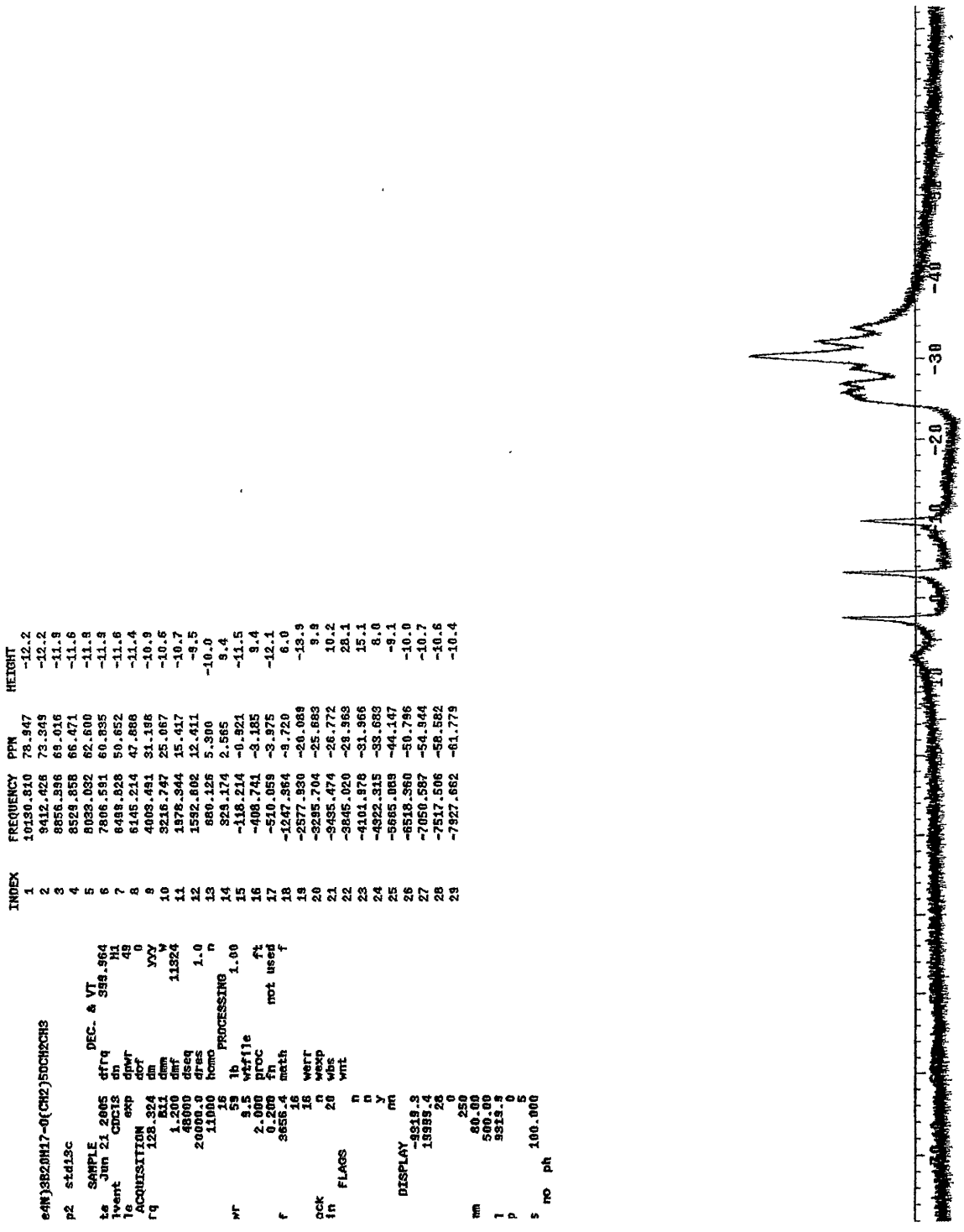
^{13}C NMR of $Rb_3[B_{20}H_{17}O(CH_2)_5]$



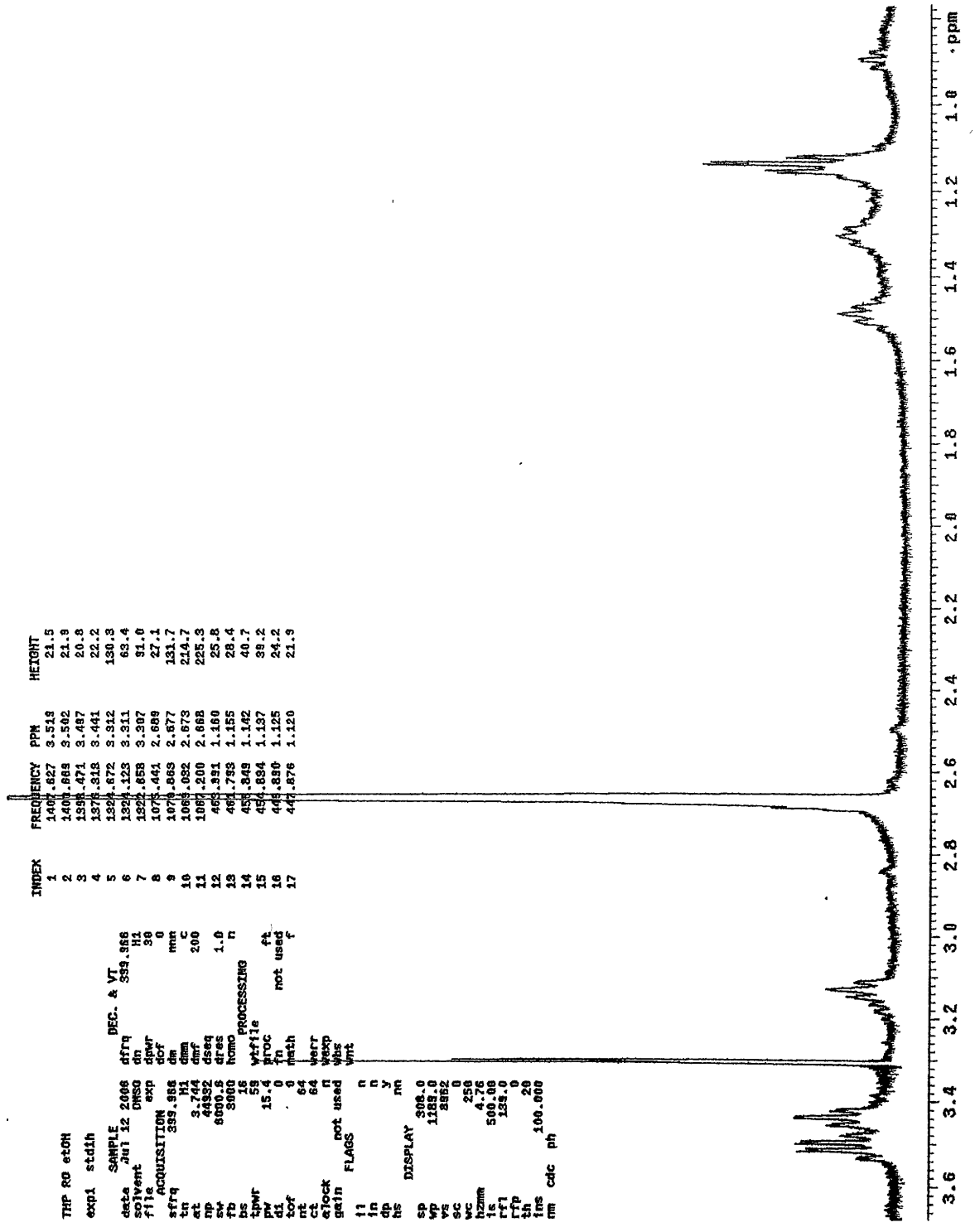
IR of $Rb_4[B_{20}H_{17}O(CH_2)_5OCH_2CH_3]$



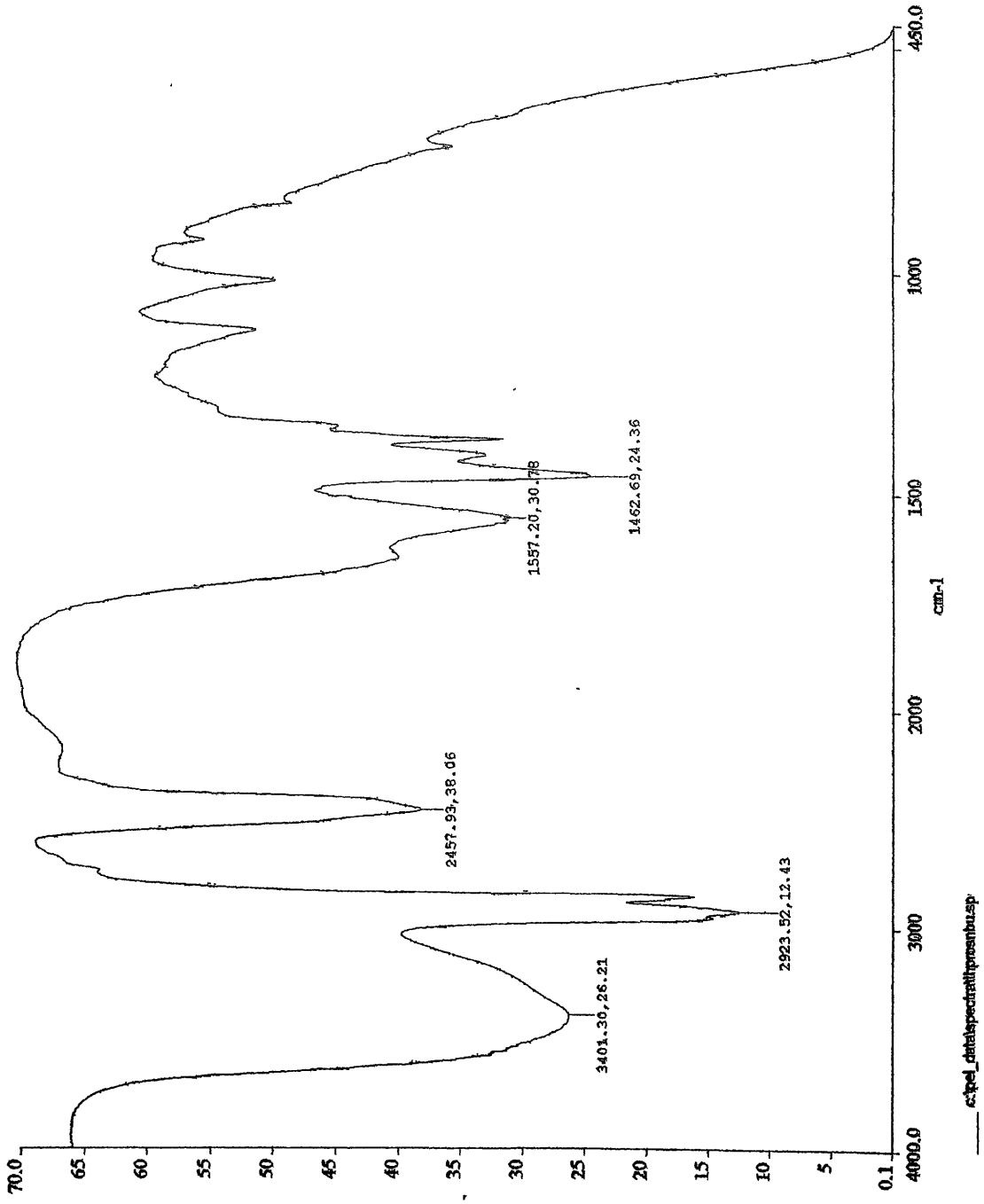
^{11}B NMR of $[(CH_3)_4N]_4[B_{20}H_{17}O(CH_2)_5OCH_2CH_3]$



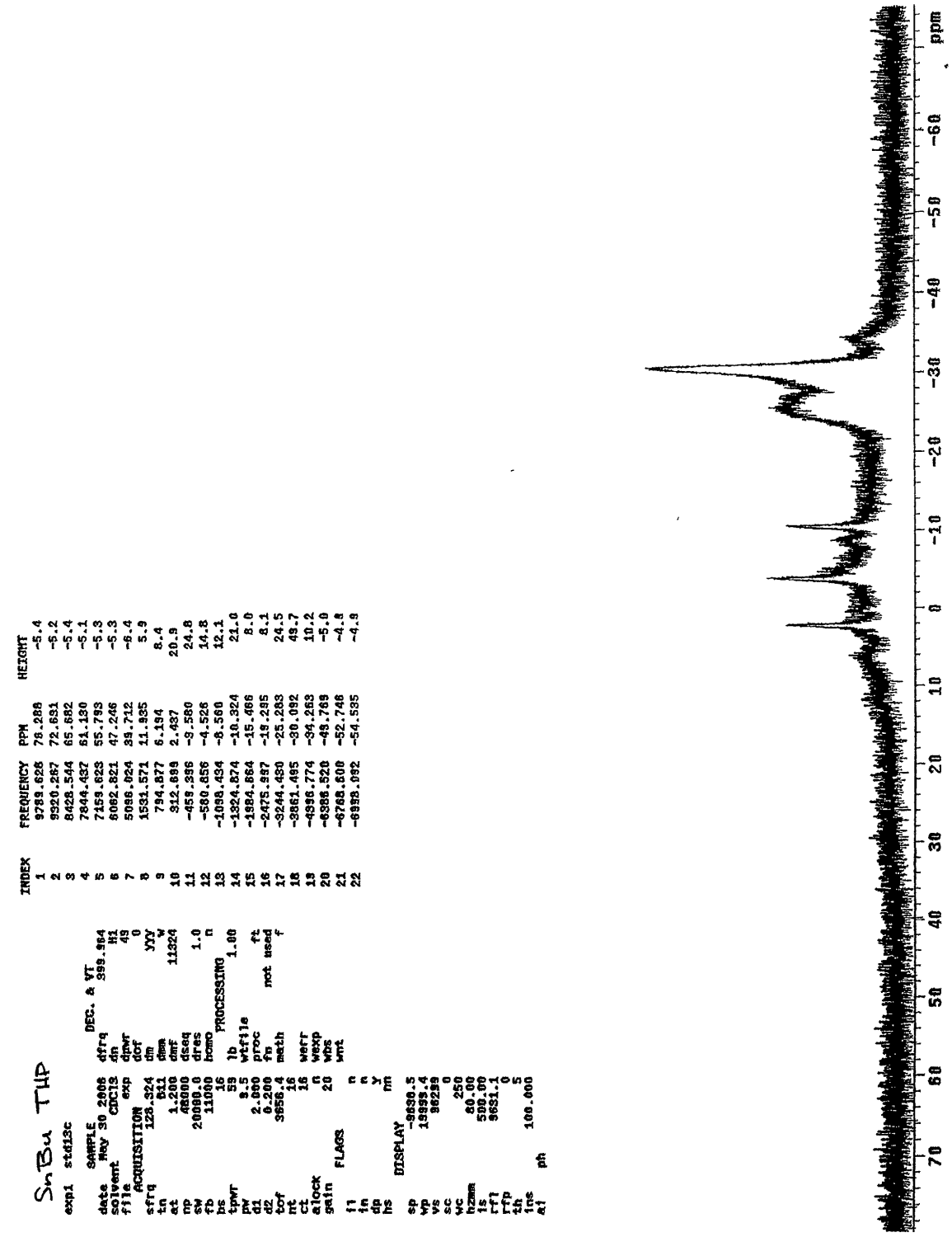
^{1}H NMR of $Rb_4[B_{20}H_{17}O(CH_2)_5OCH_2CH_3]$



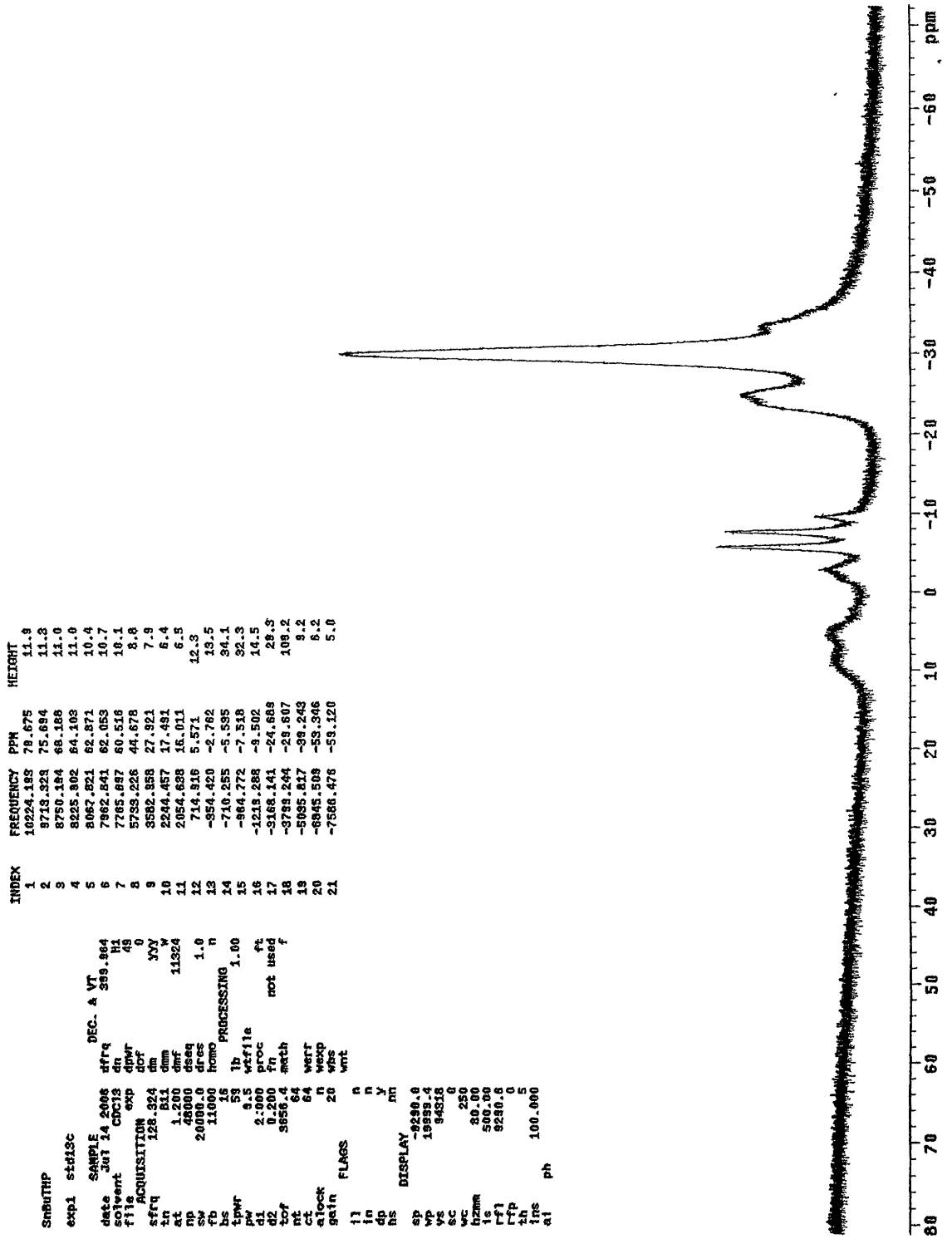
IR of $K_4[B_{20}H_{17}O(CH_2)_5S(CH_2)_3CH_3]$



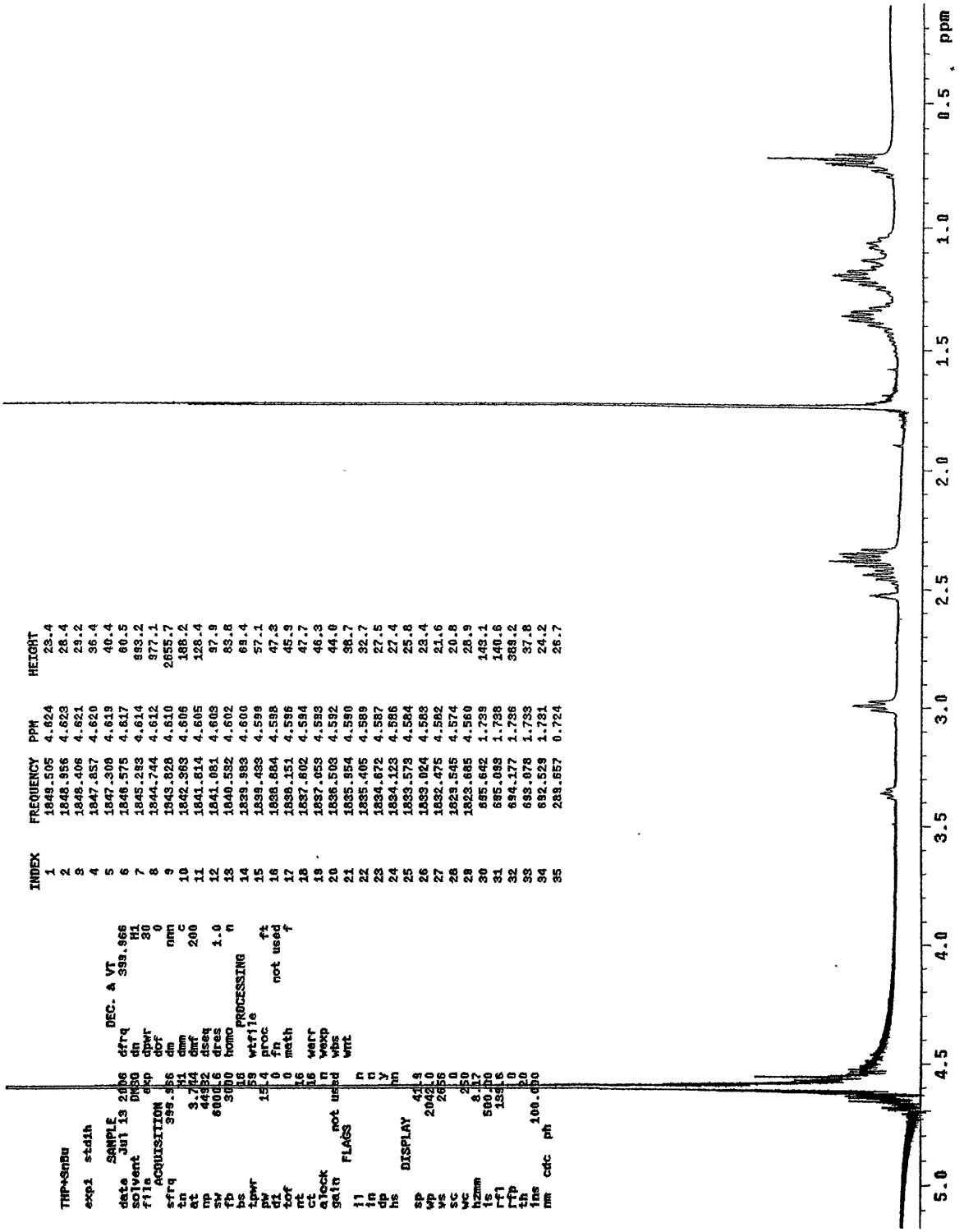
^{11}B NMR of $K_4[B_{20}H_{17}O(CH_2)_5S(CH_2)_3CH_3^*]$



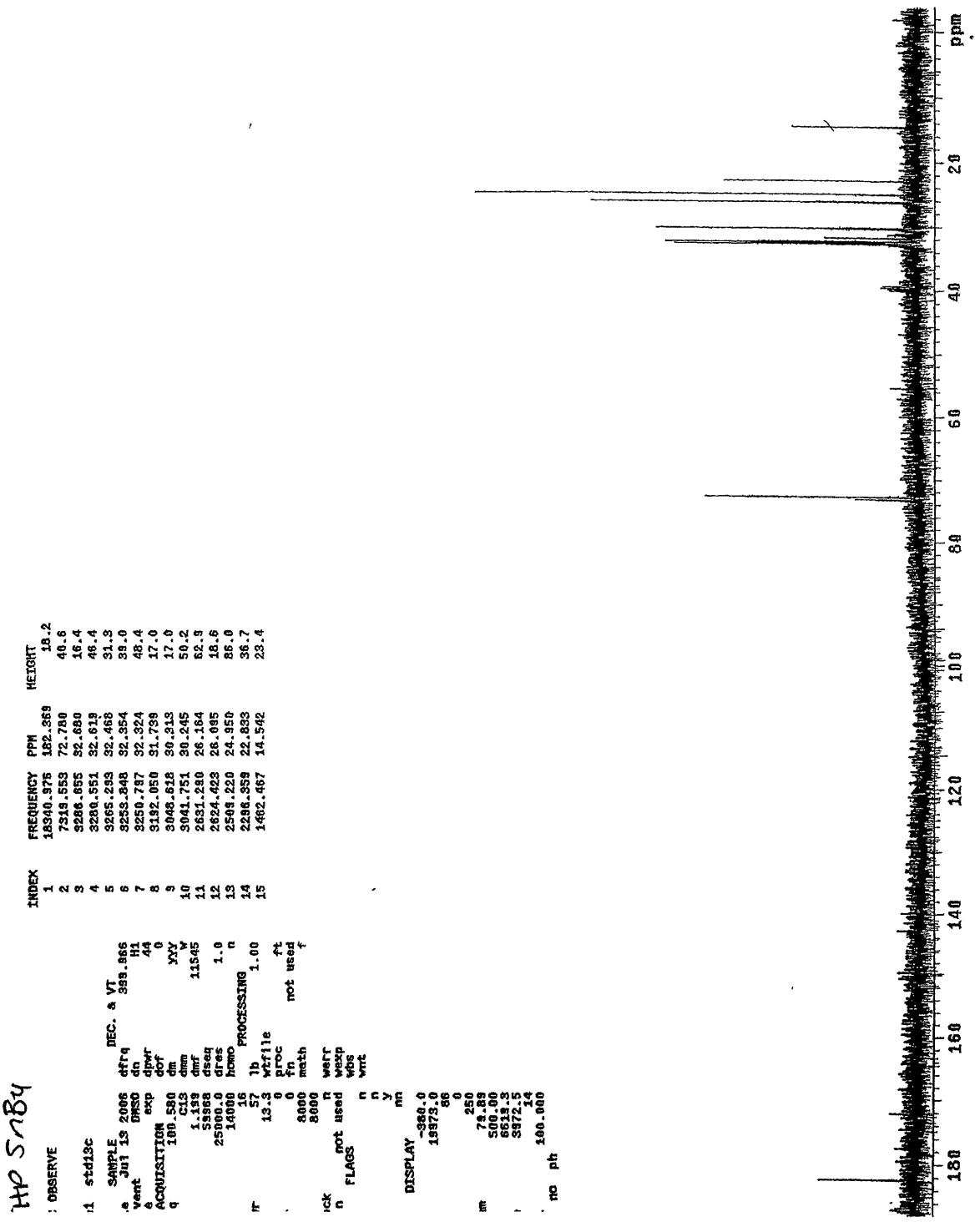
^{11}B NMR of Recrystallized $K_4[B_{20}H_{17}O(CH_2)_5S(CH_2)_3CH_3]$



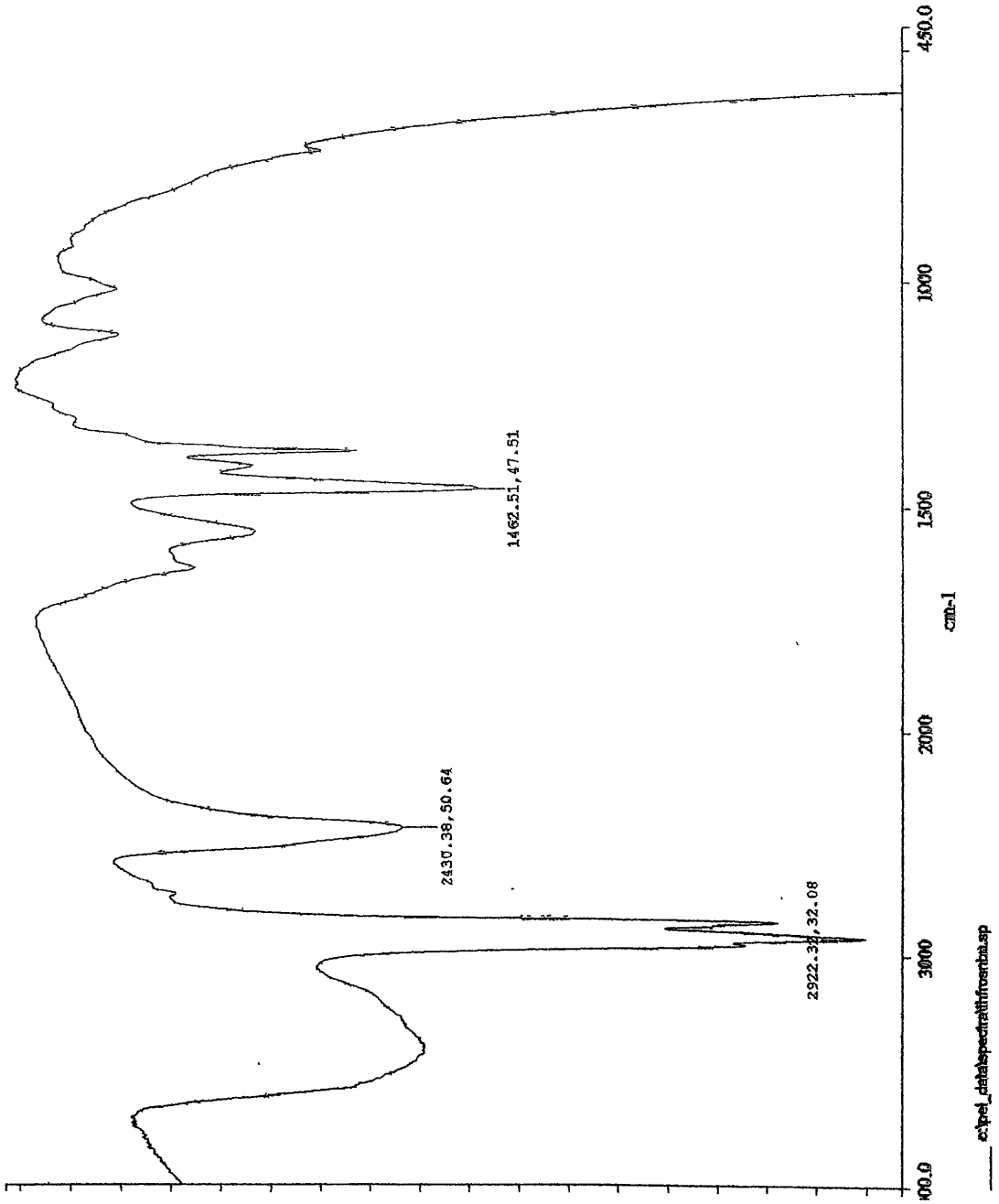
^{1}H NMR of $K_4[B_{20}H_{17}O(CH_2)_5S(CH_2)_3CH_3]$



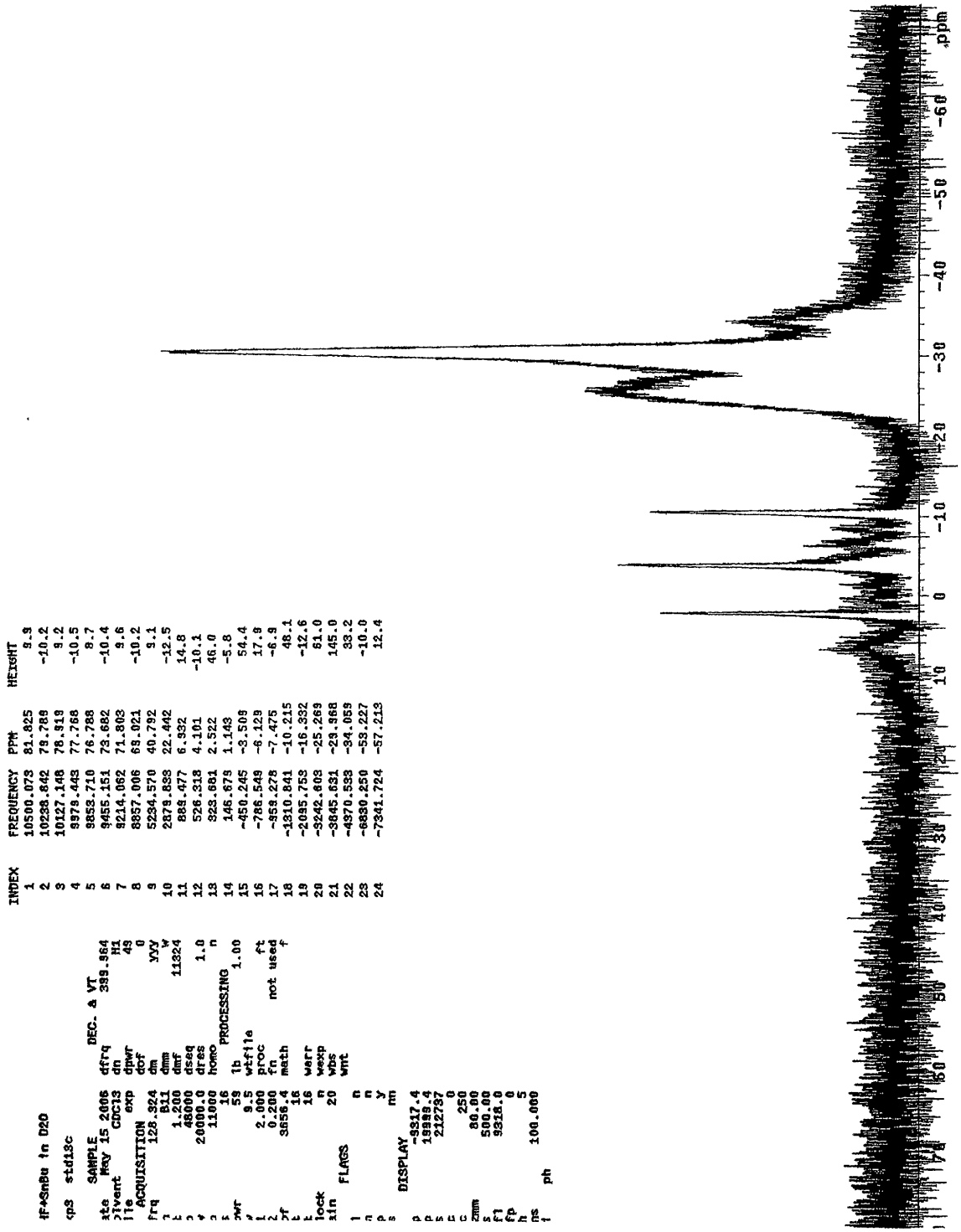
^{13}C NMR of $K_4[B_{20}H_{17}O(CH_2)_5S(CH_2)_3CH_3]$



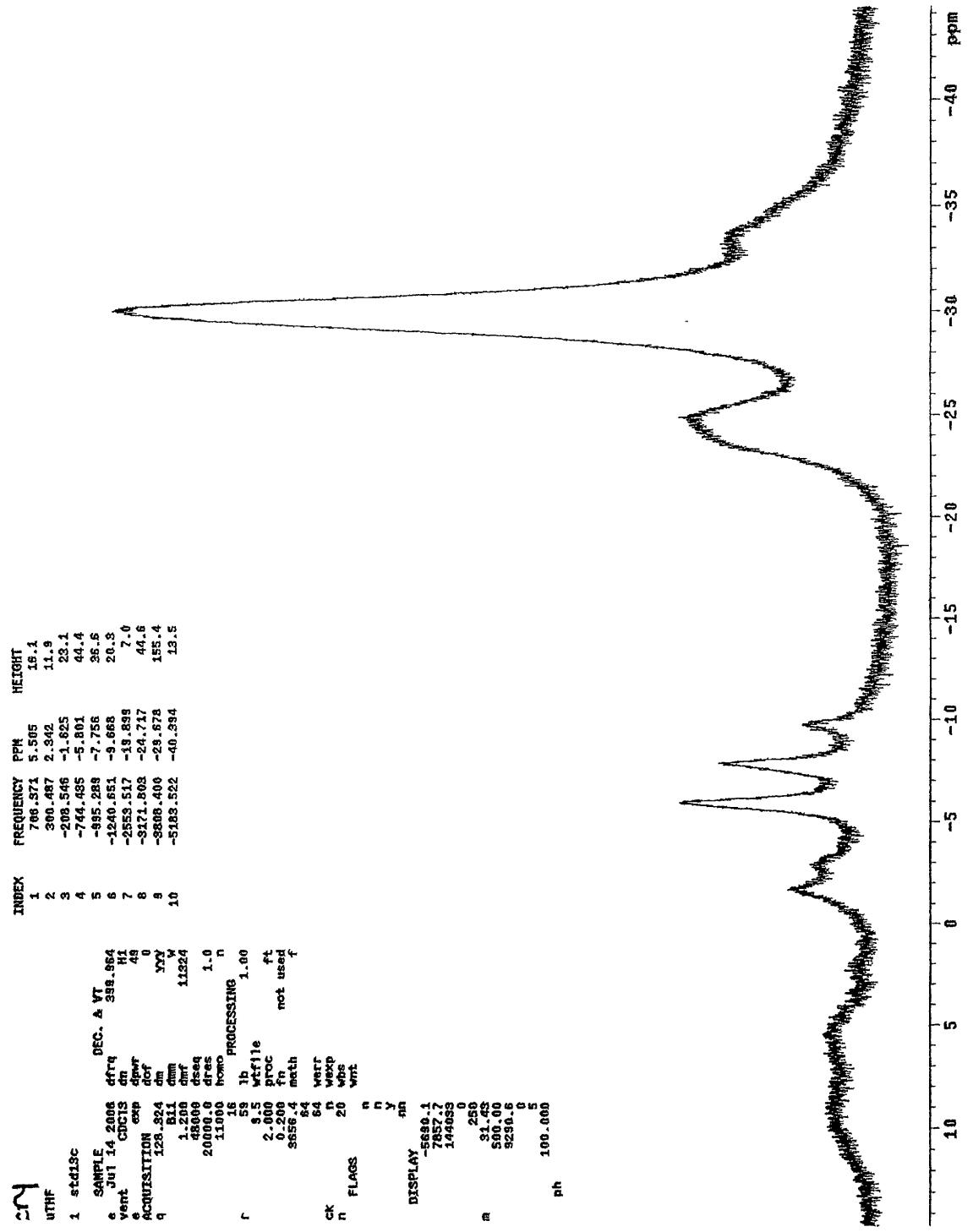
IR of $K_4[B_{20}H_{17}O(CH_2)_4S(CH_2)_3CH_3]$



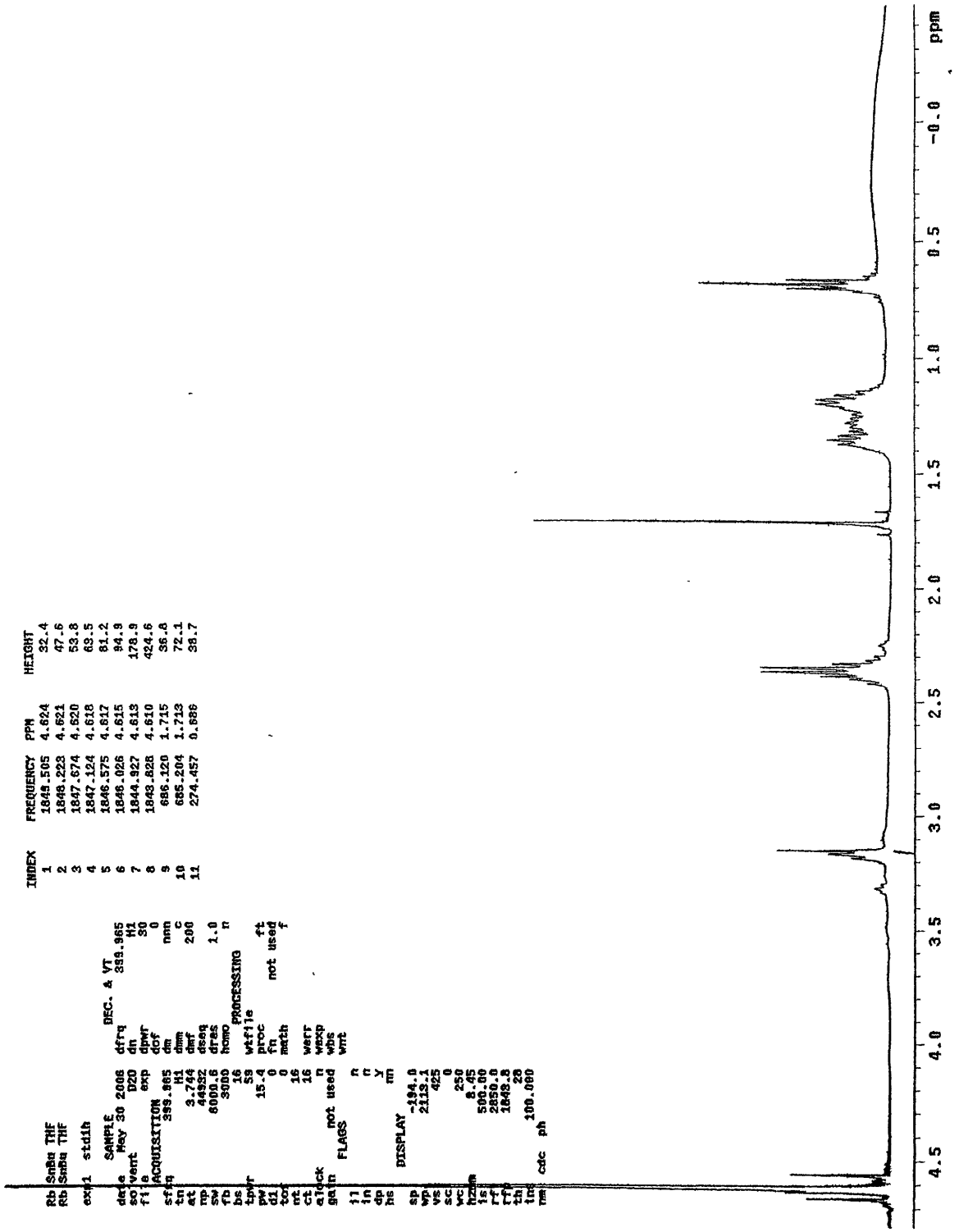
^{11}B NMR of $K_4[B_{20}H_{17}O(CH_2)_4S(CH_2)_3CH_3]$



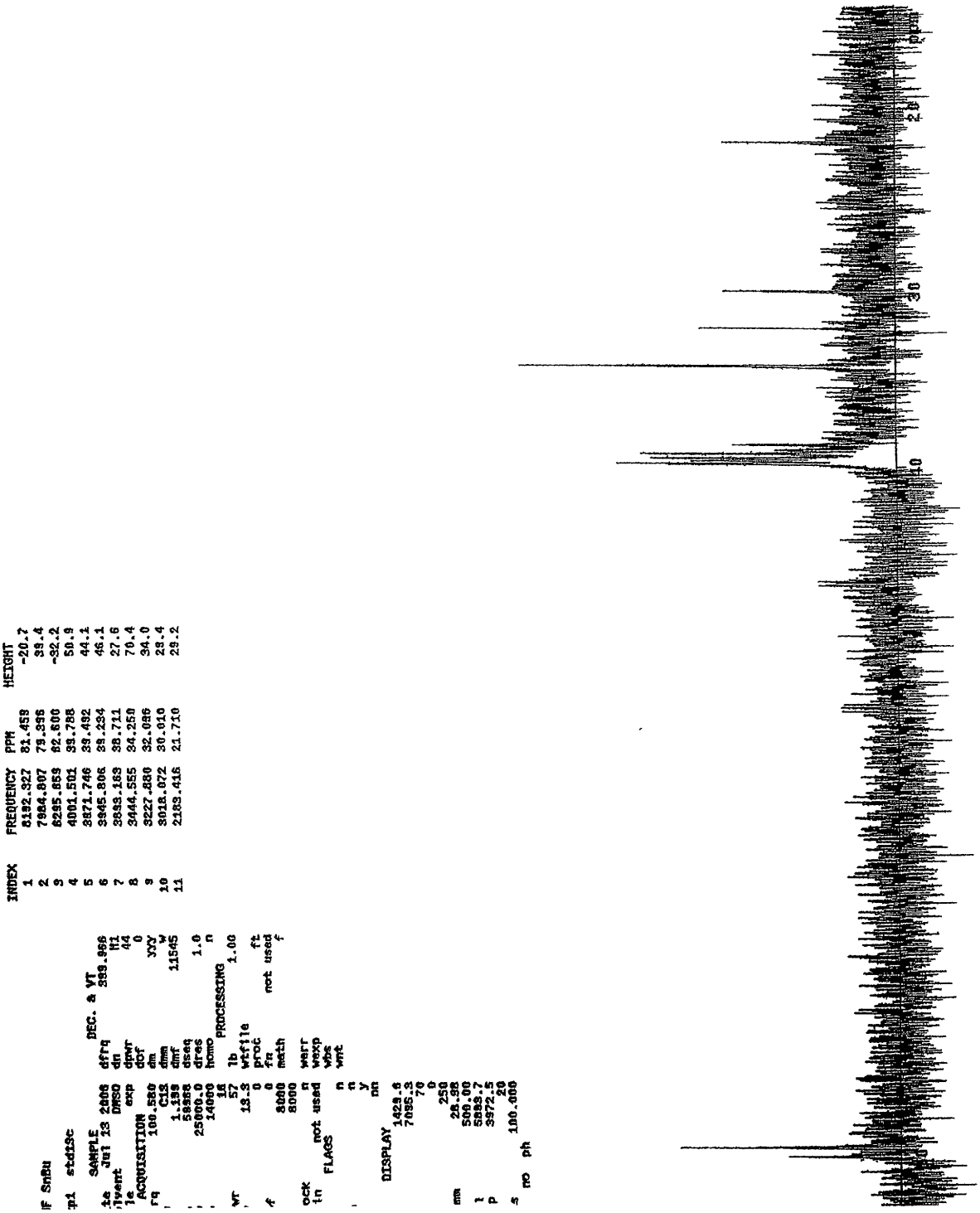
Recrystallized ^{11}B NMR of $K_4[B_{20}H_{17}O(CH_2)_4S(CH_2)_3CH_3]$



^{1}H NMR of $K_4[B_{20}H_{17}O(CH_2)_4S(CH_2)_3CH_3]$



^{13}C NMR of $K_4[B_{20}H_{17}O(CH_2)_4S(CH_2)_3CH_3]$



VITAE

Jacqueline Patricia Smits was born in Frankfurt Germany on August 13, 1982. She began her undergraduate studies at Texas State University-San Marcos in 2000, graduating with a Bachelors of Science in Chemistry in 2004. In 2004, she began Graduate School and, under the supervision of Dr. Debra A. Feakes, fulfilled the requirements for the degree Master of Science in Chemistry in 2006.

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This thesis was typed by Jacqueline Smits.