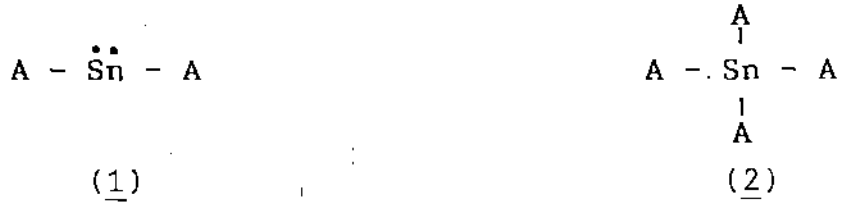
PART -- I SECTION - A

Preparation and characterisation (spectral and elemental) of a series of α,β-unsaturated (olefinic and acetylenic) triorganostannyl carboxylates and their regioselective reaction with mercury(II) salts.

Covalences of two and four would them be expected for these elements in neutral molecules. The two covalent state of tin, i.e., Sn(II) and Sn(IV) may be represented as in structure(1) and (2) respectively, where A is any covalently bound atom or group. These two states are not at all analogous



(1) (2)

chemically. Because of sp^3 hybridisation, the organometallic compounds of Group IV A are relatively stable and possess relatively low chemical reactivity. The marked increase in stability of R_4Sn compounds over R_2Sn types demonstrates the effect of increased hybridisation. Thus, the organic chemistry of tin is essentially restricted to the +4 oxidation state[2].

A bond between M-C, where M is carbon, there is possibility of forming double bond ($p\pi$-$p\pi$). When M substitutes other element of this group such as silicon, germanium, tin or lead, there is enough evidence that the d orbitals of these elements are used for bonding ($d\pi$-$p\pi$). A simple example illustrates this phenomenon. With the four acids of the type p-$R_3M.C_6H_4.COOH$, where M represents carbon, silicon germanium or tin, carbon is the most electronegative of the four elements and should enhance the acid strength to

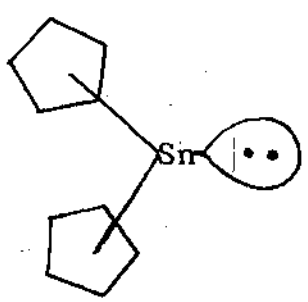
the greatest extent. Actually the carbon compound shows the lowest acid strength, indicating that $d\pi$-$p\pi$ bonding is operative in the other three compound[3].

Because of the considerable difference in electronegativity when M is shifted from carbon to silicon and other elements of this group, the polarity of the M-C bond increases. The increment is more as the M is descended in the group and the bond becomes more sensitive to attack by polar reagents[4]. In other words, the metal—carbon bond strengths decrease and the bond distances increase going down the group, resulting in progressively decreasing thermal stability.

Organotin compounds are defined as those that contain at least one Sn — C bond, the carbon atom being part of an organic group. The first reports of the existence of "Organic bodies of tin", as they were then known, appeared in 1852[5,6]. One was by Carl Lowig[5], the other by Edward Frankland[6]. The search to isolate a series of dialkyltin(R_2Sn) compounds in the second half of the 19th century was destined to be unsuccessful could only be established by experiment, and in the course of experimental studies of this point, there were a number of erroneous reports[7,8]. The isolation of diethyltin and diphenyltin are now known to be polymers of tin(IV), that is, $(Et_2Sn)_n$ and $(Ph_2Sn)_2$[9].

The search for organotin(II) species did, however, lead to an improvement in the indirect method of preparing tetraethyltin. In 1879, Frankland[10] studied the reaction between stannous chloride and diethylzinc, hoping by analogy with results obtained by Buckton[11] simply to displace the chlorides with ethyl groups. The product, however, was not diethyltin, Et_2Sn, but Et_4Sn. As a route to Et_4Sn, this reaction proved superior to Buckton's original method[11], which used $SnCl_4$. This new reaction remained the method of choice for preparing tetraalkyltins until the early years of the 20th century, when Pope and Peachey[12] first made use of the action of a Grignard reagent on stannic chloride. The early history of organotin chemistry has been recently reviewed by N. W. Nicholson[13].

However, organotin(II) species are known either where attached to bulky ligands[9,14] or where the organic substituent is cyclopentadiene[15], e.g., as in (3). Chambers and

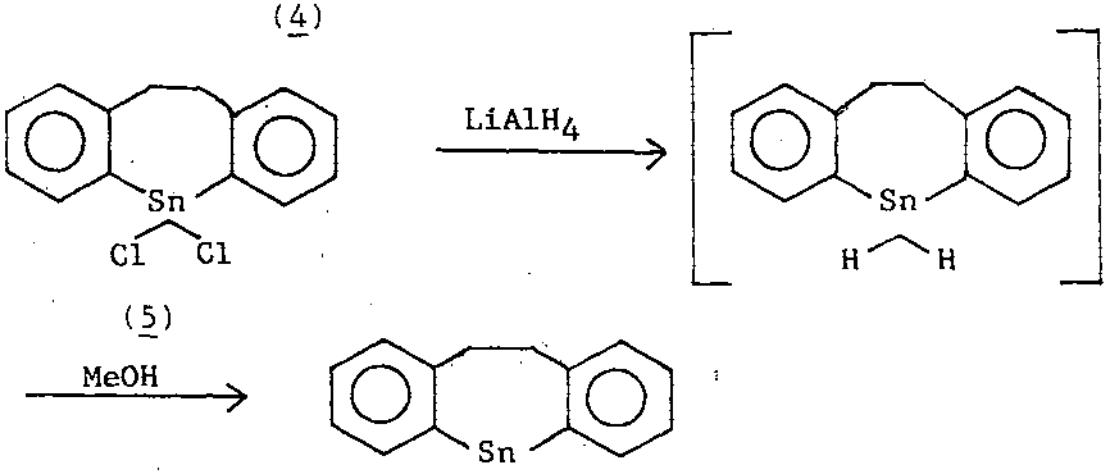


(3)

Scherer[16] prepared diphenyltin in the monomolecular form by warming diphenyltin dihydride(4) at room temperature. This reaction was also used to prepare 10, 11 dihydrodibenzo[b,f] stannoepin(6) from the corresponding tin dichloride(5) by reduction with $LiAlH_4$[17].

$$(C_6H_5)_2SnH_2 \longrightarrow (C_6H_5)_2Sn + H_2$$

(4)



(5)

(6)

The first review of organotin compounds was achieved in 1937 by Drause and Van Grosse[18]. Later the field of organotin chemistry was reviewed by Gilman et al. in 1960[4], with comprehensive tables of the compounds which were then known. In 1967, Richard Weiss[19] published his review of different class of organotin compounds with their properties and references. Afterwords, several monographs by J.J.Zuckerman(Ed)[20], by Newmann[9] and by Poller[21], and a multi-author work edited by A. K Sawyer[22] were published in 1970 and Davies and Smith in 1980[23a] and 1982[23b].

A volume of Houben-Weyl deals particularly with preparative method[24], and recent volumes of Gmelin have covered several classes of organotin derivatives[25]. Structural aspects of this class of compounds have been reviewed[26] and a comprehensive bibliography of X-ray diffraction studies is available from the International Tin Research Institute[27]. The use of organotin compounds in organic synthesis was reviewed by Pereyre in 1976[28].

Because of diverse applications in industry and in basic research, the chemistry of organotin compounds has gained considerable importance[23b,29]. Many interesting, versatile aspects of inorganic and organic tin chemistry have been unravelled by using the powerful array of physical techniques. Investigations can be performed by the general techniques such as UV[21], IR[21,30] ^{1}H-NMR[21,31], ^{13}C-NMR[32], Mass spectroscopy[33] and also by the specialised techniques of ^{119}m Sn Mossbauer Spectroscopy[21,23b] and ^{119}Sn NMR[23b,34] spectrometry. These two techniques provide complementary information on the structure of organotin molecule in the solid state and in solution. During the present work, application of these spectroscopic investigations(except ^{119}mSn Mossbauer Spectroscopy) have been carried out on several α,β -unsaturated tin carboxylates and other organotin compounds.

The ascension of organotin compounds into the domain of synthetic organic chemistry has been dramatically documented over the past decades[35-39]. In their central role

as reagents for the construction of C-C bond, they have demonstrated remarkable virtuasity in the myriad of reaction pathway available. Among these several stand out for their generality and utility such as 1) tin-lithium exchange[40], 2) transtion metal-catalysed coupling[41], and radical reaction[9,42]. Various aspects of electrophilicity of these organotin compounds, their stereoselection with respect to enantio-, diastereo- and regioselectivity have become the important and vital features for using these organotin compounds as reagents in synthetic organic chemistry[39].

While many different organotin derivatives engage in these processes, the allyl and vinyltins enjoy widespread applications due presumably to their enhanced reactivity and latent functionality (Our studies related to benzyltins have been presented in the **Part-II** of this dissertation). However, apart from these unsymmetrical tetraorganotins of the type $R'SnR_3$, organotin esters of organic carboxylic acids comprise one of the most important class of compounds in the ever expanding field of organotin chemistry.

Since a major part of the present work, embodied in **Part-I, (SECTION-A, B & C)**, included studies with several organotin carboxylates, earlier studies on this type of organotin compounds may be briefly reviewed with varying degree of details in respect of preparative modes, Structural chemistry, biological activities and their uses in synthetic

organic chemistry. The biocidal activities are discussed in the **SECTION-C** of this **Part-I** in connection with our studies[43] on fungicidal activities, phytotoxicity of several previously known and newly synthesised α,β - unsaturated tin esters.

I.A-2: Organotin Carboxylates :

The compounds containing -OCOR' groups bonded to tin are defined as organotin esters which may be either monomeric or polymeric and of three general types viz. $R_3SnOCOR'$, $R_2Sn(OCOR')_2$ and $RSn(OCOR')_3$, where R and R' may be same or different groups. Tin tetracarboxylates, $Sn(OCOR')_4$, are not organotin compounds in the strict sense of the term, that organotin compounds consist of at least one tin-carbon bond.

I.A-2.1: Preparative Methods :

Among the preparative methods of these organotin esters, the most common and important being reaction between organotin oxides (or hydroxides) and organic carboxylic acids or anhydrides (equations 1-3)[44].

$$R_3Sn\text{-}O\text{-}SnR_3 + 2R'COOH \longrightarrow 2R_3SnOCOR' + H_2O \quad .....(1)$$

$$R_3Sn\text{-}O\text{-}SnR_3 + (R'CO)_2O \longrightarrow 2R_3SnOCOR' \quad .....(2)$$

$$R_2SnO + 2R'COOH \longrightarrow R_2Sn(OCOR')_2 + H_2O \quad \ldots\ldots (3)$$

Esterifications are usually achieved by azeotropic dehydration of the reactants in boiling benzene or toluene, using a Dean-Stark seperator. Alternatively, the reactants are heated in neat mixture until the evolution of water ceased, e.g., (equation 4)[45].

$$(Bu_3Sn)_2O + 2\text{-}o\text{-}HO\text{-}C_6H_4\text{-}COOH \xrightarrow[\text{Neat mixture}]{100\text{-}110^\circ C} 2\text{-}o\text{-}OH\text{-}C_6H_4COOSnBu_3 + H_2O \quad \ldots\ldots (4)$$

Another general method involves the reaction of organotin halides with metal salts of carboxylic acids[46] or organotin sulfides with silver salts of carboxylic acids[47] (equation 5).

$$R_{4-n}SnX_n + mM(O_2CR')_q \longrightarrow R_{4-n}Sn(O_2CR')_n + mMX_q \quad \ldots\ldots (5)$$

X = halogen or sulfer, and

M = Na, K, Ag, Pb or Tl.

Organotin carboxylates are prepared by direct reaction of tetraorganotins with metal salts of carboxylic acids[48] as well as the cleavage of one or more organic groups from tetraorganotins by carboxylic acids[48,49] (equation 6).

In the acidolysis reaction (equation 6), vinyl groups are cleaved more readily than saturated alkyl groups, but less readily than phenyl[4], successive groups are lost with increasing difficulty. Tetraallyltin is more reactive than tetravinyltin[50]. Tetramethyltin is found to react with mercury(I) acetate in methanol at room temperature to form trimethyltin acetate (equation 7)[51].

$$R_4Sn + n\ R'COOH \longrightarrow R_{4-n}Sn(OCOR')_n + n\ RH \quad \ldots(6)$$

$$2Me_4Sn + Hg_2(OCOCH_3)_2 \longrightarrow 2Me_3SnOCOMe + 2Hg + C_2H_6 \quad \ldots(7)$$

Another method includes the reaction between organotin hydride and carboxylic acid with evolution of hydrogen, as shown in equations (8, 9)[52].

$$Bu_2SnH_2 + 2\ MeCOOH \xrightarrow[Et_2O]{4.5h} Bu_2Sn(OCOMe)_2 + 2H_2 \quad \ldots(8)$$

$$Ph_3SnH + EtCOOH \xrightarrow[60°C\ /3h]{Et_2O} Ph_3SnOCOEt + H_2 \quad \ldots(9)$$

Muettertin et al.[53] showed that organotin halocarboxylates, $R_2Sn(X)OCOR'$, may be prepared conveniently by heating together, in an inert solvent, equimolar proportion of a dihalide and dicarboxylates (equation 10).

$$Bu_2SnBr_2 + Bu_2Sn(OCOMe)_2 \longrightarrow 2\ Bu_2Sn(Br)OCOMe \quad ....(10)$$

Finally, during the present study, we developed a method by which alkyl or aryl esters (carboxyl group attached to primary or tertiary carbon atom) may be transesterified to triorganotin carboxylates (equation 11)[54].

$$R^1\text{-}COOR^2 + (R_3Sn)_2O \longrightarrow R^1\text{-}COOSnR_3 + R^2OSnR_3 \quad ...(11)$$

The details of this procedure have been described in Part-I, SECTION-B of this dissertation.

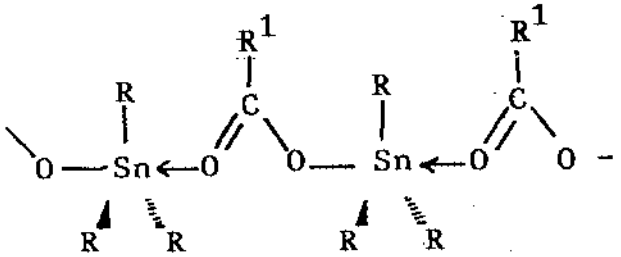
Several other methods are known, but including the methods described in equations (8-10) are not used extensively from preparative point of view.

I.A-2.2: Structure and Reactivity :

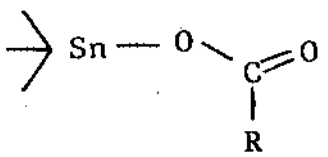
The structure of the organotin carboxylates have been determined by spectroscopy in solution phase as well as in solid phase and by crystallography in solid phase. IR and NMR spectroscopy have been extensively used to investigate structure of organotin esters.

The organotin carboxylates are known to exist in polymeric associated form, as in (7a) in the solid phase. This

chain polymer, involving bridging carboxylate groups and planar or near-planar R_3Sn moieties, has been demonstrated crystallographically for $Me_3SnOCOMe$[55], $Me_3SnOCOCF_3$[55], $Me_3SnOCHO$[56], $Bz_3SnOCOMe$[57] and $(CH_2{=}CH)_3SnOCOCH_3$[58]. Sterically



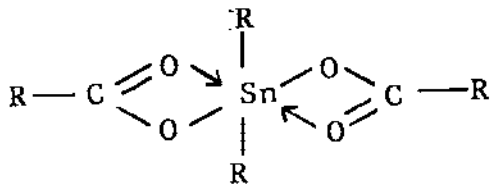
In the solid state (7a)



In dilute solution (7b)

hindered groups, however, prevent this association e.g., Alcock et al.[59] showed that $Cy_3SnOCOMe$ is present as monomer with the tin atom occupying a distorted tetrahedral geometry.

Okawara et al.[60] and several other workers[60c] investigated the structural aspects of triorganotin carboxylates by infrared and far-infrared spectroscopy in the solid state and in solution phase. They came up with the conclusion that on dilution of the associated triorganotin carboxylates in organic solvents usually produces oligomeric and finally monomeric species containing tetrahedral tin atom and free ester carbonyl functionality (7a & 7b)[60,61]. Dialkyltin dicarboxylates were suggested to be monomeric with hexacoordinate tin(8)[62].



(8)

From proton magnetic resonance data on organotin carboxylates, attempts have been made to correlate tin-proton coupling constants with the structures of these compounds and it is now generally accepted that the values of $J(^{119}Sn\text{-}C\text{-}H)$ increase with increasing percent s-character of the Sn-C bond[63]. However, carbon-13 spectroscopy has certain advantages over proton spectroscopy in the elucidation of structure of organotin esters[64]. For example; (i) the differences in the coupling constant $^{1}J(C\text{-}Sn)$ are much greater than those in $^{2}J(H\text{-}Sn)$; (ii) since the carbon of the alkyl or aryl group is directly bonded to tin, the variations in $^{1}J(C\text{-}Sn)$ more accurately reflect rehybridisation at the tin atom than do those in $^{2}J(H\text{-}Sn)$; (iii) for alkyl groups like propyl, butyl etc., it is possible to measure $^{1}J(C\text{-}Sn)$ accurately where $^{2}J(H\text{-}Sn)$ can not be measured under normal conditions; (iv) for such long-chain alkyl groups the identity of the compound and within limits, its purity can be established without doubt.

Of the ten naturally occuring isotopes of tin, only ^{119}Sn(abundance 8.58%), ^{117}Sn(abundance 7.57%) and ^{115}Sn (abundance 0.34%) have a nuclear spin $I=\frac{1}{2}$ and are, therefore,

amenable to study by NMR spectroscopy. In practice, the isotope of choice is usually ^{119}Sn, due to its higher abundance and its greater sensitivity to NMR detection.

Early measurements of ^{119}Sn chemical shifts were carried out by the heteronuclear double resonance technique[65], more recently, the advent of pulsed Fourier Transform (FT) technique enabled high quality ^{119}Sn NMR spectra[34]. The ^{119}Sn chemical shifts values alongwith the $^{n}J(^{119}Sn-^{13}C)$ data have been used to describe the structure of organotin compounds, the coordination number of tin etc. In the recent years, solid phase NMR spectroscopic data have been used to assign structure and coordination number of tin of several organotin esters[66-69].

Since a vast literature on the structure of organotin carboxylates were covered in the review written by Davies et al.[23b] and on ^{119}Sn-NMR spectroscopy by P. J. Smith & A. P. Tupciauskas[34a] and by B. Wrackmeyer[34b], it seemed reasonable to discuss the literature observations (including the recent works) only pertaining to our present work, wherever necessary.

With regard to reactivity of Sn-C bond, the electronegativity of C and Sn are 2.5 and 1.8 (in the Pauling scale) respectively indicating highly covalence in nature. However,

Sn-C bond can readily participate in ionic reactions through polarisation, where the carbon acts as a nucleophile and the tin atom acts as an electrophilic centre. On the other hand, the bonds between tin and heteroatoms (Sn-X, where X=N, O, F, Cl, Br etc.) are thermodynamically quite stable, but are chemically highly labile and readily participate in various substitution reactions. The large size of tin atom (covalent radius 1.4A°), the greater polarisability of the Sn-X bond relative to that of C-X bond and the possible participation of the tin 3d orbitals appear to be the major factors responsible for the greater ease of substitution reaction at tin than at carbon[35]. In view of this, several workers have utilised organotin compounds in modern organic synthesis. The synthetic efforts directed towards the utilisation of organotin carboxylates are presented briefly in the next few pages.

The thermal decarboxylation of triorganotin esters[30] was utilised in the preparation of unsymmetrical tetraorganotin compounds of the type $R'SnR_3$, where the R—Sn bond formation was taken place. Trialkyltin formate, however, led to the formation of trialkyltin hydride with the formation of Sn-H bond (equation 12)[71].

$$H\text{-}COOSnR_3 \xrightarrow[(R = Pr,\ Bu)]{100\text{-}170^\circ C} R_3Sn\text{-}H + CO_2 \quad \ldots\ldots \quad (12)$$

$$R_3SnO\text{-}CO\text{-}C{\equiv}C\text{-}CO\text{-}O\text{-}SnR_3 \xrightarrow[(R=Et,\ Pr,\ Bu)]{\sim 160^\circ C} R_3Sn\text{-}C{\equiv}C\text{-}SnR_3 + 2CO_2 \quad [72]$$

$$Ph\text{-}C{\equiv}C\text{-}CO\text{-}OSnBu_3 \xrightarrow{\sim 60^\circ C} Ph\text{-}C{\equiv}C\text{-}SnBu_3 \quad [71]$$

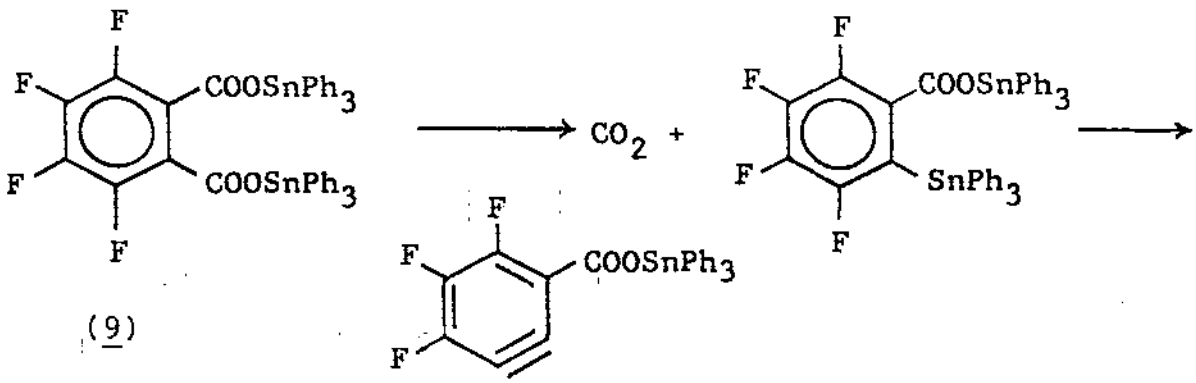
van der Kerk and Luijten[73] showed that organotin compounds containing a cyanomethyl group attached to the tin atom could be prepared by heating trialkyltin or triphenyltin cyanoacetates. e.g.,

$$NC\text{-}CH_2\text{-}CO_2SnPh_3 \xrightarrow[\text{vacuum}]{140^\circ C/\text{under}} \underset{49\%}{NC\text{-}CH_2\text{-}SnPh_3}$$

In 1977, Deacon and Farquharson[74] prepared several polyfluorophenyl stannanes utilising this thermal decarboxylation in boiling pyridine. They also reported that thermal decomposi-

$$RCOOSnPh_3 \xrightarrow{Py/\text{boiling}} R\text{-}SnPh_3 + CO_2$$
$$(R = C_6F_5,\ p\text{-}MeO.C_6F_4,\ p\text{-}EtOC_6F_4 \text{ or } o\text{-}HC_6F_4)$$

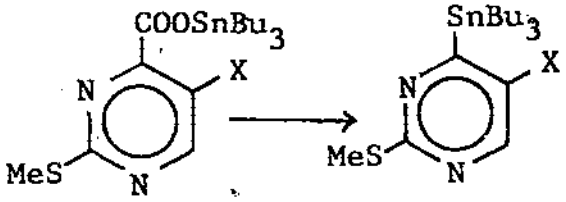
tion of bis(triphenyltin) tetrafluorophthalate(9) gave an insoluble high melting solid, identified as Ph_3SnF by IR spectroscopy[75]. They proposed a possible reaction path comprising hemidecarboxylation[76] followed by elimination of the fluorine ortho to the bulky triphenyltin substituent[77]. However, the aryne(10) was not isolated or characterised[74].



(9)

(10)

Recently, K. Undheim and his collaborators[78] reported that the decarboxylation can be catalysed by Pd(II) complex and thereby getting better yield, e.g., thermal decarboxylation of the 2-methylthio derivatives(11) and (12) in refluxing anisole gave the 4-stannylated products in only 30-40% yield. Free-radical conditions, AIBN and illumination did not significantly affect the yield. Metal catalysis did influence the reaction; Pd(II) complexes were best. Use of bis (acetonitrile) and bis(triphenylphosphine) palladium(II) dichloride increased the yield of 4-stannylated product up to 70% after refluxing in anisole for 4-6 hours.



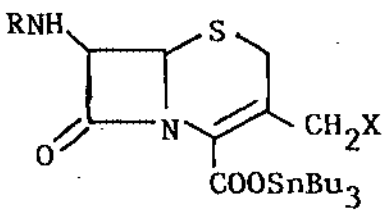
(11) X = Cl

(12) X = Br

Reaction condition	Yield
(i) 190-225°C, neat at 10mm Hg/3hr.	30-40%
(ii) $(MeCN)_2PdCl_2$/ PhOMe/ 4-6hr.	70%

Tris(triphenylphosphine) rhodium(I) chloride, however, which is a decarbonylation catalyst, had only a slight effect on the decarboxylation reaction ; yield 50%.

As a masking group of organic carboxyl function, triorganostannyl(-SnR_3) moiety has certain advantages over alkyl group (discussed in SECTION-B, p.106). Conversion of 7-amino cephalosphoranic acids to their tributylstannyl esters(13)., by treatment with bis(tributyltin) oxide in refluxing benzene increased the solubility of these acids in the reaction medium, and at the end of a reaction sequence involving the ester(13), the free acid was reprecipitated by hydrolysis.

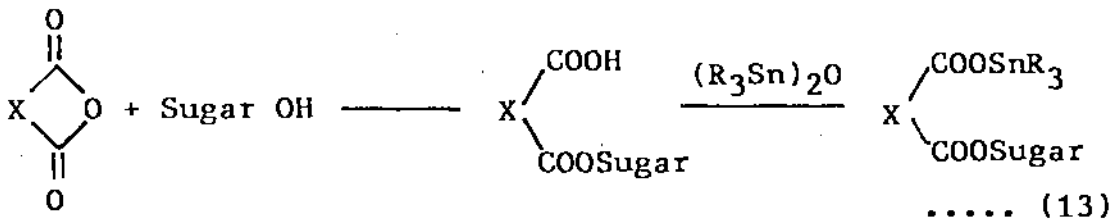


R = R^1CO or H

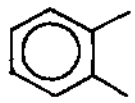
X = $MeCO_2$, N_3 or H

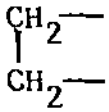
(13)

In a recent study, Poller et al.[79] reported that direct phthalation and succinylation of sugars gave mono esters (14, 15) which were converted to stannyl sugar esters (16, 17) having enhanced biocidal properties (equation 13).

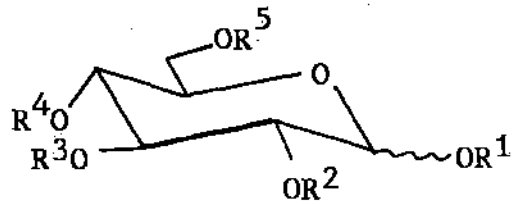


..... (13)

X =  (14), Monoester (16), Diester

X =  (15), Monoester (17), Diester

In compounds (18-22), they demonstrated that a tributyltin function can have a dual role, first to activate sugar hydroxyl groups towards phthalation and second to confer high biocidal activity on the product.



(18) $R^1 = R^4 = R^5 = Bu_3Sn$, $R^2 = R^3 = H$;

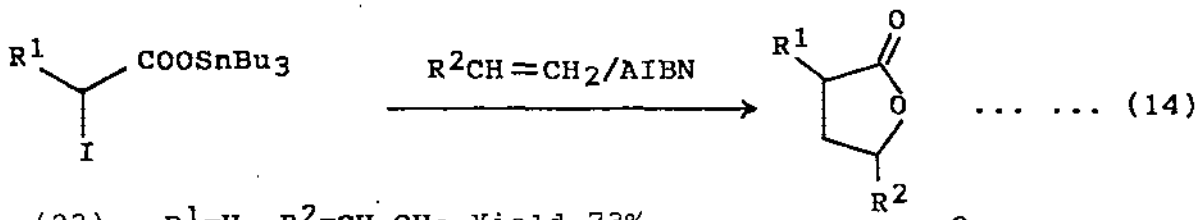
(19) $R^1 = R^5 = O\text{-}COC_6H_4COOSnBu_3$, $R^2 = R^3 = R^4 = H$;

(20) $R^1 = R^5 = O\text{-}COC_6H_4COOMe$, $R^2 = R^3 = R^4 = Ac$;

(21) $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = O\text{-}COC_6H_4COOSnBu_3$

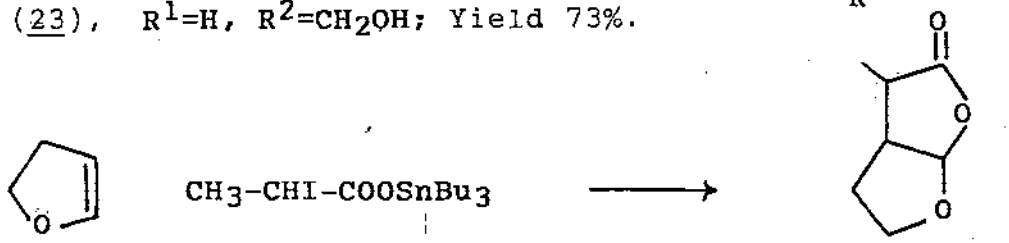
(22) $R^1 = R^2 = R^3 = R^4 = Ac$, $R^5 = O\text{-}COC_6H_4COOMe$;

Lactones are important functionality incorporated in many natural products. Electron-rich alkenes are found to react with α-iodo triorganotin esters in the presence of radical initiator to produce γ-lactone as depicted in equation (14). AIBN was found to be more effective and convenient than any other initiation procedure[80].



... ... (14)

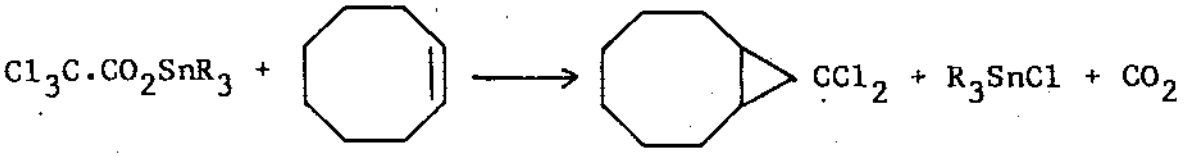
(23), R^1=H, R^2=CH_2OH; Yield 73%.



(72%) (24)

According to authors, the process probably involved first the generation of a radical which then added to the alkene before cyclisation, with concomitant elimination of the tributylstannyl radical. Regardless of the mechanism, this reaction proved to be of high synthetic value. α-Bromo esters, however, gave lower yield of the lactone.

The organotin esters of haloacetic acid are known to produce carbenes. Seyferth and his associates[81] observed that organotin esters of trichloroacetic acid, when heated, were able to transfer dichloro carbene being reacted with unsaturated substrates (equation 15).



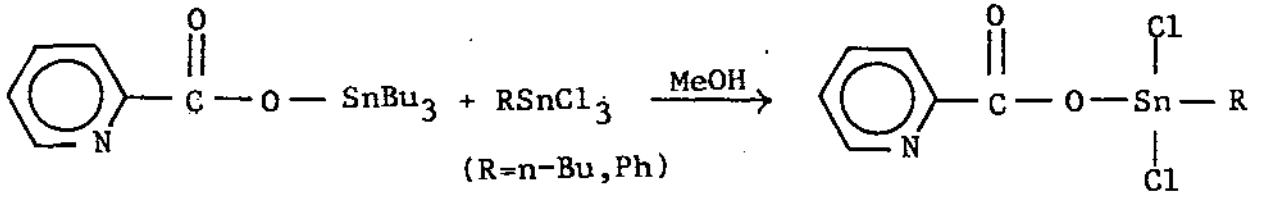
... ... (15)

Although it was not clear, the reaction might involve either R_3SnCl_3 as intermediate or decarboxylation and carbene transfer simultaneously in a concerted manner.

Mono-[82], di-[60c] and tri-[83] organotin carboxylates are known to undergo exchange reactions with other organotin compounds to yield mixed carboxylates derivatives (equations 16, 17).

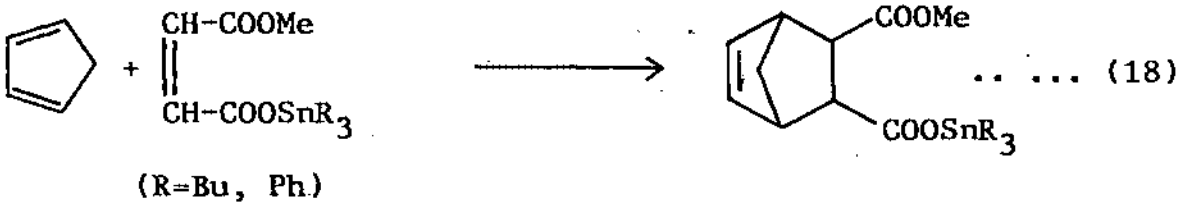
$$R_2Sn(OCOR^1)_2 + R_2SnX_2 \longrightarrow 2R_2Sn(OCOR^1)X \quad \ldots\ldots (16)$$

(X=halogen, OR, H etc.)

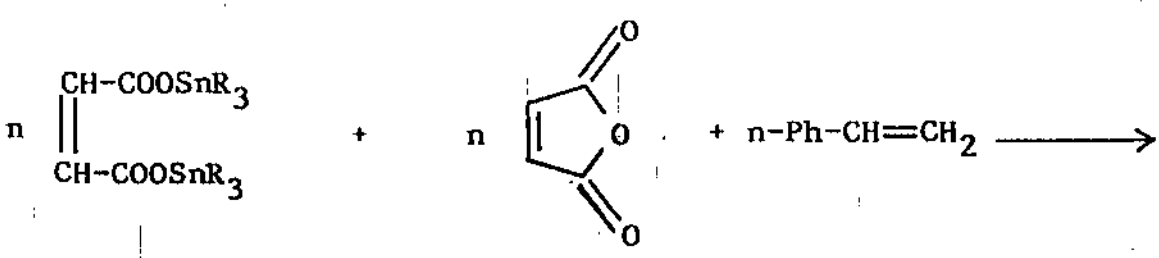


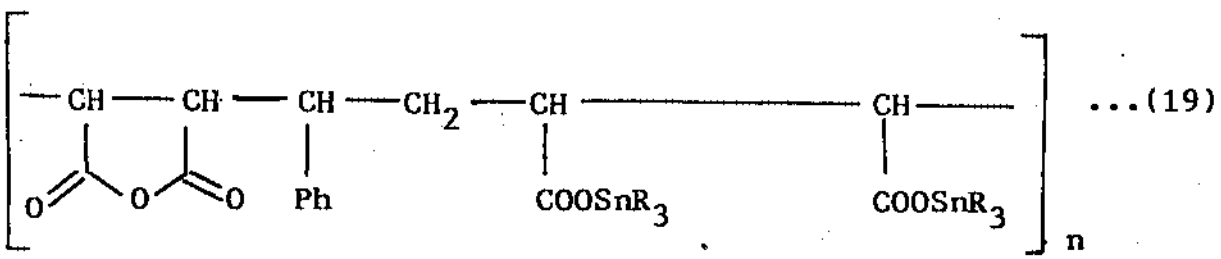
+ Bu_3SnCl ... .. (17)

Poller et al.[84] showed that the unsaturated organotin esters are capable of participating in Diels-Alder reaction as dienophile. For example, organotin alkyl maleates reacted with cyclopentadiene (equation 18). In some cases the tin esters were copolymerised to form polymers with pendant trialkylstannyl groups (equation 19).[85]



.. ... (18)





...(19)

The polymerisation reactions were achieved by the use of heat or free radical initiator and the resulting organotin polymers (where R=Bu or Ph) have important commercial outlets

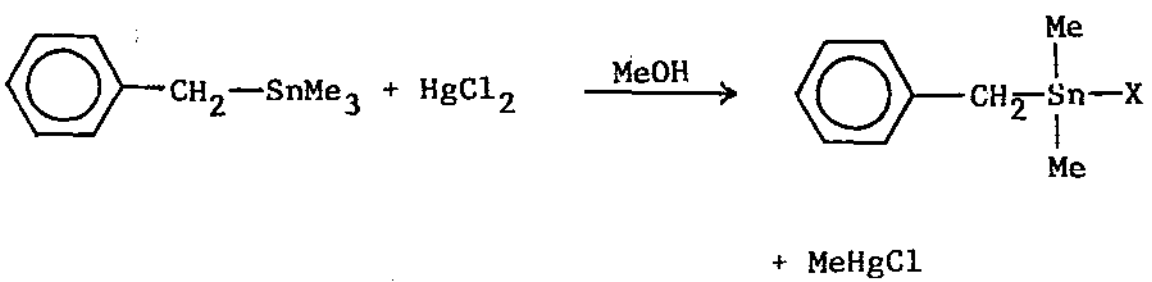
in biocidal paints[86] for protecting ship's hulls. Recently, Babu et al.[87] described the copolymerisation of functional and alkyl methacrylates with tributyltin methacrylates and showed that the presence of functional units in the copolymers can be utilised to selectively cross-link the polymers so that the rate of release of tin moiety can be controlled which is believed to have played a role in biocidic properties.

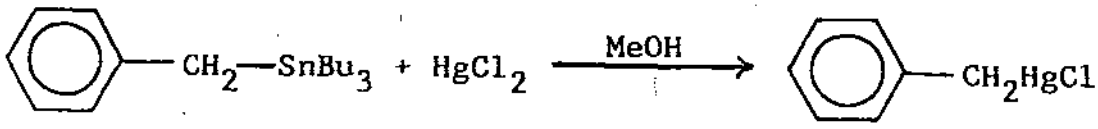
I.A-3: Present work: Background, Objective, Results and discussion

From the synthetic efforts directed towards the utilisation of organotin carboxylates delineated in the preceding pages, it is evident that apart from the broad spectrum of industrial applications of organotin esters[20,23b,29], such as, organo chemicals (fungicidal, antifeedants), antifouling biocides (in plants), disinfectants, PVC stabiliser, homogenous catalysts, anthelmintics etc., there are potentialities remain in the use of them in synthetic organic chemistry. The application of organotin carboxylates in modern organic synthesis continues to grow at an impressive rate because the tin esters are easily accessible in pure form, fairly stable, storable without special caution and they exhibit wide range of reactivity. Nevertheless, organotin carboxylates, in particular the triorganotin carboxylates are hydrolytically more

stable than triorganosilyl esters[35].

The action of electrophiles on the alkyltin compounds was studied in some detail. The relative reactivity of simple alkyl or aryl tins towards electrophilic reagents, like iodine, bromine and mercury(II) salts, was ascertained in the studies of Abraham et al.[88-90] and of several other workers[91-93]. In 1980, Abraham and his coworker[88] reported the sequence of reactivity of R-Sn bond in $R\text{-}SnR_3$ towards mercury(II) salts in methanol: Ph(1.4×10^5) > Me(430) > $PhCH_2$(11) > Et(1) > n-Pr(0.19) > n-Bu(0.17). The reactivity of benzyl group was found to be ten times more than that of the higher n-alkyl groups. In contrast, the methyl group was observed to be substituted from tin atom ca. forty times as rapidly as the benzyl group. Therefore, it was concluded that for benzyltrimethyltin, the methyl group should preferentially be removed at ca. one hundred twenty times (taking into account a statistical factor) faster the rate of benzyl group.





+ Bu_3SnCl

We were interested to compare this action of electrophilic reagent, mercury(II) salts on triorganotin ester, $R'SnR_3$, where the tin atom is bonded to hetero atom ($-O-\overset{\overset{O}{\|}}{C}-R''=R'$). In this area, Roy and Ghosh[94,95] from this department carried out a search during 1977-1978. They reported that triorganotin carboxylates upon treatment with mercury(II) salts resulted in the formation of polymeric tin-containing products alongwith the formation of corresponding acids, alkyltin halides, organomercuric halides etc. They described[95] this reaction as demetallation reaction and proposed the probable pathways, based on chemical evidence.

A)

1. $nR'COOSnR_3 + nHgX_2 \longrightarrow nR'COOSnR_2X + nRHgX$
2. $nR'COOSnR_2X + nR'COOSnR_3 \longrightarrow n(R'COO)_2SnR_2 + nR_3SnX$
3. $n(R'COO)_2SnR_2 + nHgX_2 \longrightarrow n(R'COO)_2SnRX + nRHgX$
4. $n(R'COO)_2SnRX + 2nHOH \longrightarrow [R'COOSnR(OH)_2] + nHX + nR'COOH$

$$R'COOSnR_3 + HgX_2 + H_2O \longrightarrow \frac{1}{2n}[R'COOSnR(OH)_2]_n + \tfrac{1}{2}R_3SnX + RHgX + \tfrac{1}{2}HX + \tfrac{1}{2}R'COOH$$

(Where (i) R=Ph ; R'=H ; X=Cl, (ii) R=Ph ; R'=H, CH_3, CH_2CH_3 ; X=Br, I and (iii) R=Pr, Bu ; R'=CH_3 ; X=Cl).

However, when R=Ph ; R'=CH_3, CH_2CH_3 and X=Cl, the reactions take the following course after the 3rd step of the above sequence (A):

B)

4. $n(R'COO)_2SnRX + nR'COOSnR_3 \longrightarrow n(R'COO)_3SnR + nR_3SnX$
5. $n(R'COO)_3SnR + nHgX_2 \longrightarrow n(R'COO)_3SnX + nRHgX$
6. $n(R'COO)_3Snx + 4nHOH \longrightarrow [Sn(OH)_4]_n + nHX + 3nR'COOH$

The overall reaction, therefore, is

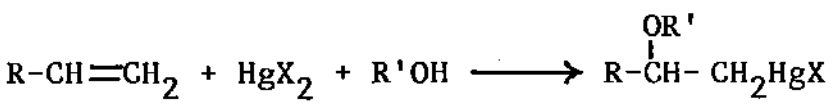
$$R'COOSnR_3 + HgX_2 + \frac{4}{3}H_2O \longrightarrow \frac{1}{3n}[Sn(OH)_4]_n + \frac{2}{3}R_3SnX + RHgX + \frac{1}{3}HX + R'COOH$$

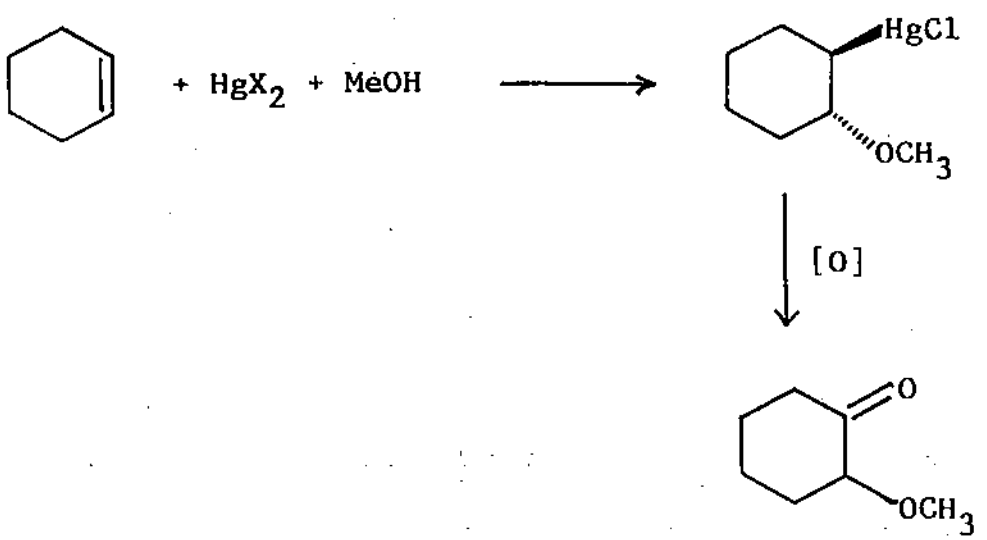
Roy and Ghosh[95] reasoned that the preference for the hydrolysis of substituted organotin esters(4th step in A) or substituted tin ester(6th step in B) could be attributed to the difference in acid strength of the carboxylic acids of the corresponding organotin carboxylates. Thus the more acidic formic acid ester underwent ready hydrolysis after the 3rd step(A) producing the tin polymer. On the other hand, triphenyltin acetate and propionate reacted with mercury(II) chloride to form the intermediates $(R'COO)_2SnPhCl$ [R'=CH_3, Et] that preceded the hydrolysis and underwent further

substitution to form the acid finally in the 6th step(B).

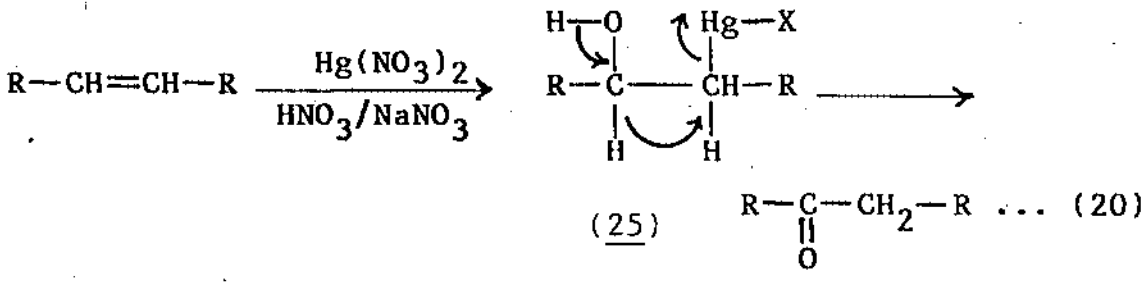
At this point, it occurred to us that the reaction of an unsaturated tin carboxylates with mercury(II) salts could be interesting since the unsaturated function is also capable of reacting with mercuric salts. There might be a competition between the unsaturation and tin ester function present in the same molecule to react with mercuric salts.

The reaction of an alkene with mercury(II) salt in presence of a solvent is commonly known as solvomercuration[96]. The resulting organomercurials have found many applications in organic synthesis[97,98]. For exmaple ;





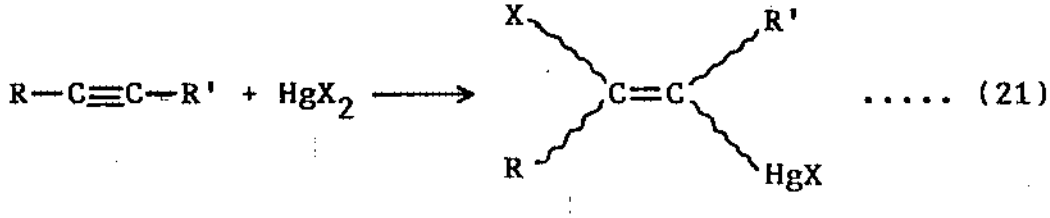
Sometimes solvomercuration of an alkene resulted in the formation of β-hydroxymercurial(25) which could be involved in solvolytic rearrangement producing ketones[99] (equation 20).



(25) $R-\overset{\overset{O}{\|}}{C}-CH_2-R$ ... (20)

In neutral or acidic media, terminal and internal alkynes often added to mercury salts to afford vinyl mercurials (equation 21).

Alkynes reported to add mercuric halides include acetylene[100], propyne[101], cyclooctyne[102], vinyl acetylene[101,103], alkynyl ethers[104], propergylic alcohols[105,106] and halides[105,107]. Mercuric acetate[108] and



..... (21)

X=F, Cl, OAc, SCN

thiocyanide[109] also added to a variety of internal alkyl or aryl acetylenes to generate vinyl mercurials. Several α,β -unsaturated ketones[110], acids[111,112] and esters[111,113,114] are known to undergo mercuration with Hg(II) salts. As for example, solvomercuration of α,β -unsaturated alkyl ester was utilised in the preparation of dl-serine[115].

$$CH_2{=}CHCO_2CH_3 \xrightarrow[CH_3OH]{Hg(OAc)_2} CH_3OCH_2\overset{CH}{\underset{}{}}(HgOAc)CO_2CH_3 \xrightarrow{KBr}$$

$$CH_3OCH_2CH(HgBr)CO_2CH_3 \xrightarrow{Br_2} CH_3OCH_2CHBrCO_2CH_3 \xrightarrow[H_2SO_4]{NaOH}$$

$$CH_3OCH_2CHBrCO_2H \xrightarrow{NH_3} CH_3OCH_2CH(NH_2)CO_2H \xrightarrow{HBr}$$

$$HOCH_2CH(NH_3Br)CO_2H \xrightarrow{NH_3} HOCH_2CH(NH_2)CO_2H$$

α,β -unsaturated acetylenic ester also undergoes solvomercuration, the organomercurial being treated with bromine to afford α,α-dibromo-β-keto ester[116].

$$R-C\equiv C-COOR' \xrightarrow[ii)\ Br_2]{i)\ Hg(OAc)_2} R-\overset{O}{\overset{\|}{C}}-\overset{Br}{\underset{Br}{\overset{|}{\underset{|}{C}}}}-COOR'$$

Recently, R. C. Larock had reviewed[98] in detail this mercuration reaction to prepare organomercurials and their uses in organic synthesis.

It, therefore, seemed appropriate to investigate the reaction of α,β-unsaturated stannyl esters with various mercuric salts with a view to figure out the nature of reactivity of both of these two functions (unsaturation and tin carboxylate group) towards mercury(II) salts.

I.A-3.1: Preparation and characterisation of α,β-unsaturated triorganostannyl carboxylates and their reactivity towards Hg(II) salts

The present study dealt with the preparation, characterisation(by spectroscopy, elemental analysis) of a series of unsaturated (both olefinic and acetylenic) tri-n-butyltin carboxylates and triphenyltin carboxylates and their reaction behaviour towards mercury(II) salts (HgX_2 ; X=Cl, OAc) under different reaction conditions.

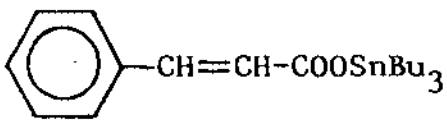
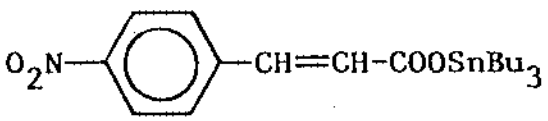
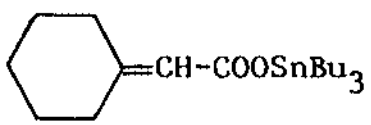
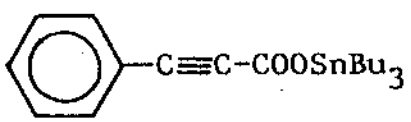
The unsaturated tin carboxylates(26-30 & 32, 33), (TABLE-I) were prepared in the usual procedure[21] from their corresponding acids with bis tri-n-butyltin oxide in refluxing benzene using a Dean-Stark water seperator. The cyclohexylidene acetic acid, however, afforded the corresponding tri-n-butyltin ester(31) while mixing the reagents at room temperature. Similarly, the triphenyltin carboxylates

(34-38) were prepared in the same procedure by using bis(triphenyltin) oxide. The esters were purified either by column chromatography or by crystallisation directly and obtained in good to excellent yield (see Experimental). They were characterised by spectral and elemental analyses data.

Infrared spectral data for organotin carboxylates are useful in comparing solid and solution state structures. The carbonyl group stretching frequency in the series of alkyl ester derivatives generally shifts to higher values with respect to free carboxylic acid carbonyl group. A lowering of ν(CO) would be expected if the carbonyl oxygen is involved in coordination. The influence of conjugated unsaturation would be effective equally both in non-coordinated or coordinated carbonyl function. Moreover, the asymmetric carboxyl stretch, $\nu_{asym}(CO_2)$ is most sensitive to structural changes in the carboxylate group coordination[117] and in addition the $\nu_{sym}(CO_2)$ frequencies are also considered.

The detailed infrared spectral studies of these organotin carboxylates(26-38) were not carried out since the present investigation was mainly aimed to study their nature of reaction toward electrophilic reagents, such as mercury(II) salts. However, the IR spectra of these tin carboxylates(26-38) were recroded in nujol and important observed frequencies were given in TABLE-I.

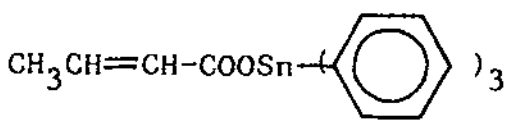
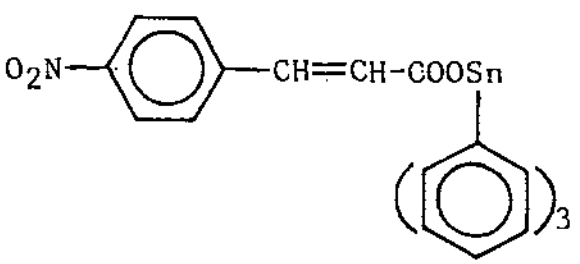
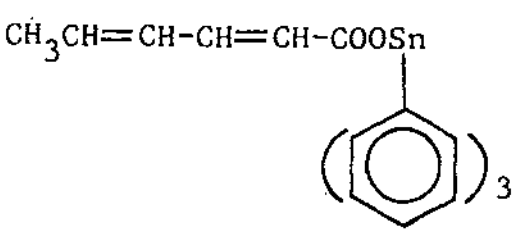
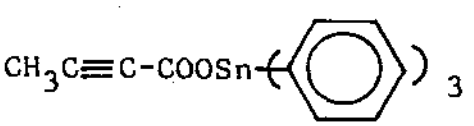
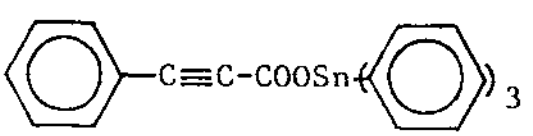
TABLE-I

No.	Triorganotin Carboxylates	IR spectral data	
		$\nu_{asym}(CO_2)$/C=C/ aromatic ring (in cm^{-1})	$\nu_{sym}(CO_2)$ (in cm^{-1})
(26)	$CH_2{=}CH\text{-}COOSnBu_3$	1645, 1655	1530, 1550
(27)	$CH_3CH{=}CH\text{-}COOSnBu_3$	1655	1535, 1555
(28)		1640	1540, 1555, 1580
(29)		1635	1550, 1563, 1595
(30)	$CH_3CH{=}CH\text{-}CH{=}CH\text{-}COOSnBu_3$	1600, 1625	1500
(31)		1625	1548, 1567
(32)	$CH_3C{\equiv}C\text{-}COOSnBu_3$	1560, 2250(C≡C)	1540
(33)		1560, [2125, 2310 (C≡C)]	1505

Contd...

Contd....

TABLE-I

No.	Triorganotin Carboxylates	IR spectral data	
		$\nu_{asym}(CO_2)$/C=C/ aromatic ring (in cm^{-1})	$\nu_{sym}(CO_2)$ (in cm^{-1})
(34)		1650	1515, 1545, 1570
(35)		1610, 1640	1590
(36)		1610, 1635	1575
(37)		1565, 2250(C≡C)	1510
(38)		1570 2220(C≡C)	1515

Assignments of bands associated with $\nu_{asym}(CO_2)$ mode of these compounds(26-38) were ambiguous owing to the presence of stretching vibration of both C-C double bond and the aromatic ring in the same region of the spectrum.

For compounds(26,27 & 34), the $\nu(CO_2)$ in nujol appeared at the regions 1650-1655cm^{-1} and 1530-1545cm^{-1}, while for tri-n-butyl cyclohexylidene acetate(31), the $\nu(CO_2)$ displayed at 1625, 1567 and 1548 cm^{-1}. The higher range could be attributable to $\nu_{asym}(CO_2)$ and the lower range was due to $\nu_{sym}(CO_2)$.Tri-n-butyltin cinnamate(28), p-nitro cinnamate(29) and sorbate(30) showed infrared absorptions at the regions 1625-1640cm^{-1} and 1500-1563 cm^{-1}, a lower range of frequency than that in stannyl acrylate(26) and crotonates(27 and 34). This could be explained probably on the basis of more conjugation available through the phenyl ring or the C-C double bond (in sorbate ester). The corresponding triphenyltin esters of p-nitro cinnamic(35) and sorbic(36) acids showed $\nu_{asym}(CO_2)$ at 1575-1590 cm^{-1}. An additional band appeared at 1610 cm^{-1}, in each compound, (35) and (36), could be assigned for phenyl ring or the C-C double bond.

Sorbic acid, for example, the $\nu_{asym}(CO_2)$ for acid was reported[118a] at 1690 cm^{-1}, its ethyl ester at 1710cm^{-1} and its tri-n-butyltin(30) and triphenyltin(36) ester displayed corresponding bands at the region 1600-1635 cm^{-1}. Similarly, $\nu_{asym}(CO_2)$ for p-nitro cinnamic acid was observed[118b] at 1690cm^{-1} while its tri-n-butyltin ester(29)

showed band at 1635 cm^{-1} and the corresponding triphenyl p-nitro cinnamate(35) gave $\nu_{asym}(CO_2)$ at 1640, 1610 cm^{-1} indicating a lowering of frequency than the acid. However, in 1988, Sharma et al.[69] reported that $\nu_{asym}(CO_2)$ for tri-n-butyl p-methoxy cinnamate was observed at 1585 cm^{-1}, in the solid state and suggested bridging bidentate nature for the carboxylate group[119,120]. This band had shifted to 1625 cm^{-1} in solution state, indicating cleavage of weak intramolecular bridges on dissolution. On the other hand, the triphenyltin p-methoxy cinnamate showed $\nu_{asym}(CO_2)$ frequency at 1620 cm^{-1}, both in solid and solution phase and they assigned that this was associated with a unidentate carboxylate group.

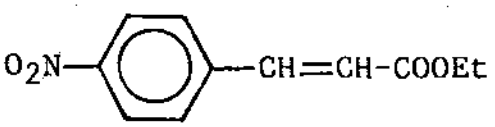
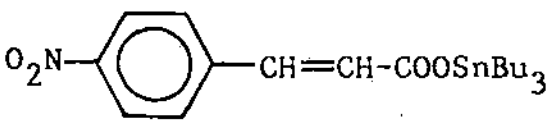
The α,β-unsaturated tin carboxylates, included in the present studies, displayed the $\nu_{asym}(CO_2)$ frequency at the region 1625-1655 cm^{-1}, in nujol. As compared to the observations of Sharma et al.[69] for triorganostannyl α,β-unsaturated (olefinic) carboxylates, it could be suggested the tri-n-butyltin esters(26-31 , 34-36) were probably associated with unidentate carboxylate group.

Since, we extended our investigation to α,β-unsaturated acetylenic tin carboxylates, the infrared spectra for the compounds (32, 33, 37 and 38) were also recorded in nujol mull and summarised in **TABLE-I.** The infrared absorption bands for C—C triple bond were found as expected[121], at the region

2220-2250 cm^{-1} for the esters (32, 37 and 38). However, compound(33) exhibited the C≡C band at 2310 cm^{-1}, 2125 cm^{-1}. The $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ bands were observed at the regions 1560-1570 cm^{-1} and 1505-1540 cm^{-1} respectively. Compared to α,β-unsaturated(olefinic) tin carboxylates, a bridging bidentate nature for the carboxylate group could be suggested. However, their infrared absorption in solution phase could provide more information regarding structure, which were not performed.

The proton and carbon-13 NMR chemical shifts values for these organotin esters(26-38) were assigned by comparison with the related compounds[63,64,69,122,123]. A comparative observation of a few proton chemical shifts, in particular the α- and β- olefinic hydrogens, between the stannyl and alkyl esters revealed no appreciable shifting. As for example, α- and β- protons for ethyl sorbate appeared[124] at δ 5.65 and δ 7.20 respectively, whereas those in tributyltin sorbate(30) resonanced at δ 5.79 and δ 7.15. Similarly, for ethyl crotonate the α- and β-protons appeared[125] at δ 5.82(d) and δ 7.00(m) respectively while the corresponding tri-n-tutyltin ester(27) exhibited doublet (with small allylic coupling) for α-H at 5.84 and multiplets for β-H at δ 6.84. In case of ethyl p-nitro cinnamate, the α- and β- protons displayed[125] at δ 6.60 and δ 7.73 respectively whereas, for the tri-n-butylstannyl p-nitro cinnamate(29), the α- and β-

protons appeared at δ 6.58 and δ 7.59.

Compound	α-H δ-ppm	β-H δ-ppm
$CH_3CH{=}CH{-}CH{=}CH{-}COOEt$	5.65	7.20
$CH_3CH{=}CH{-}CH{=}CH{-}COOSnBu_3$	5.79	7.15
$CH_3{-}CH{=}CH{-}COOEt$	5.82	7.00
$CH_3{-}CH{=}CH{-}COOSnBu_3$	5.84	6.84
	6.60	7.73
	6.58	7.59

For the studies of tin-proton coupling constant values it was suggested[63,126] that the J values are a measure of the percentage of s-character in the tin-carbon bond. However, as described earlier(p.13), the $^{n}J(^{119}Sn{-}^{13}C)$ values provide more accurate informations on the hybridisation of tin-carbon bond than the J values of ^{119}Sn-C-H bond.

For n-butyltin esters, the butyl protons appeared as follows : C_1, and C_3, protons in the range of δ 1.04-1.48 as a multiplets, the protons attached to C_2, displayed in the region of δ 1.48-1.74 as a multiplet and C_1, protons exhibited triplet in the range of δ 0.83-0.92. The chemical shifts for protons attached to carbons C_1,-C_4, were shown in TABLE-II The proton chemical shifts for the butyl protons were found to be consistent with the literature data[31,69].The other proton chemical shifts were given in the experimental section of this Part-I, SECTION-A.

For triphenyltin esters of crotonic(34), p-nitro cinnamic(35), sorbic(36), but-2-ynoic(37) and phenylpropynoic (38) acids, the aromatic protons appeared as multiplets and therefore, the individual aromatic proton chemical shifts could be assigned.

Carbon-13 magnetic resonance spectra of these organotin esters(26-38) were recorded and analysed during this study. The carbonyl carbon appeared in the range δ173.85-170.87 for the tin esters(26-30 & 34-36) whereas the corresponding carbon for compound(31) appeared at δ 177.50. In the series of acetylenic tin esters(32, 33, 37 & 38), the carbonyl carbon displayed in the range of δ 156.75-159.77, lower range than the olefinic compounds. This might be attributable to the presence of triple bond which made the

TABLE-II

Compound No.	$H-C_1$, & $H-C_3$, (as multiplet) δ ppm	$H-C_2$, (as multiplet) δ ppm	$H-C_3$, (as triplet) δ ppm
(26)	1.18-1.43	1.49-1.62	0.84(J=7.21 Hz)
(27)	1.20-1.39	1.54-1.74	0.85(J=7.25 Hz)
(28)	1.27-1.42	1.58-1.71	0.92(J=7.22 Hz)
(29)	1.15-1.48	1.57-1.71	0.90(J=7.23 Hz)
(30)	1.10-1.44	1.53-1.72	0.88(J=7.22 Hz)
(31)	1.04-1.41	1.48-1.66	0.83(J=7.22 Hz)
(32)	1.09-1.40	1.49-1.68	0.84(J=7.19 Hz)
(33)	1.20-1.46	1.58-1.70	0.91(J=7.21 Hz)

upfield shifting. The n-butyltin carbons($C_{1'}$-$C_{4'}$) were given in **TABLE-III** and the carbons of the aromatic ring(C_i-C_o-C_m-C_p) attached to tin atom were summarised in **TABLE-IV.**

As described previously, ^{13}C-[127,128] and ^{119}Sn-NMR had been used by several workers in the recent years to examine coordination geometry of the tin atom in some tri-n-butyltin compounds[64,69,122,129]. In 1984, Lycka and his associates[122] made an extensive investigation on ^{13}C- and ^{119}Sn-NMR spectra of a set of tri-n-butyltin(IV) compounds and their complexes in coordinating and non-coordinating solvents. They found that the chemical shifts $\delta(^{13}C)$ and $\delta(^{119}Sn)$ and the coupling constants $^{1}J(^{119}Sn-^{13}C)$ depend significantly on the coordination number of the tin atom and on the geometry of its coordination sphere. For compounds $n\text{-}Bu_3SnX$ as neat liquids and $CDCl_3$ solution the $^{1}J(^{119}Sn-^{13}C)$ values were obtained in the range of 326.7-386.7 Hz and they suggested that this range are typical of sp^3-sp^3 character of Sn-C bond in non-planar Bu_3Sn grouping. The tri-n-butyltin esters(26-33) included here showed $^{1}J(^{119}Sn-^{13}C)$ values in the range of 351.21-379.39 Hz. This was in good agreement with literature[122] values and thus suggested unidented tetrahedron structure for the n-butyl esters. Also the chemical shifts $\delta[^{13}C(1') - C(4')]$ in all the compounds were found(**TABLE-III**) within the ranges of tri-n-butyltin(IV) carboxylates reported[64,69,122,129] earlier. Again, the

TABLE-III

Compound No	C_1,	C_2,	C_3,	C_4,	$^1J(^{119}Sn-^{13}C)$	$^3J(^{119}Sn-^{13}C)$	^{119}Sn
	δ in ppm				in Hz	in Hz	δ ppm
(26)	16.46	27.64	27.00	13.60	351.84	64.66	-
(27)	16.41	27.67	27.02	13.62	356.12	64.91	-
(28)	16.57	27.72	27.09	13.68	353.66	65.41	-
(29)	16.65	27.82	27.03	13.63	379.39	64.53	+120.258
(30)	16.46	27.68	27.02	13.61	351.21	64.40	+106.576
(31)	16.41	27.83	27.00	13.62	355.42	64.03	+108.213 +100.281
(32)	16.81	27.69	27.02	13.56	353.98	65.66	+131.811
(33)	16.96	27.75	27.06	13.61	351.71	65.91	-

$^{3}J(^{119}Sn-^{13}C)$ coupling constant values were observed to be in the range of 64.03-65.91 Hz and compatible with published values. From the ^{13}C-NMR spectra available to us, we could not calculate the coupling constant values $^{n}J(^{119}Sn-^{13}C)$ when n=2,4. Furthermore, since we had to depend on the external sources for magnetic resonance spectra, the variation of chemical shift values with respect to concentration and various coordinating solvents could not be undertaken during this study.

However, a comparative table (TABLE-V) comprising of similar class of tri-n-butyltin carboxylates may be given here for corroborating our assigned structures.

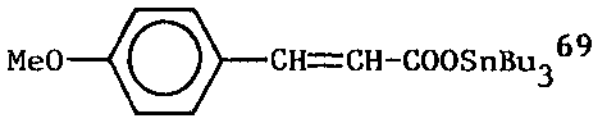
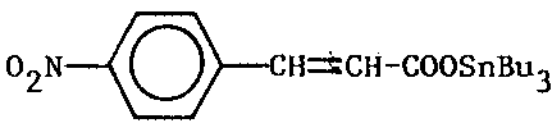
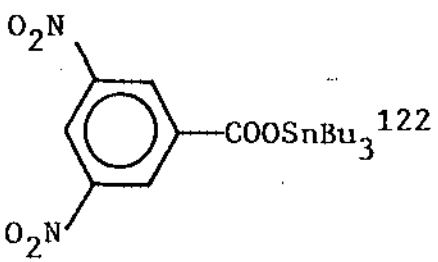
The chemical shifts $\delta(^{119}Sn)$ for a few tributyltin esters(29), (30) and (31) in $CDCl_3$ solution were found in the range δ 100.281 to 120.258 ppm, indicating tetrahedral arrangement[122] with four coordinate tin. However, the compound(31) showed two $\delta(^{119}Sn)$ values at 108.213 and 100.281 ppm.

The important ^{13}C- and ^{119}Sn-NMR spectral data for triphenyltin esters(34-38) were compiled in TABLE-IV. The chemical shifts $\delta(^{13}C)$ of the carbon atoms in the ipso-positions of the phenyl groups varied over a range of §137.58 - 142.64. It was observed by Lycka et al.[123] that the

TABLE-IV

Compound No.	C_i	C_o	C_m	C_p	$^2J(^{119}Sn-^{13}C)$	$^3J(^{119}Sn-^{13}C)$	In ppm
	δ in ppm				in Hz	in Hz	$\delta_{(^{119}sn)}$
(34)	138.59	136.92	128.89	130.07	48.11	63.40	-182.664
(35)	138.04	136.93	129.06	130.37	48.30	63.65	-103.37
(36)	138.69	136.94	128.89	130.06	48.18	63.21	-160.846
(37)	142.64	136.08	128.34	128.96	45.66	74.28	-250.807
(38)	137.58	136.95	129.08	130.45	48.18	68.87	-

TABLE-V

Tri-n-butyltin Carboxylates	Solvent	C_1, C_2, C_3, C_4, δ in ppm				$n_J(^{119}Sn-^{13}C)$(Hz) n=1	n=2	n=3	^{119}Sn δ in ppm
	$CDCl_3$	27.56	27.73	26.88	13.45	-	-	-	+104.7
	$CDCl_3$	16.65	27.82	27.03	13.63	379.39	-	64.53	+120.258
	$CDCl_3$	16.57	27.39	26.61	13.11	351.6	22.0	66.0	+140.0

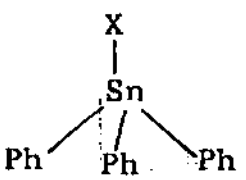
δ -values for the carbon at ipso-position shifted downfield for the five coordinate tin compounds from those for four coordinate tin compounds. It thus seemed probable that the Sn-C(phenyl) bond becomes more polar with increasing coordination of tin atom. Triphenyltin but-2-ynoate(37) showed the ipso-carbons at δ 142.64, downfield than the ipso-carbons at δ 137.58-138.69 and by comparison it was expected that compound(37) might possess penta-coordinate tin atom being coordinated with D_6-DMSO.

The value of coupling constant, reflecting spin-spin coupling of neighbouring atoms joined by a simple bond, depends mainly on the magnitude of the Fermi-contant term. In the case when none of the participating bonding atoms have a lone electron pair, the ^1J values are directly proportional to the s-character of their hybrid orbitals[130]. Therefore, the triphenyltin(IV) compounds (sp^2 hybrid carbon orbital) have higher ^1J values than analogous trialkyltin (sp^3 hybrid orbital) compounds. For the same reason and in accordance with Bent's rule[131] in all the compounds with a Ph_3Sn-halogen bond the $^1J(^{119}Sn-^{13}C)$ values decrease in the order Cl>Br>I. The proportion of s-character in the tin hybrid orbitals provides a satisfactory explanation of the obtained $^1J(^{119}Sn-^{13}C)$ values of the triphenyltin(IV) compounds of the suggested structural types.

Unfortunately, from our ^{13}C-NMR spectra of the

compounds(34-38) we could not be able to calculate the $^{1}J(^{119}Sn-^{13}C)$ values. However, $^{n}J(^{119}Sn-^{13}C)$; n=2, 3 values were calculated and found compitable with Lycka's[123] observations.

According to Lycka et al.[123], for a group of compounds of similar compositions, the $\delta(^{119}Sn)$ chemical shifts seemed to depend mainly on the total electron density on the central tin atom. The Ph_3SnX compounds having the values $\delta(^{119}Sn)$ shifted downfield in the range of -40 to -120 ppm compared with that of Ph_4Sn (^{119}Sn δ=-128.1) should have four-coordinate tin and tetrahedral arrangement of phenyl and X substituents [structural type (39)].



(Four-coordinate tin)
Tetrahedron

(39)

Although precise interpretation of the chemical shifts $\delta(^{119}Sn)$ of these tin carboxylates(34-38) studied here was difficult, in the case of triphenyltin p-nitro cinnamate (35), the p-nitro group being strongly electron withdrawing, reduced electron density on the central tin atom. Thus, the $\delta(^{119}Sn)$ value obtained for the tin cinnamate(35) at δ -103.37 came well within the range (-40 to 120 ppm)

observed by Lycka and his collaborators[123]. Keeping conformity with Lycka's observations it might be tentatively assumed that the possible structural arrangement for compound(35) would be tetrahedral with four-coordinate tin.

The ^{119}Sn chemical shifts for compounds triphenyltin crotonate(34) and triphenyltin butynoate(37) were exhibited at δ -182.664 and δ -250.807 ppm respectively. On the basis of the values of chemical shifts $\delta(^{119}Sn)$ and the coupling constants $^{1}J(^{119}Sn-^{13}C)$, Lycka et al.[123] concluded that the possible structural arrangements for compounds(Ph_3SnX) with (^{119}Sn) values (δ -180 to -200) and (δ -200 to -260) were characterised by having cis and trans trigonal bipyramidal geometry respectively with five-coordinate tin atom in both cases.

It was difficult to conclude the structural arrangement for compound(34) by only checking $\delta(^{119}Sn)$ value and moreover it was appeared at δ -182.664, merginally within the range of cis trigonal bipyramidal geometry(δ -180 to 200). However, as suggested earlier from the $\delta(^{13}C)$ value of the ipso-carbon (appeared downfield) for compound(37), the $\delta(^{119}Sn)$ value at -250.807 ppm also corroborated that the triphenyltin but-2-ynoate(37) should possess five coordinate tin atom and having trans trigonal bipyramidal geometry. However, for making a conclusion about the geometry and coordination number of tin atom of these α,β-unsaturated tin

carboxylates, a more detailed NMR investigation was necessary. Because of the lack of these instruments facility in this department we could not be able to undertake such measurements.

Having prepared the unsaturated triorganostannyl carboxylates(26-28), we turned our attention to investigate the reaction behaviour of these esters with mercuric chloride or mercuric acetate in different solvents. The nature of solvents employed in the present study included protic polar (methanol) aprotic polar(acetonitrile) and aprotic non-polar (benzene). Initially we attempted this reaction with a few α,β -unsaturated(olefinic) tri-n-butyltin esters(26, 27, 28, 29, 30 and 31). Among these esters the double bond was either unsubstituted(26), or β-monosubstituted(27), (28), or β-monosubstituted with extended conjugation through another olefinic C—C bond(30) or β,β-disubstituted olefinic and cyclic compound(31), (TABLE-I).

In all the cases, treatment with mercuric chloride in different solvents at different temperature afforded with the formation of butylmercuric chloride(BuHgCl) and the corresponding unsaturated acids alongwith other products as mentioned previously(p.25-26). The formation of BuHgCl and the carboxylic acid were beleived to take place by demetallation of the C-Sn bond with the eventual hydrolysis

of the resulting substituted intermediates. However, the C—C double bond was found to be unreacted from mercuration.

Treatment of these unsaturated tin carboxylates(26-31) with mercuric acetate also afforded with the formation of BuHgCl and the corresponding unsaturated acids alongwith other products and again, mercuration of the C—C double bond was not observed. The formation of BuHgCl in the case of mercuric acetate was probably occurred during washing of the reaction mixture with brine(aqueous NaCl solution).

Thus, it was found that the ester function underwent demetallation preferentially over the mercuration of C—C double bond when α,β-unsaturated stannyl esters were treated with mercuric chloride or mercuric acetate. Since C—C double bonds are quite reactive towards mercury(II) salts, as depicted earlier (p.27-29), we considered that this reaction might portend certain potentials in organic synthesis.

The C—C triple bonds are also reactive towards mercury(II) salts and therefore we extended our studies to examine the reaction of acetylenic unsaturated tin esters with mercuric salts.

The acetylenic compounds(32, 33) were treated with mercury (II) chlorides and mercury(II) acetates in different solvents. Similar observations were found by isolating the

corresponding acetylenic unsaturated acids and BuHgCl. However, in the case of tri-n-butylstannyl but-2-ynoate(32), immediately after the treatment of mercury(II) acetate in methanol, large amount of solid was appeared. The solid was filtered off after the reaction time (TABLE-VI) was over and the filtrate was concentrated and worked-up to furnish the but-2-ynoic acid in only 26% yield.

It was stated[95] that these demetallation reactions of triorganotin carboxylates with Hg(II) salts depend on the nature of the organic groups bonded to tin. We chose to observe the effect of phenyl group attached to tin atom. Accordingly, similar reactions were attended with both olefinic triphenyltin esters(34, 35, 36) and acetylenic triphenyltin esters(37, 38) and the results were summarised in **TABLE-VI.** Though, Roy and Ghosh[95] obtained some contrasting behaviour of mercuric acetate towards triphenyltin esters, we observed almost comparable results both by using mercuric acetate and mercuric chloride.

In terms of yield of the acids it seemed that two factors could be of importance, besides the role of solvents. Firstly, Abraham et al.[88] observed that in the electrophilic substitution at the carbon centre bonded to tin atom, the aryl-tin bond underwent cleavage more rapidly than the cleavage of alkyl-tin bond when treated with mercury(II)

TABLE-VI

Compound	HgX_2	Solvent	Time/Temp.	Yield(%) of BuHgCl or PhHgCl	Yield (%) of acid
(26)	X=Cl	MeOH	48h/r.t.	89	42
	X=Cl	CH_3CN	6h/reflux	86	40
	X=OAc	MeOH	48h/r.t.	84	30
	X=OAc	CH_3CN	6h/reflux	82	42
(27)	X=Cl	MeOH	48h/r.t.	40	45
	X=Cl	PhH	4h/reflux	88	43
	X=OAc	CH_3CN	4h/reflux	96	47
	X=OAc	PhH	4h/reflux	84	48
(28)	X=Cl	MeOH	48h/r.t.	96	45
	X=Cl	CH_3CN	6h/reflux	94	48
	X=OAc	MeOH	48h/r.t.	85	46
	X=OAc	CH_3CN	6h/reflux	90	49
(29)	X=Cl	PhH	4h/reflux	72	30
	X=OAc	MeOH	48h/r.t.	70	32
(30)	X=OAc	MeOH	48h/r.t.	71	50
	X=Cl	PhH	4h/reflux	76	43
	X=Cl	CH_3CN	6h/reflux	92	59

Contd...

Contd...

TABLE-VI

Compound	HgX_2	Solvent	Time/Temp.	Yield(%) of BuHgCl or PhHgCl	Yield (%) of acid
(31)	X=OAc	MeOH	48h/r.t.	73	48
	X=Cl	PhH	4h/reflux	78	44
(32)	X=Cl	CH_3CN	4h/reflux	55	28
	X=OAc	MeOH	48h/r.t.	50	26
(33)	X=OAc	MeOH	48h/r.t.	86	46
(34)	X=Cl	CH_3CN	4h/reflux	80	42
	X=OAc	MeOH	48h/r.t.	78	40
(35)	X=Cl	CH_3CN	4h/reflux	92	60
	X=OAc	MeOH	48h/r.t.	85	48
(36)	X=Cl	CH_3CN	4h/reflux	92	59
	X=OAc	MeOH	48h/r.t.	78	40
(37)	X=Cl	CH_3CN	5min/reflux	98	62
(38)	X=Cl	PhH	1h/reflux	90	58

salts. Similar observations were noticed by Roy and Ghosh[94,95] in the case of triorganotin carboxylates. However, Roy and Ghosh [95] suggested that the ultimate hydrolysis of the resulting substituted intermediates (reaction pathway, p.25-26) would be governed by the polarity of the Sn-O bond of the organotin carboxylates. The more polar bond, or in turn the more acid strength of the corresponding acid, contraction of the 'd' orbital of the tin atom should be more pronounced. This could enhance the probability of the attack of a nucleophile, e.g., water, at the tin atom resulting in carboxylate hydrolysis. They came up with this conclusion from their finding among the triphenyltin esters of formate, acetate and propionate. The triphenyltin formate, the corresponding acid being more acidic, reacted with $HgCl_2$ to produce the intermediate[$(HCOO)_2SnPHX$] and the latter was attacked by water and hydrolysed to form acid and polymeric tin compound. On the other hand, $CH_3COOSnPh_3$ and $CH_3CH_2COOSnPh_3$ produced the corresponding acids in better yield through the intermediate[$(R'COO)_3SnX$; ($R'=CH_3$, Et)] alongwith tin hydroxide and other compounds.

From our observations with phenyltin and n-butyltin carboxylate it seemed difficult to make any generalisation in respect of yields of the acids. On some occasion, such as triphenyltin p-nitro cinnamate(35), underwent demetallation upon treatment with Hg(II) salts furnishing the

corresponding acids in much better yield than tri-n-butyltin ester(29). This was in conformity with Abraham's observation[88] that the phenyl substituents attached to tin undergo electrophilic substitution faster than alkyl groups attached to tin. Similar observations were found in the case of acetylenic compounds. For example, the tri-n-butyltin but-2-ynoate(32) furnished the acid in 26-28% yield while its triphenyltin ester(37) gave 62% acid in much less time when treated with Hg(II) salts under identical conditions. On the other hand, the stannyl sorbates did not produce any remarkable reactivity difference between its n-butyl (30) and phenyl(36) esters. The formation of organomercuric chloride (BuHgCl or PhHgCl) was evident from the reaction sequence, reported by Roy et al.[95](p.25-26).

In respect of role of solvents used here, it may be pointed out that although methanol required a lower temperature to bring about the reaction, use of aprotic polar solvent, such as acetonitrile, afforded the acid in better yield in less reaction time in many cases (**TABLE-VI**).

I,A-3.2: Conclusion :

The present approach therefore revealed that while the alkyl esters of α,β-unsaturated(olefinic/acetylenic) acids, upon treatment with mercury(II) salts, undergo solvo -

mercuration of C—C double/triple bond, the corresponding stannyl esters, upon similar treatment, react preferentially and regioselectively at the ester function keeping the olefinic bond unreacted. Thus by using the stannyl esters we were able to protect the C—C double/triple bond and thereby providing a useful approach for preferential and regioselective reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts[136,137]. The result was the formation of the corresponding acids and alkyl mercuric halides and thus this reaction also provided a mild and neutral condition for hydrolysis of alkyl/aryl esters since these tin esters could be prepared from these alkyl/aryl esters[54] (SECTION-B of this dissertation).

Finally, it may be assumed that the phenyl group attached to the tin atom and the acidity of the carboxylic acid in aprotic polar solvent might govern the overall reaction pathway leading to higher yield of the carboxylic acid.

I.A-4: Experimental

Note : The compounds described are all racemates. Melting points were taken in an open capillary in sulfuric acid bath. M.p.s. and b.p.s. are not corrected. IR spectra were recorded on Pye Unicam SP 3-300S and on Perkin-Elmer model PE 298 spectrophotometer in nujol mull (unless otherwise stated). For recording UV spectra a Shimadzu UV-240 spectrophotometer was used. ^{1}H-NMR spectra were taken at 60 MHz on a Varian T-60A or Varian EM-360 and at 250 MHz on a Bruker's spectrometer. ^{13}C-NMR spectra were measured at 62.896 MHz on a Bruker's spectrometer. ^{119}Sn-NMR were obtained on a VXR-300S equipped with multinuclear probe and operating at 111.862 MHz. The chemical shifts in NMR spectra were determined relative to internal Tetramethylsilane for ^{1}H- and ^{13}C- and to external tetramethylstannane for ^{119}Sn-NMR respectively. In the ^{1}H- and ^{13}C- NMR spectra, $C_{1'}$-$C_{4'}$ correspond to the n-butyl group attached to tin and C_i, C_o, C_m, C_p correspond to the phenyl ring attached to tin. Tin was estimated gravimetically as SnO_2. column chromatography were performed on silica gel (60-120 mesh) or neutral alumina (Brockman grade I). Extracts were dried over anhydrous Na_2SO_4. Light petroleum refers to the fraction of b.p. 60-80°C. Ether refers to diethylether. Product purities were routinely checked by TLC using silica gel IB-F (Baker-flex), made by J. T. Baker Inc., Phillipsburg, N. J.

Solvents and commercial reagents were purified and dried by conventional methods before use. Bis (triphenyltin) oxide used here was prepared by the reaction of triphenyltin chloride with 50% excess of sodium hydroxide, as described by McLean et al. [K. A. Elegbede and R. McLean, J. Organomet. Chem., 20, 387 (1955)].

In IR spectra, the abbreviations s, m, w stood for strong, medium and weak bands. In NMR spectra, s, d, t, m, br., were used for singlet, doublet, triplet, multiplet and broad peaks respectively. The chemical shifts(δ) values were expressed in ppm.

Preparation of a few acids used here following the literature procedures.

1) Hexa-2,4-dienoic acid (Sorbic acid) :

In a 100 ml round bottom flask fitted with reflux condenser, crotonaldehyde (10g, 0.1426 mole), malonic acid (15g, 0.1441 mole) and 15 ml dry pyridine (b.p. 113-115°C) were taken. The reaction mixture was heated on a water bath for 3 hours. At the end of that period the vigorous evolution of carbon dioxide was ceased. After cooling, the reaction mixture was acidified by adding dropwise cold dilute sulfuric acid with caution and gentle shaking in an ice-cold condition. Yellow coloured crystalline solid was started to separate immediately from the mother liquor. For the completion of crystallisation it was kept overnight in the refrigerator. Next day, the solid was separated by filtration and washed with ice-cold water. After drying, it was recrystallised from benzene to afford pure sorbic acid (4.8g, 30%), m.p. 132-133°C(lit.[121] m.p. 134°). IR: ν_{max} 1690 cm^{-1}.

2) p-nitro cinnamic acid :

A mixture of 4.2g (0.0277 mole) of p-nitro benzaldehyde (m.p. 105-108°C), 2.9g (0.0279 mole) of malonic

acid (m.p. 135-137°C) and 3 ml dry pyridine (b.p. 113-115°C) were taken in a 50 ml round bottom flask attached to a reflux condenser. A few drops of piperidine was added to the reaction mixture, red colour appeared. Then it was heated over water bath and within 10-15 minutes the reaction mixture became solidified, warming was continued for the next 2 hours. After cooling to room temperature it was acidified by dropwise addition of dilute sulfuric acid in the ice-cold condition. Solids were allowed to settle down by keeping it in refrigerator for 4 hours. Yellow crystals were separated out by filtration and the crystals were washed with ice-cold water and dried in open air. Recrystallisation from benzene afforded pale yellow crystal of p-nitro cinnamic acid (4.8 g, 90%), m.p. 289° (dec.)[lit[132] 289° (dec.) IR: ν_{max} 1635, 1690cm^{-1}.

3) But-2-ynoic acid:

a) 3-Methylpyrazole-5-one :

To a magnetically stirred solution of ethyl acetoacetate(25g, 0.1921 mole) in absolute ethanol (15.3 ml) was added dropwise slowly 99% hydrazine hydrate (9.66 g, 0.5 mole). Exothermic reaction was ensured and the temperature of the reaction mixture was maintained at 60°C. After the addition was complete, the mixture was stirred for another hour at room temperature. It was then cooled in an ice-bath

to complete the crystallisation. Colourless, needle shaped crystalline 3-Methylpyrazole-5-one was filtered off and dried in open air, (16.9 g, 90%), m.p. 220-221°C (phase changed at 195°C), (lit.[121] m.p. 222°C).

b) 4,4-Dibromo-3-methylpyrazole-5-one :

A solution of the aforementioned crude 3-methylpyrazole-5-one (16g, 0.1631 mole) in 64 ml of glacial was taken in a 250 ml round bottom flask and stirred magnetically 26 g (0.1631 mole) of bromine in 16 ml of glacial acetic acid was added dropwise via pressure equiliser to the stirred solution. On completion of that addition, 40 ml of water and 26 g (0.1631 mole) of bromine in 16 ml glacial acetic acid were added to the reaction mixture. Clear solution was obtained at the end of second lot addition of bromine. The reaction mixture was permited to stand overnight at room temperature. Crystals of dibromo pyrazolone was separated out on addition of water. The product was filtered under water suction and washed with distilled water until the washings were neutral. The air-dried product (30, 79g, 78%) had m.p. 128-130° (lit.[121] m.p. 130-132°) and was used directly for the next step.

c) But-2-ynoic acid :

In a 1L round bottom flask, a solution of sodium hydroxide in 440 ml of water was prepared and stirred magnetically in an ice-bath until the temperature of the solution reached 0-5°C. 30g (0.1239 mole) of 4,4-Dibromo-3-methylpyrazole-5-one was added portionwise over a period of 10 minutes. The bromoketone was dissolved to give an orange-red solution which evolve nitrogen gas; the temperature of the solution during the addition showed only a slight tendency to rise. The reaction mixture was stirred for 1 hour at 0-5°C and then at room temperature for 1 hour. The solution was cooled and acidified with concentrated hydrochoric acid. Then it was extracted with diethyl ether (3 x 75 ml) and the combined ethereal layer was washed with brine and dried (Na_2SO_4). Evaporation of the solvent afforded a residue which was kept in a vacuum desiccator. After 3 days crude orange crystals of but-2-ynoic acid were appeared. Then the crystals were extracted with boiling light petroleum successively and the solution was concentrated to furnish yellow crystalline acid. Recrystallisation from benzene furnished but-2-ynoic acid (5.2 g, 50%), m.p. 72-73° (lit.[121] m.p. 75-76°C). IR : ν_{max} 1690, 2240, 2950 cm^{-1}.

4. Cyclohexylidene acetic acid :

a) Preparation of Ethyl cyclohexylidene cyano acetate :

A mixture of cyclohexanone (8.65 g, 0.0884 mole) and ethyl cyanoacetate (10g, 0.0884 mole) was dissolved in benzene (50 ml) and a few drops of piperidine were added to it. The mixture was refluxed for 2 hours using a Dean-Stark water separator. The solution was cooled and acidified with 3(N) dilute hydrochloric acid to maintain the pH as neutral. The organic part was washed with aqueous sodium bicarbonate solution carefully and then washed with brine and dried over anhydrous Na_2SO_4. Solvents were distilled off to afford an oily brown residue which was distilled under reduced pressure and collected the condensation product, ethyl cyclohexylidene cyano acetate at 117-121°/2mm Hg(15.35 g, 90%). IR(Neat): ν_{max} 1598(s, C=C), 1710(s,C=C-COOEt), 2220(s, C=C-CN)cm^{-1}.

b) Hydrolysis of Ethyl cyclohexylidene cyano acetate :

The foregoing ethyl cyclohexylidene cyano acetate (10g, 0.0518 mole) was treated with glycollic potassium hydroxide solution (prepared from 12g KOH in minimum volume of water and then added 120 ml of ethylene glycol) and refluxed for 5 hours. After cooling to room temperature the reaction mixture was poured into crushed ice and extracted with ether (3 x, 50ml) to eliminate any neutral unreacted part. The aquous layer was separated and acidified with ice-

cold dilute hydrochloric acid (3N). The acid was extracted with ether (2 x 50 ml) after saturation with sodium chloride and combined etherial layer was washed with brine and dried (Na_2SO_4). Evaporation of the solvent afforded the dark red acid (5.6 g, 71%).

c) Cyclohexylidene acetic acid :

The aforementioned crude dicarboxylic acid (3.0 g, 0.0197 mole) was taken in a sublimation tube and heated at 180° for minutes in a sublimation chamber. The desired acid was sublimed at 140-150°C/6-5 mm Hg(1.93 g, 70%), IR : ν_{max} 1685 cm^{-1}.

5. Phenylpropynoic acid :

a) 2,3-Dibromo-3-phenylpropanoate :

To a solution of ethyl cinnamate (42g, 0.2496 mole) (prepared from cinnamic acid) in carbon tetrachloride (25 ml) in 1l r.b. flask was added bromine (40g, 12.5 ml, 0.25 mole) at 0°C (ice-bath) during 30 minutes. The bromine was found to disappear rapidly at first, but more slowly towards the end of the reaction. The reaction mixture was allowed to stand for 1 hour and then poured into a large evaporatory dish so that the excess of bromine and carbon tetrachloride were evaporated. The crude ethyl 2,3-Dibromo-3-phenylpropanoate

remained as a solid cake, which was dried by pressing between large filter papers. The crude product (70g, 83%), m.p. 65-69°C (lit.[121] m.p. 66-71°C) was directly used for the next step.

The crude dibromo ester (80g, 0.2357 mole) was added to an ethanolic solution of KOH (prepared from 61g KOH in 285 ml of rectified spirit by heating). An initial exothermic reaction was set in, subsided after a short while, and then heated under gentle reflux for 6 hours on a steam-bath. The contents were poured into a large beaker, cooled and neutralise by adding concentrated hydrochloric acid with stirring until neutral to litmus. After cooling at 0°C, the precipitated solids were filtered off at the pump and washed with a little chilled alcohol. The solid compound(A) was set aside. The filtrate was transfered into the original flask and the liquid was distilled out until the temperature of the vapour reached 95°C. The residue was combined with the solid obtained earlier(A) dissolved in 200 ml of water and 200 g of crushed ice and cooled in an ice-bath. To this was added 20% sulfuric acid slowly until the solution became strongly acid to congo red. Allowed to stand for 20 minutes when the dark-coloured crude phenylpropynoic acid was separated out and filtered off, washed with three 10 ml portions of 2% sulfuric acid. The solid acid was dissolved in 150 ml of 5% sodium carbonate solution, 3 g of decolourising charcoal was added,

and heated on a water bath for 30 minutes with occasional shaking. The charcoal was eliminated by filtering off. Then the filtrate was cooled in ice-bath and 50 g of crushed ice was added to it. 20% sulfuric acid was added slowly to mechanically stirred solution until acid to congo red. After 30 minutes, the precipitate was filtered off by suction and washed with 10 ml of ice-cold 2% sulfuric acid, then with a little water and dried in the air. The yield of phenylpropynoic acid was 45% (15 g), m.p. 132-133°C (lit.[121] m.p. 134-135°C).

I.A-4.1: Preparation of α,β-Unsaturated Stannyl Carboxylates (26 - 38)

Tri-n-butylstannyl acrylate (26)

This ester was prepared from its methyl ester by transesterification method[54]. A mixture of freshly distilled methyl acrylate (1 g, 0.0116 mole) and bis tri-n-butyltin oxide (6.92g, 0.0116 mole) was gently refluxed in neat for 2 hours with very gentle heating at 60°C. It was then cooled to room temperature and colourless crystalline solid appeared which was purified by silica-gel column chromatography. Elution with 25% benzene-light petroleum afforded fine

crystals of tri-n-butylstannyl acrylate(26), (3.85g, 92%), m.p. 69-70°C(lit.[133] m.p. 69-70°C).

UV(EtOH): λ_{max} 215(ε 834).

IR: ν_{max} 1530(s), 1550(s), 1645(m), 1655(m)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.84(t, J= 7.21 Hz, 9H, C_4,), 1.18-1.43(m, 12H, C_1, & C_3,), 1.49-1.62(m, 6H, C_2,), 5.65(dd, J=2.29 & 9.80 Hz, 1H, C3), 6.07(dd, J=9.80 & 17.24 Hz, 1H, C2), 6.22 (dd, J=2.29 & 17.24 Hz, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.60(C_4,), 16.46(C_1,), 27.00(C_3,), 27.64 (C_3,), 129.18(C2), 130.35(C3), 171.36(C1).

% Analysis for $C_{15}H_{30}SnO_2$:

Found :	C	49.60	H	8.27	Sn	32.90
Calcd.:	C	49.89	H	8.37	Sn	32.87

General Procedure - I :

A solution of unsaturated acid (20 m mole) and bis tri-n-butyltin oxide (10 m mole) in dry benzene(30 ml) was heated under reflux for 3 hours with azeotropic removal of water using a Dean - Stark trap. The volatiles were removed under vacuo and the residue was purified as described below:

Tri-n-butylstannyl crotonate (27) :

A mixture of crotonic acid (1.5g, 0.0174 mole) and

bis tri-n-butyltin oxide (5.19g, 0.0087 mole) was refluxed in benzene (30 ml) following the general procedure I. The residue was crystallised twice from light petroleum to furnish(27) as colourless needles, 5.62g (86%), m.p. 81°C (lit.[134] m.p. 84°C).

UV (EtOH) : λ_{max} 224(ε=1, 618).

IR : ν_{max} 1535(s), 1555(s), 1655(s) cm^{-1}.

^{1}H-NMR ($CDCl_3$) : δ 0.85(t, J=7.25 Hz, 9H, C_4,), 1.20-1.39(m, 12H, C_1, & C_3,), 1.54-1.74(m, 6H, C_2,), 1.81(d, J=1.70, small allylic coupling, and 6.90 Hz, 3H, C4), 5.84(d, J=1.7 Hz, small allylic coupling, and 15.40 Hz, 1H, C2), 6.84(m, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.62(C_4,), 16.41(C_1,), 17.75(C4), 27.02 (C_3,), 27.67(C_2,), 124.30(C2), 143.22(C3), 171.81(C1).

% Analysis for $C_{16}H_{32}SnO_2$:

Found :	C	51.12	H	8.46	Sn	31.50
Calcd.:	C	51.23	H	8.59	Sn	31.64

Tri-n-butylstannyl cinnamate (28) :

The reaction was carried out with 2g(0.0134 mole) of cinnamic acid and 4.02g(0.0067 mole)of bis tri-n-butyltin oxide in refluxing benzene (20 ml) following the general procedure I. The residue was purified by silica-gel column

chromatography. Elution with 25% benzene-ligh petroleum afforded colourless needles or the desired compound(28), (5.31g, 90%), m.p. 71°C (lit.[134] m.p. 69-70°C).

UV(EtOH): λ_{max}215(ϵ=5,250), 270(ϵ=6,700).

IR : ν_{max} 1540(s), 1555(s), 1580(m), 1640(s)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.92(t, J=7.22 Hz, 9H, C_4,), 1.27-1.42(m, 12H, C_1, & C_3,), 1.58-1.71(m, 6H, C_2,), 6.49(d, J=15.94 Hz, 1H, C2), 7.33-7.39(m, 3H, Aromatic), 7.47-7.52(m, 2H, Aromatic), 7.61(d, J=15.94 Hz, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.68(C_4,), 16.57(C_1,), 27.09(C_3,), 27.72 (C_2,), 120.06(C6 & C8), 127.93 & 128.77(C4 & C2), 129.72(C5 & C9), 135.04(C7), 143.84(C3), 172.12(C1).

% Analysis for $C_{21}H_{34}SnO_2$:

Found :	C	57.45	H	7.68	Sn	27.23
Calcd.:	C	57.69	H	7.84	Sn	27.14

Tri-n-butylstannyl p-nitro cinnamate(29)

It was prepared from 3g(0.0155 mole) of p-nitro cinnamic acid and 4.6g(0.0077 mole) of bis tri-n-butyltin oxide dissolved in 25 ml benzene following the general Procedure I. Residue was crystallised twice from

light petroleum afforded yellow coloured crystals of tri-n-butylstannyl p-nitro cinnamate(29), (6.29g, 84%), m.p. 76°C.
UV(EtOH) : λ_{max} 232(ϵ=41,622), 305(ϵ=78,709).
IR : ν_{max} 1550(s), 1563(s), 1595(s), 1635(m)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.90(t,J=7.23 Hz, 9H, C_4,), 1.15-1.48(m, 12H, C_1, & C_3,), 1.57-1.71(m, 6H, C_2,), 6.58(d, J=15.99 Hz, 1H, C2), 7.59(d, J=15.99 Hz, 1H, C3), 7.63(dd, J=1.8 & 8.80 Hz, 2H, C5 & C9), 8.20(dd, J=1.8 & 8.80 Hz, 2H, C6 & C8).

^{13}C-NMR($CDCl_3$): δ 13.63(C_4,), 16.65(C_1,), 27.03(C_3,); 27.82(C_2,), 124.06(C6 & C8), 124.76(C2), 128.40(C5 & C9), 140.61(C4), 141.40(C3), 148.17(C7), 170.87(C1).

^{119}Sn-NMR($CDCl_3$): δ +120.258

% Analysis for $C_{21}H_{33}NSnO_4$:

Found :	C	52.43	H	6.73	N	2.81	Sn	24.73
Calcd. :	C	52.31	H	6.89	N	2.90	Sn	24.61

Tri-n-butylstannyl sorbate (30) :

A mixture of 2g(0.0178 mole) of sorbic acid and 5.31g(0.0089 mole) of bis tri-n-butyltin oxide was refluxed in 30 ml benzene following the general procedure I. The

residue was purified by recrystallisation from light petroleum to furnish colourless, neddle-shaped crystals of the desired compound(30) (6.08g, 85%), m.p. 84-85°C.

UV(EtOH): λ_{max} 252(ϵ=28,559).

IR: ν_{max} 1500(s), 1600(s), 1625(m)cm^{-1}

^{1}H-NMR($CDCl_3$): δ 0.88(t, J=7.22 Hz, 9H, C_4,), 1.10-1.44(m, 12H, C_1, & C_3,), 1.53-1.72(m, 6H, C_2,), 1.80(d, J=6.14 Hz, 3H, C6), 5.79(d, J=15.22 Hz, 1H, C2), 5.96-6.21(m, 2H, C5 & C4), 7.15(dd, J= 13.76 & 15.22 Hz, 1H, C3).

^{13}C-NMR($CDCl_3$): δ 13.61(C_4,), 16.46(C_1,), 18.51(C6), 27.02 (C_3,), 27.68(C_2,), 120.87(C2), 130.10(C4), 137.58(C5), 144.19(C3), 172.46(C1).

^{119}Sn-NMR($CDCl_3$): δ +106.576

% Analysis for $C_{18}H_{34}SnO_2$:

Found :	C	54.05	H	8.73	Sn	29.73
Calcd. :	C	53.89	H	8.54	Sn	29.59

Tri-n-butylstannyl but-2-ynoate (32) :

A mixture of but-2-ynoic acid (1.5g, 0.0178 mole) and bis-tri-n-butyltin oxide (5.31g, 0.0089 mole) was refluxed in 30 ml benzene following the general procedure I.

Volatiles were removed and an oily mass was obtained. On scratching it was solidified. Solids were dissolved in minimum volume of light petroleum. Evaporation of solvent afforded the colourless crystal of(32), (5.19g, 78%), m.p. 65-66°C.

UV($CHCl_3$): λ_{max} 240(ϵ=182).

IR: ν_{max} 1540(s), 1560(s), 2250(s) cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.84(t, J=7.19 Hz, 9H, C_4,), 1.09-1.40(m, 12H, C_1, & C_3,), 1.49-1.68(m, 6H, C_2,), 1.88(s, 3H, C4).

^{13}C-NMR($CDCl_3$): δ 3.75(C4), 13.56(C_4,), 16.81(C_1,), 27.02(C_3,), 27.69(C_2,), 73.84(C2), 82.79(C3), 158.54(C1).

^{119}Sn-NMR($CDCl_3$): δ +131.811

% Analysis for $C_{16}H_{30}SnO_2$:

Found :	C	51.72	H	8.23	Sn	31.60
Calcd.:	C	51.50	H	8.10	Sn	31.81

Tri-n-butylstannyl phenylpropynoate (33)

A solution of 2.5g (0.017 mole) phenylpropynoic acid and 5.10g(0.0085 mole) of bis tri-n-butyltin oxide was heated under reflux in 30 ml benzene following the general

procedure I. Solvents were removed and an oily mass was obtained. The residue was dissolved in minimum amount of light petroleum and kept in refrigerator. After few days crystals were appeared which was separated out by filtration and washed with little amount of chilled light petroleum to furnish colourless crystals of (33), (4.24g, 57%) m.p. 56-57°C (lit.[135] m.p. 57-58°C).

UV($CHCl_3$): λ_{max} 252(ϵ=12,448), 264(ϵ=10,968).

IR: ν_{max} 1505(s), 1560(m), 2125(w), 2310(w)cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.91(t, J=7.21 Hz, 9H, $C_{4'}$), 1.20-1.46(m, 12H, $C_{1'}$ & $C_{3'}$), 1.58-1.70(m, 6H, $C_{2'}$), 7.32-7.38(m, C6, C7 & C8), 7.55(d, J=6.72 Hz, 2H, C5 & C9).

^{13}C-NMR($CDCl_3$): δ 13.61($C_{4'}$), 16.96($C_{1'}$), 27.06($C_{3'}$), 27.75($C_{2'}$), 82.26(C2), 83.93(C3), 120.66(C6), 128.39(C4), 129.91(C5), 132.82(C7), 158.74(C1).

% Analysis for $C_{21}H_{32}SnO_2$:

Found :	C	57.81	H	7.63	Sn	27.01
Calcd.:	C	57.96	H	7.41	Sn	27.27

Tri-n-butylstannyl cyclohexylidene acetate (31) :

The reaction was carried out by mixing 1.5g(0.0107

mole) cyclohexylidene acetic acid and 3.19g(0.0053 mole) bis tri-n-butyltin oxide in neat. An immediate exothermic reaction was ensured. Crystals were appeared from the clear reaction mixture at room temperature and within a few minutes the whole reaction mixture became solidified. The residue was crystallised from light petroleum afforded needle shaped colourless crystals of tri-n-butylstannyl cyclohexylidene acetate (31), (3.67g, 80%), m.p. 80°C.

UV(EtOH): λ_{max} 225(ϵ=943).

IR: ν_{max} 1548(s), 1567(s), 1625(m) cm^{-1}.

^{1}H-NMR($CDCl_3$): δ 0.83(t, J=7.22 Hz, 9H, $C_{4'}$), 1.04-1.41(m, 16H, Cyclohexenyl, $C_{1'}$ & $C_{3'}$), 1.48-1.66(m, 6H, $C_{2'}$), 1.94 (br. s, 4H, Cyclohexenyl), 2.87(br. s, 2H, C4), 5.47(s, 1H, C2).

^{13}C-NMR($CDCl_3$): δ 13.62($C_{4'}$), 16.41($C_{1'}$), 22.12(C6), 22.84 (C7), 25.30(C5), 27.00($C_{3'}$), 27.83($C_{2'}$), 28.38(C8), 44.30 (C4), 124.55(C2), 132.49(C3), 177.50(C1).

^{119}Sn-NMR($CDCl_3$): δ +108.213 and +100.281

% Analysis for $C_{20}H_{38}SnO_2$:

Found :	C	55.73	H	9.07	Sn	27.71
Calcd.:	C	55.97	H	8.92	Sn	27.65

General Procedure - II

To a solution of unsaturated acid(20 mmole) in either dry benzene or toluene (30 ml), bis triphenyltin oxide(10 mmole) was added. A slightly milky white solution was obtained which was turned into a clear solution after reflux for 4 hours azeotropically with a Dean-Stark water separator. After cooling to room temperature a small amount of powdery solid was precipitated which was removed by filtration. Volatiles were distilled out, the residue was dried in vacuo and purified as described below:

Triphenylstannyl Crotonate (34)

1.5g(0.0174 mole) of crotonic acid and 6.23g (0.0087 mole) of bis triphenyltin oxide were dissolved in 30 ml toluene and refluxed following the general procedure II. The residue was crystallised twice from chloroform-benzene mixture afforded colourless solids of (34), (6.06g, 80%), m.p.141-142°C.

UV($CHCl_3$): λ_{max} 241(ϵ=1,182).

IR: ν_{max} 1515(s), 1545(s), 1570(m), 1650(s)cm^{-1}.

^{1}H-NMR($CDCl_3$) δ 1.87(d, J=1.7 & 6.9 Hz, 3H, C4), 5.97(d, J=1.70 Hz, small allylic coupling, & 14.0 Hz, 1H, C2), 7.06 (m, 1H, C3), 7.37-7.50(m, 9H, Aromatic), 7.62-7.89(m, 6H, Aromatic).

^{13}C-NMR($CDCl_3$): δ 18.02(C4), 122.75(C2), 128.89(C_m), 130.07(C_p), 136.92(C_o), 138.59(C_i), 145.86(C_3), 173.07(C1).

^{119}Sn-NMR($CDCl_3$): δ -182.664

% Analysis for $C_{22}H_{20}SnO_2$:

Found :	C	60.59	H	4.47	Sn	27.19
Calcd.:	C	60.73	H	4.63	Sn	27.28

Triphenylstannyl p-nitro cinnamate (35)

A mixture of 2.5g(0.0129 mole) of p-nitro cinnamic acid and 4.63g(0.0064 mole) of bis triphenyltin oxide was heated under reflux in benzene following the general procedure II. The residue was recrystallised from acetone-petroleum mixture provided shining yellow crystals of (35), (6.17g, 88%), m.p. 178-179°C.

UV(EtOH): λ_{max} 222(ϵ=24,191), 305(ϵ=24,558).

IR: ν_{max} 1590(s), 1610(m), 1640(w) cm^{-1}.

^1H-NMR($CDCl_3$): δ 6.68(d, J=16.2 Hz, 1H,, C2), 7.37-7.54(m, 9H, Aromatic), 7.63(dd, J=1.80 & 8.80 Hz, 2H, C5 & C9), 7.75(d, J=16.2 Hz, 1H, C3), 7.78-7.83(m, 6H, Aromatic), 8.21 (dd, J=1.8 & 8.80 Hz, 2H, C6 & C8).

^{13}C-NMR($CDCl_3$): δ 123.15(C6 & C8), 124.15(C2), 128.59(C5 & C9), 129.06(C_3,), 130.37(C_4,), 136.93(C_2,), 138.04(C_1,), 140.96(C4), 142.38(C3), 148.40(C7), 171.99(C1).

^{119}Sn-NMR($CDCl_3$): δ -103.37

% Analysis for $C_{21}H_{33}NO_4Sn$:

Found :	C	52.45	H	6.64	N	2.83	Sn	24.57
Calcd.:	C	52.31	H	6.89	N	2.90	Sn	24.61

Triphenylstannyl sorbate (36)

2g (0.0178 mole) of sorbic acid and 6.38g(0.0089 mole) of bis-triphenyltin oxide were dissolved in 30 ml benzene and the solution was refluxed following the general procedure II. An oily residue was obtained after the removal of volatiles in vacuo,which on scratching for a long time was solidified. The solids were dissolved in acetone,after complete evaporation of solvent afforded crystalline off white product (36), (6.13g, 79%), m.p. 96-98°C.
UV(EtOH): λ_{max} 220(ε=88,615), 254(ε=91,076).
IR: ν_{max} 1575(w), 1610(m), 1635(w)cm^{-1}.

^1H-NMR($CDCl_3$): δ 1.73(d, J=5.84 Hz, 3H, C6), 5.80(d, J=15.56 Hz, 1H, C2), 5.94-6.16(m, 2H, C4 & C5), 7.13-7.40(m, 10H, C3

& Aromatic), 7.53-7.80(m, 6H, Aromatic).

^{13}C-NMR($CDCl_3$): δ 18.68(C6), 119.02(C2), 128.89(C_m), 130.06 (C4 & C_p), 136.94(C_o), 138.69(C_i), 139.07(C5), 146.27(c3), 173.85(C1).

% Analysis for $C_{24}H_{22}SnO_2$:

Found :	C	62.43	H	4.73	Sn	25.98
Calcd.:	C	62.51	H	4.81	Sn	25.74

Triphenylstannyl but-2-ynoate (37)

A solution of 1.5g(0.0178 mole) of but - 2- ynoic acid and 6.36g, (0.0089 mole) of bis triphenyltin oxide in 30 ml benzene was refluxed following the general procedure II. The residue was purified by crystallisation. Recrystallisation from acetone-light petroleum mixture provided colourless crystalline solids of (37), (5.87g, 76%,), m.p. 192-193°C.

UV($CHCl_3$): λ_{max} 240(ϵ=912), 258(ϵ=825).
IR: ν_{max} 1510(s), 1565(m), 2250(s)cm^{-1}.

^{1}H-NMR(D_6-DMSO):δ1.80(s, 3H, C4), 7.41-7.49(m, 9H, C_m, C_p), 7.63-7.91(m, 6H, C_o).

^{13}C-NMR(D_6-DMSO):δ 2.89(C4),76.77(C2), 79.33(C3), 128.34(C_m), 128.96(C_p), 136.08(C_o), 142.64(C_i), 156.75(C1).

^{119}Sn-NMR(D_6-DMSO):δ-250.807

% Analysis for $C_{22}H_{18}SnO_2$:

Found :	C	61.15	H	4.20	Sn	27.55
Calcd.:	C	61.01	H	4.19	Sn	27.41

Triphenylstannyl phenylpropynoate (38)

A solution of phenylpropynoic acid (2.5g, 0.0171 mole) and bis triphenyltin oxide (6.13g, 0.0085 mole) in benzene was refluxed following the general procedure II. The crude residue was recrystallised from chloroform-benzene mixture to furnish colourless needles of (38) (7.51g, 90%), m.p. 118-120°C(lit.[135] # m.p. 175-176°C).

UV($CHCl_3$): λ_{max} 258(ϵ=13,000).

IR: ν_{max} 1515(s), 1570(m), 2220(m) cm^{-1}.

^{1}H-NMR($CDCl_3$):δ 7.30-7.55((m, 14H, C5, C6, C7, C8, C9 & C_m, C_p), 7.61.7.88(m, 6H, C_o).

^{13}C-NMR($CDCl_3$): δ 81.49(C2), 86.21(C3), 120.30(C6), 128.49 (C4), 129.08(C_m), 130.27(C5), 130.45(C_p), 132.94(C7),

136.95(C_o), 137.58(C_i), 159.77(C1).

% Analysis for $C_{27}H_{20}SnO_2$:

Found :	C	65.69	H	4.12	Sn	23.62
Calcd.:	C	65.49	H	4.07	Sn	23.97

Although the melting point of compound(38) did not match with the literature value, the spectral and elemental data suggested our assigned structure to be correct.

I.A-4.2 : Reaction of α,β-unsaturated stannyl carboxylates with Hg(II) salts (X = Cl, OAc)

General Procedure

To a solution of α,β-unsaturated stannyl carboxylates (2 mmole) in a solvent(10 ml) were added mercury(II) salts (2 mmole) (HgX_2; X = Cl, OAc) and the mixture was either stirred at room temperature (in case of methanol) or heated under gentle reflux (in the case of benzene or acetonitrile) for several hours noted in TABLE-VI. A small amount of white solid was precipitated during the reaction which was filtered off. [In the case of tri-n-butyl stannyl but-2-ynoate(32), a large amount of gelatinous

precipitate appeared when its solution in MeOH was treated with mercuric acetate at room temperature. After 48 hours the deposites were filtered off]. The filtrate was diluted with ether and the organic layer was washed with aqueous sodium chloride and dried over anhydrous Na_2SO_4.Evaporation of the solvents afforded a solid residue which was crystallised from light petroleum to furnish shining flakes of BuHgCl(from tri-n-butylstannyl esters) or white leaflets of PhHgCl(from triphenylstannyl esters). BuHgCl and PhHgCl were characerised by physical/spectral data and their yields(%) were recorded in **TABLE-VI.**

Characterisation of BuHgCl :

m.p. 128°C (lit.[138] 127-130°C).

^{1}H-NMR($CDCl_3$): δ 0.95(t, 3H, J=7.29 Hz), 1.34-1.48(m, 2H), 1.67-1.78(m, 2H), 2.1(t, 2H, J=7.13 Hz).

^{13}C-NMR($CDCl_3$), ppm for APT spectra a(+) indicates 0 or 2 attached protons and a(-) indicates 1 or 3 attached protons) δ 13.47(-), 27.81(+), 30.09(+), 33.06(+).

% Analysis for C_4H_9HgCl (sublimed at 90-110°C/1 mm Hg and recrystallised from benzene-light petroleum).

Found :	C	16.08	H	3.17
Calcd.:	C	16.38	H	3.07

Characterisation of PhHgCl:

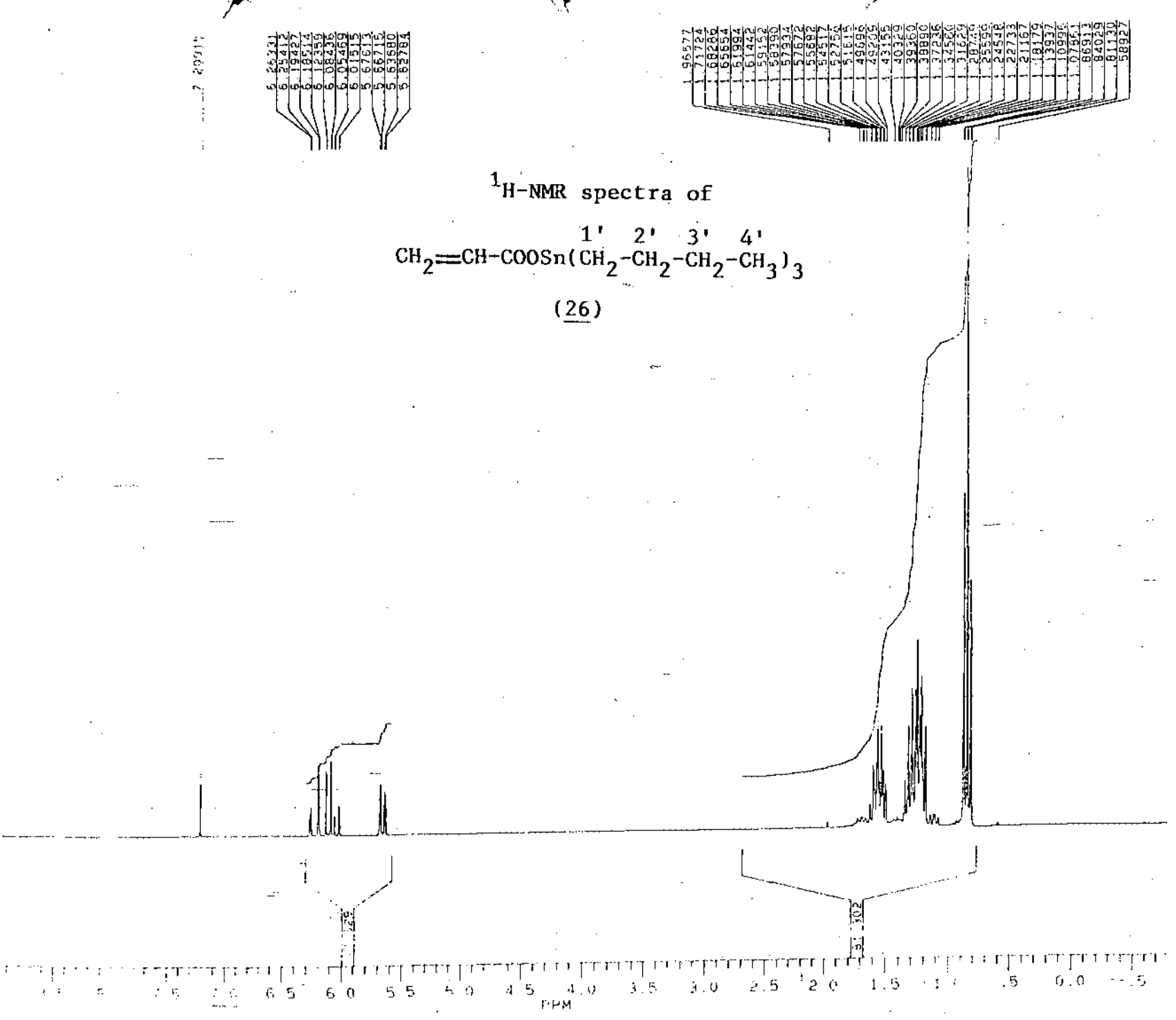
M.p.249-250°C (dec.) (lit.[139] m.p. 251°C), m.m.p. 248-249°C.

The mother liquor from the crystallisation was then diluted with ether and the acid was extracted with saturated aqueous sodium carbonate. The aqueous phase was separated and acidified with dilute hydrochloric acid(3N) under ice cold condition. The liberated acid was extracted with ether (3 x 25 ml) after saturating the aqueous part with sodium chloride. The combined ethereal layer was dried over anhydrous Na_2SO_4. The volatiles were removed and the residue was dried under vacuo. Recrystallisation from benzene-light petroleum afforded the acids, yield(%) of acids was recorded in the **TABLE-VI.** All the acids were characterised by physical and spectral data and found identical with the reported values.

^{1}H-NMR spectra of

$CH_2{=}CH{-}COOSn(\overset{1'}{C}H_2{-}\overset{2'}{C}H_2{-}\overset{3'}{C}H_2{-}\overset{4'}{C}H_3)_3$

(26)

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TIME 9:34

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O1    4311.814
SI    32768
TD    32768
SW    5000.000
HZ/PT     .305

AQ        3.277
NS       16

O2     2714.499
DP    68L PO

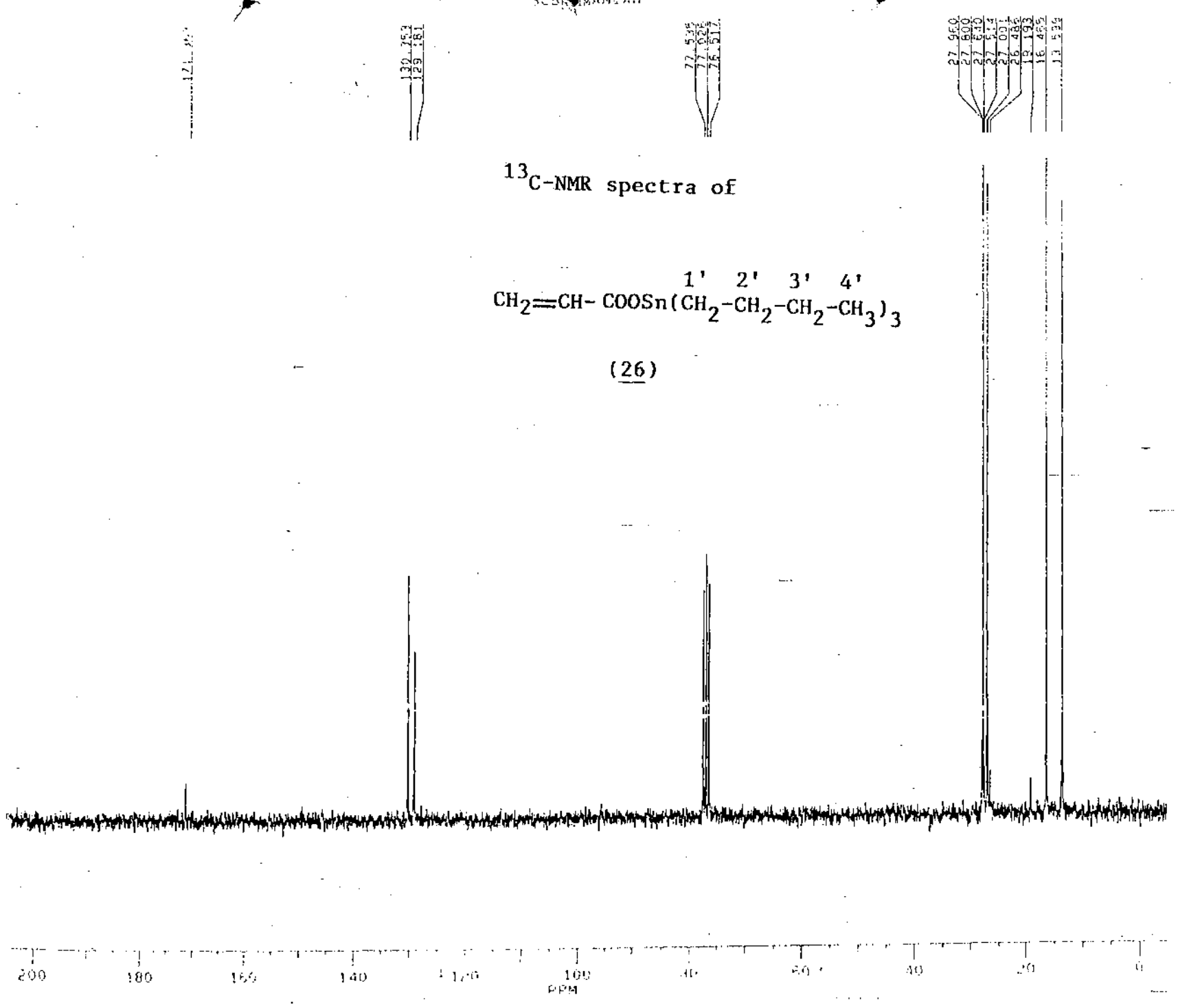
LB          .100
CX        23.50
CY        12.50
F1        9.201P
F2        -.799P
HZ/CM  106.435
PPM/CM    .426
SR     2866.81

D1     1.0000000
P0          3.
RGA
RD     0.0
PW          0.0
DE        125.00
NS          16
DS           2
```

^{13}C-NMR spectra of

$CH_2{=}CH\text{-}COOSn(CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3)_3$

(26)



BRUKER

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SF2     62.896
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SI    32768
TD    32768
SW    15625.000
HZ/PT     .954

AQ        1.049
NS      128

O2    3871.265
DP    20H 00

LB        1.600
CX       23.50
CY       12.50
F1     210.015P
F2      -4.977P
HZ/CM  575.411
PPM/CM   9.149
SR    -4045.28

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PO        2.30
RGA
RD    0.0
PW        6.0
DE       40.00
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DS
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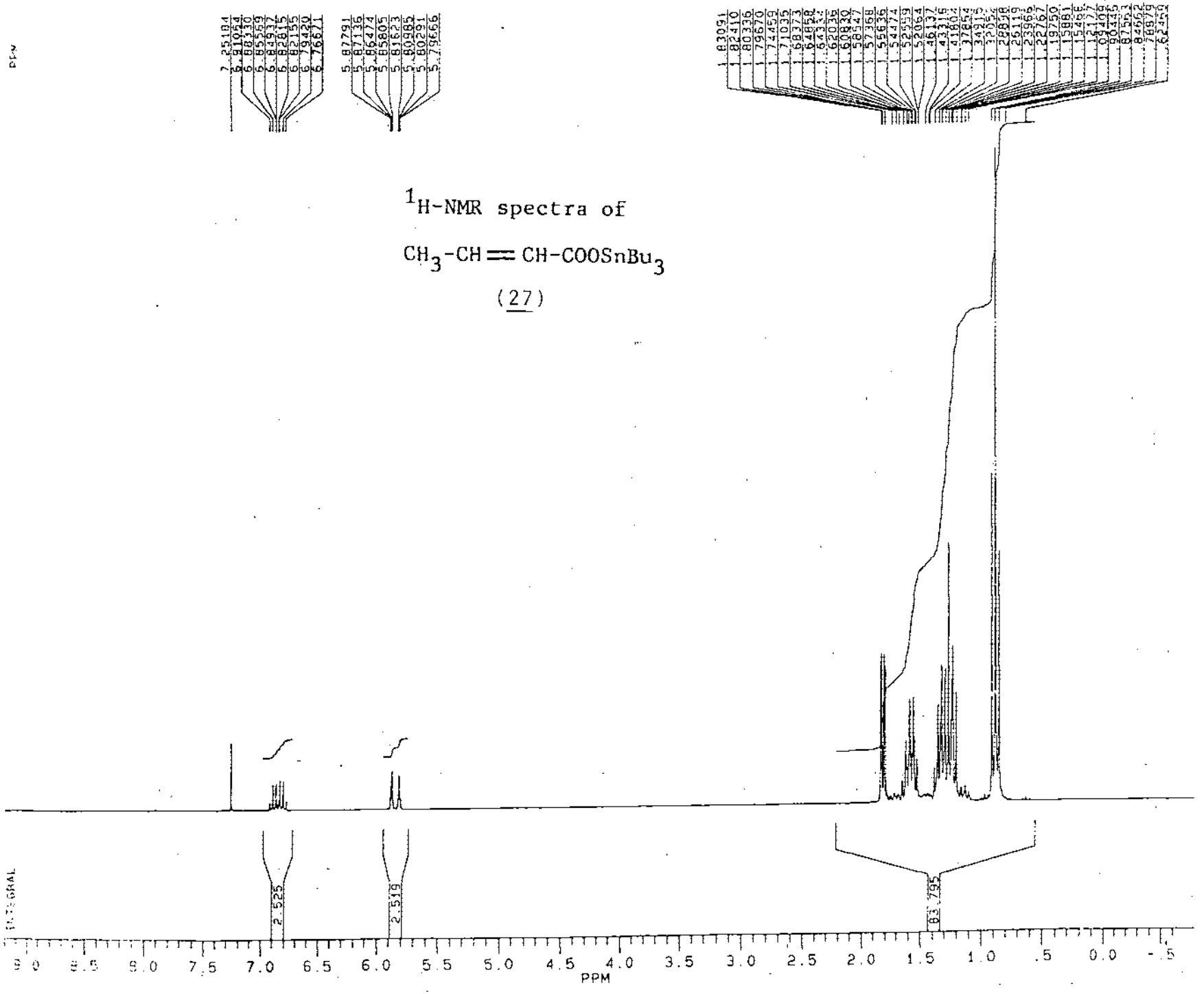
SUBRAMANIAN

^{1}H-NMR spectra of

$CH_3-CH=CH-COOSnBu_3$

(27)



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SY 100.0
O1 4311.814
SI 32768
TD 32768
SW 5000.000
SW2 5000.000
HZ/PT .305

RD 0.0
AQ 3.277
RG 2
NS 16
TE 297

DE 125.1
PW 6300
O2 2714.499
DP 63L PD

LB .100
GB 0.0
PC 2
.X 23.50
CY 12.50
F1 9.200P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2855.82

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PW 0.0
DE 125.00
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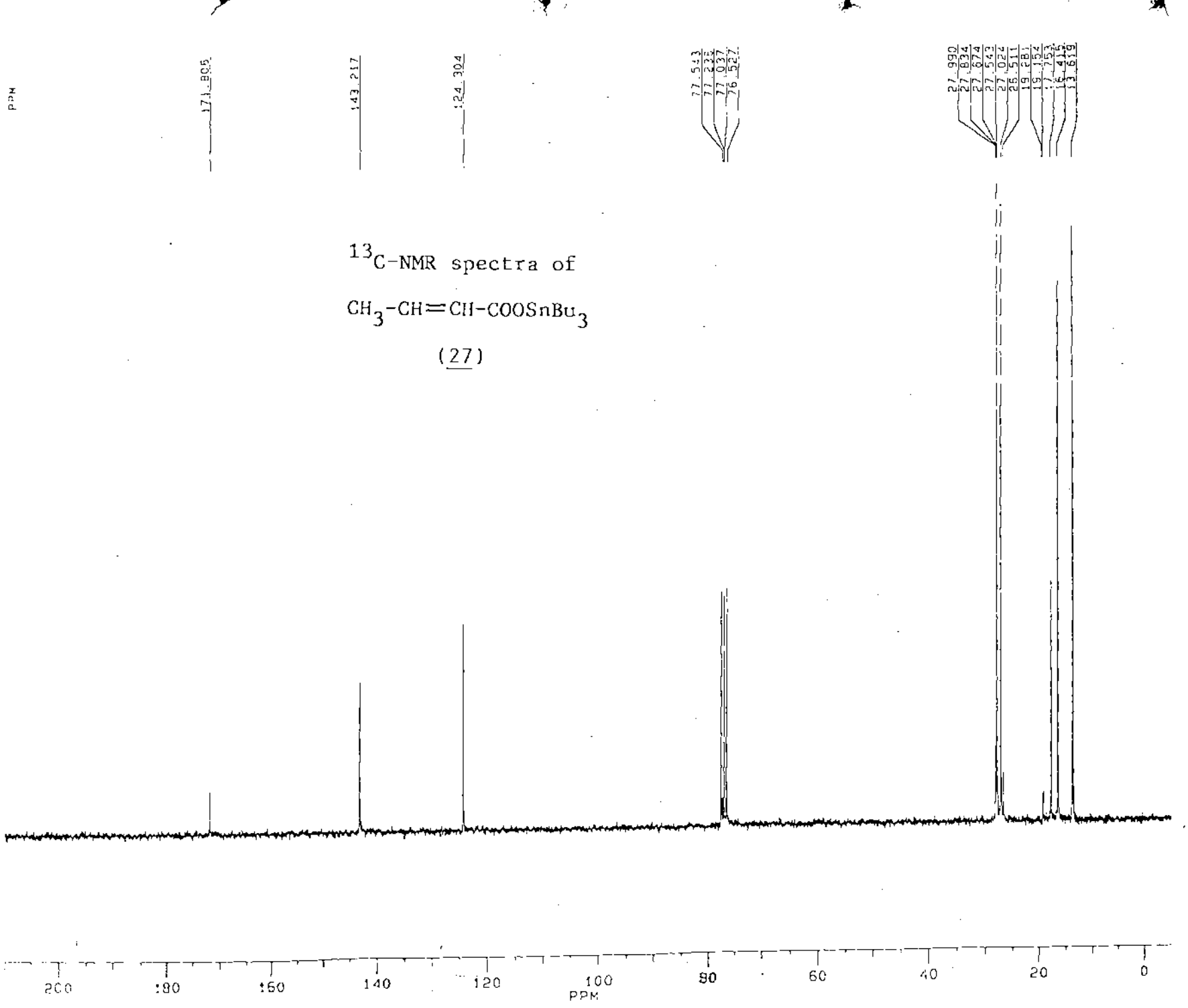
DS 2



^{13}C-NMR spectra of

CH_3-CH=CH-COOSnBu_3

(27)

BRUKER

JA1215.124
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DATE 12-1-93
TIME 19:20

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SY 62.0
O1 2268.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 512
TE 297

DE 40.0
FW 19600
O2 3871.265
DP 20H DD

LB 1.600
GB 0.0
NC 6
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
S1 16H
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RGA
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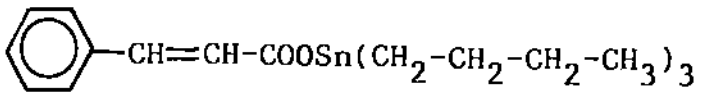
NS 512
D5 2

^{1}H-NMR spectra of



(28)

SUBRAMANIAN

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77.266
77.062
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19.427
19.300
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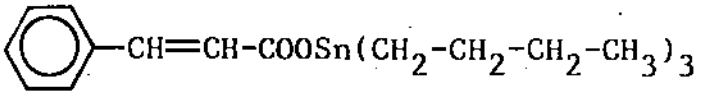

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SF2 62.896
SY 62.0
O1 2268.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 512
TE 297

DE 40.0
FW 19600
O2 3871.265
DP 20H DO

LB 1.600
GB 0.0
NC 5
C1 [illegible]
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F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

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SE 20H
PC 2.30

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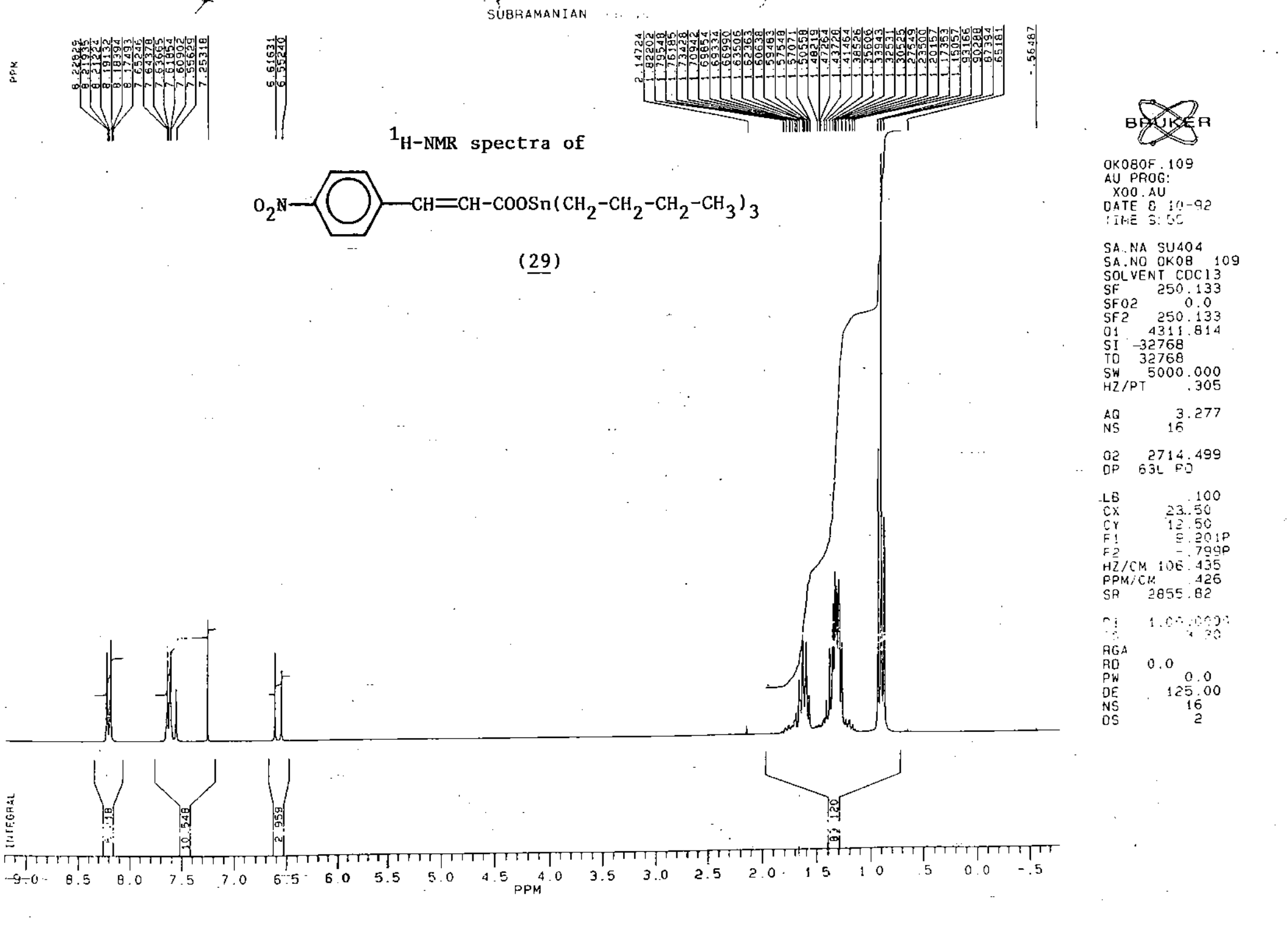

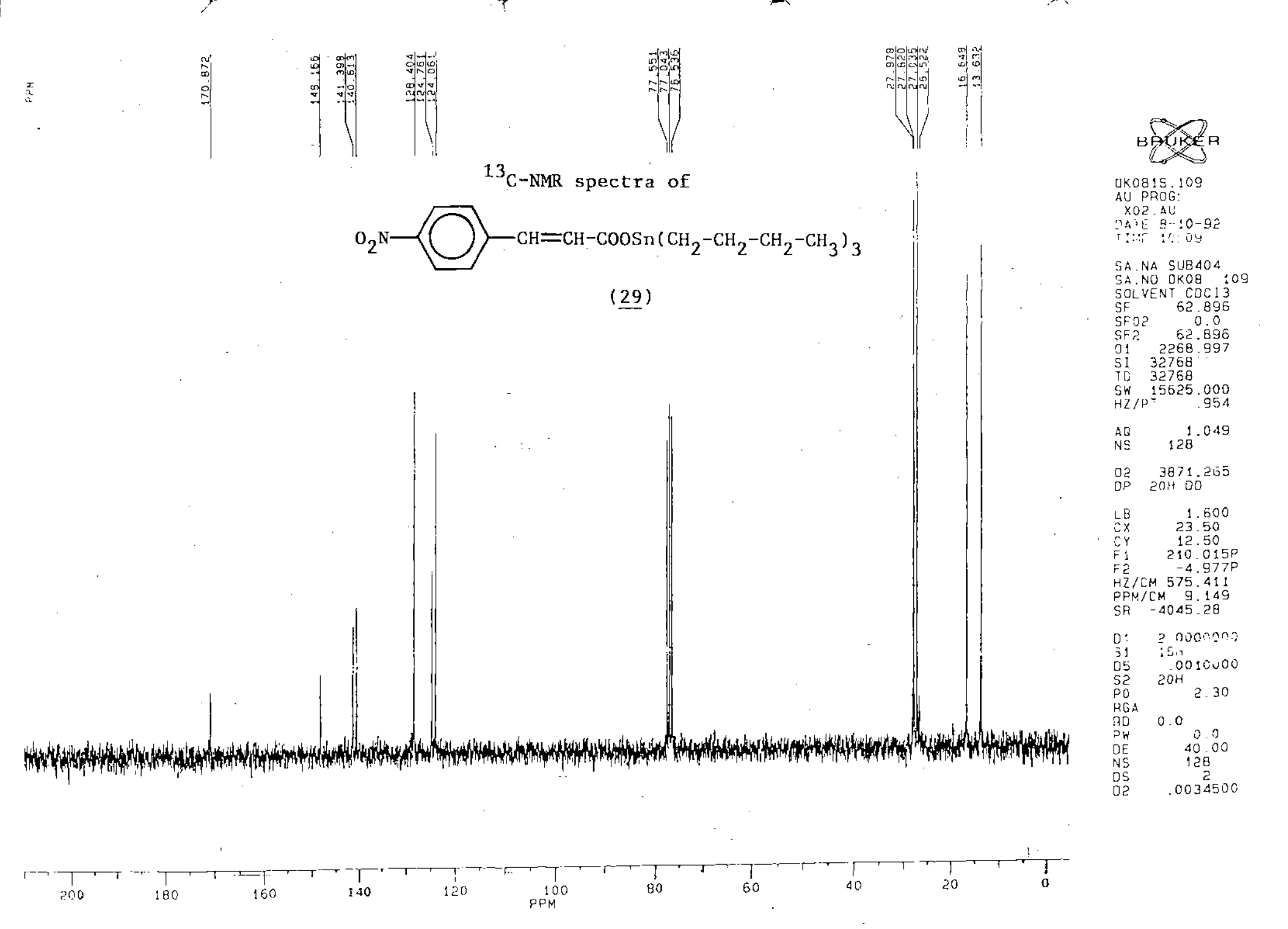

^{13}C-NMR spectra of

(29)

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DK081S.109
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X02.AU
DATE 8-10-92
TIME 10:09

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SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 128

O2 3871.265
DP 20H 00

LB 1.600
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
51 15u
D5 .0010000
S2 20H
P0 2.30
RGA
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PW 0.0
DE 40.00
NS 128
DS 2
O2 .0034500

CD/150

OBSERVE Sn:9
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Pulse width 90.0 degrees
Ambient temperature
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[illegible]
[illegible]
Decoupler gated on during acquisition
Decoupler gated off during delay
[illegible]
[illegible]
[illegible]
Total acquisition time 5 minutes

$p\text{-}NO_2\text{-}PhCH{=}CH\text{-}COOSnBu_3$

(29)

(120.258)

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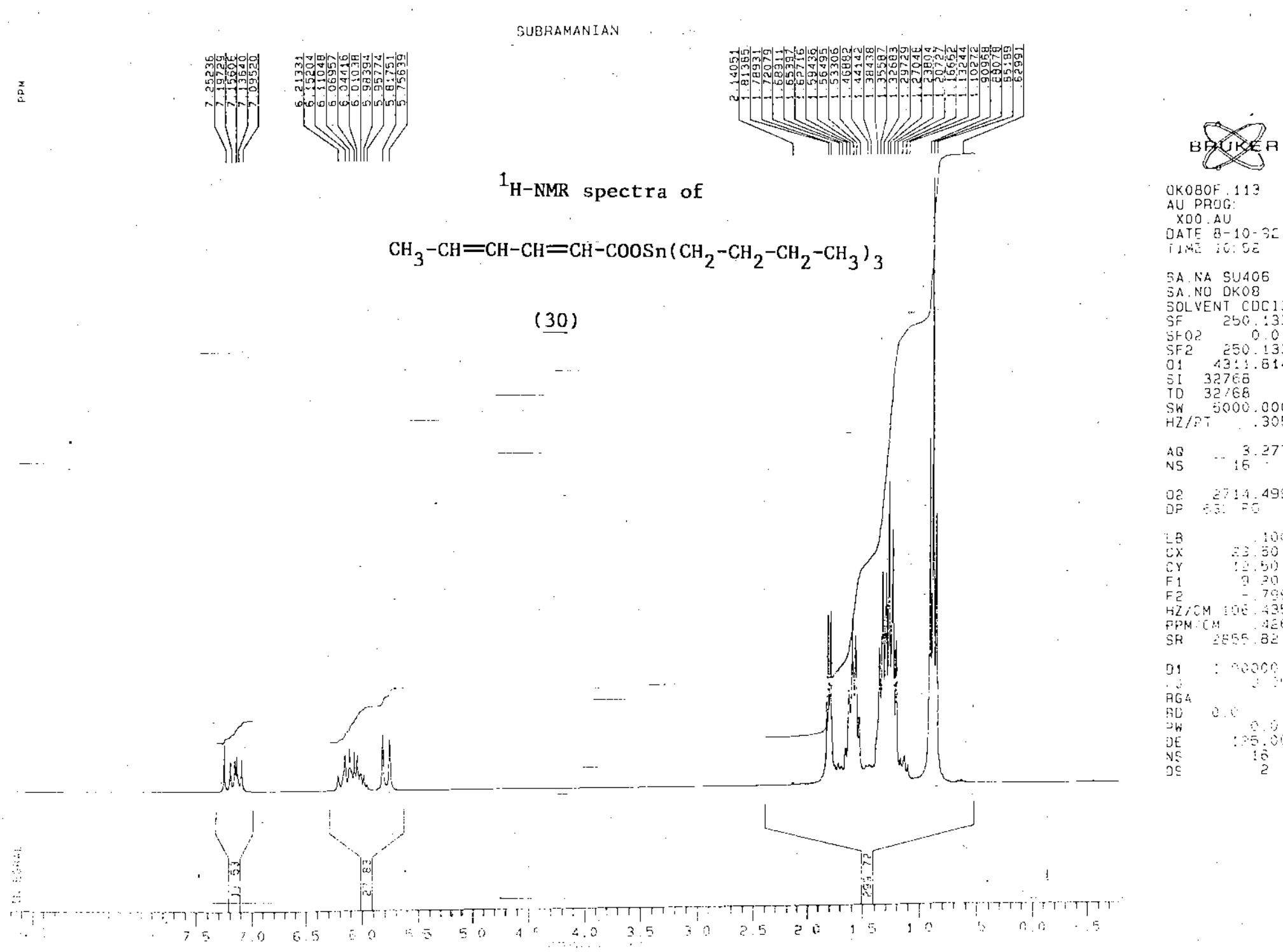
SUBRAMANIAN



^{1}H-NMR spectra of

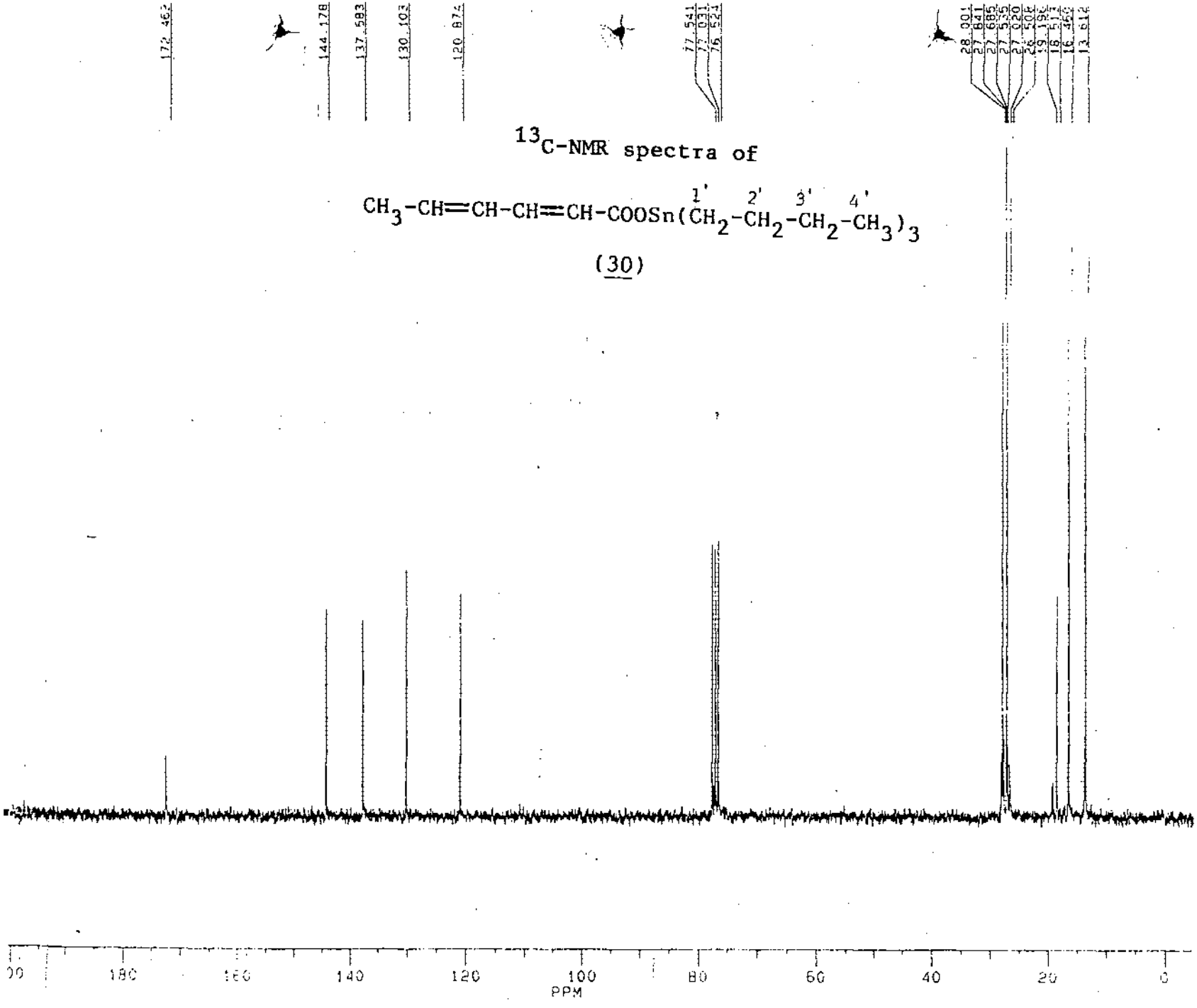
$CH_3-CH=CH-CH=CH-COOSn(CH_2-CH_2-CH_2-CH_3)_3$

(30)

^{13}C-NMR spectra of

$CH_3-CH=CH-CH=CH-COOSn(\overset{1'}{CH_2}-\overset{2'}{CH_2}-\overset{3'}{CH_2}-\overset{4'}{CH_3})_3$

(30)



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DATE 8-10-92
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SA.NO DK08 113
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SFO2
SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 256

O2 3871.265
OP 20H DO

L8 1.600
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
D4 16H
D5 .0010000
S2 20H
P0 2.30
RGA
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PW 0 0
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NS 256
DS 2
D2 .0034500

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Relaxation delay 1.000 sec
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Ambient temperature
No. repetitions 144
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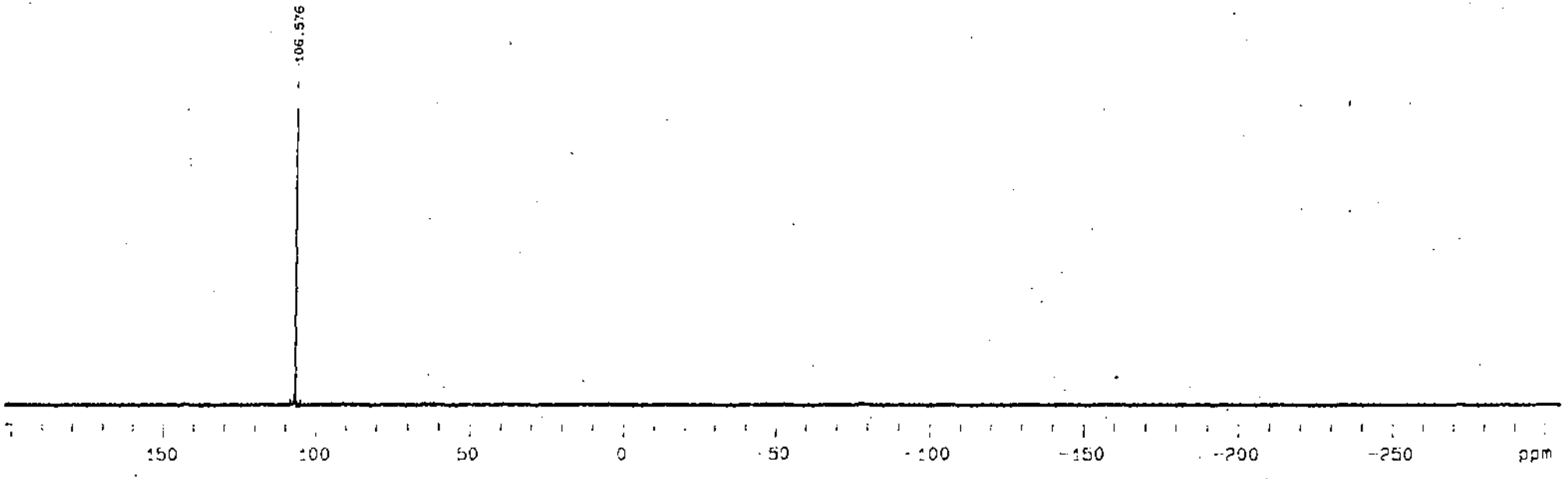
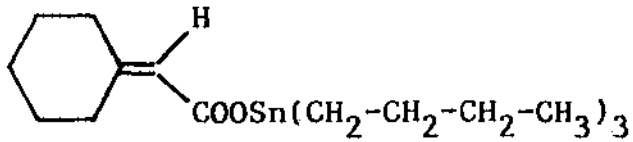
High power 50
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 262144
Total acquisition time 4 minutes

$CH_3-CH=CH-CH=CH-COOSnBu_3$

(30)



^{1}H-NMR spectra of



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BRUKER

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XQG.AU
DATE 9-10-92
TIME 10:25

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SA.NO OK08 110
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SFO2 0.0
SF2 250.133
O1 4311.814
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

AG 3.277
NS 16

O2 2714.499
DF 631.80

LB .100
GB 23.50
GC 12.80
P1 9.2019
P2 -.7998
PLW/CM 106.486
PPM/CM .426
SF 3866.50

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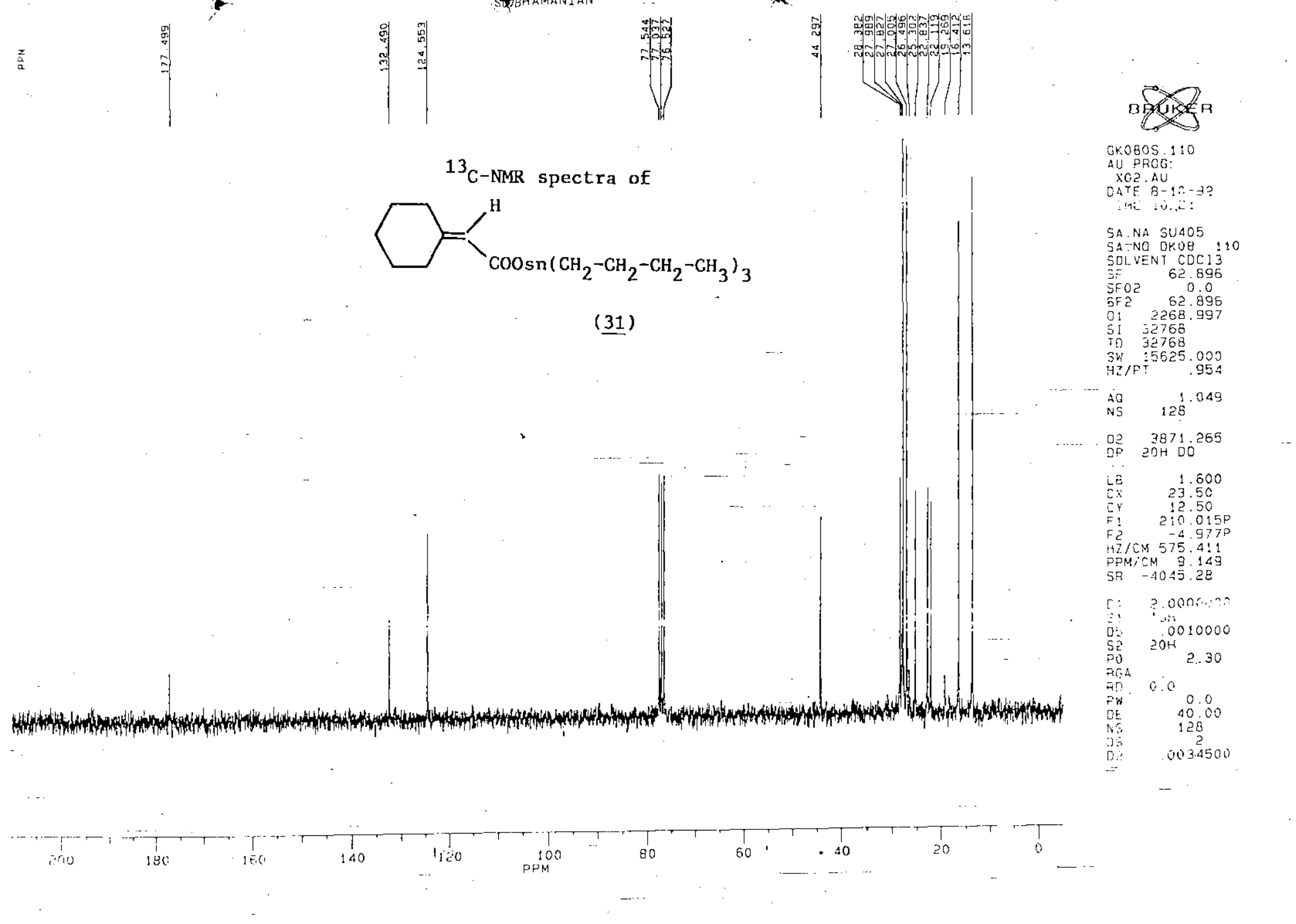
D2 3.30
RG4
RD 0.0
PW 3.0
DE 125.00
NS 16
DS 2



^{13}C-NMR spectra of

(31)

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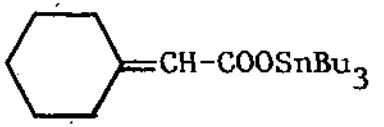
Spectral width 100.0 KHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 272
DECOUPLE H1
High power 50
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 262144
Total acquisition time 9 minutes



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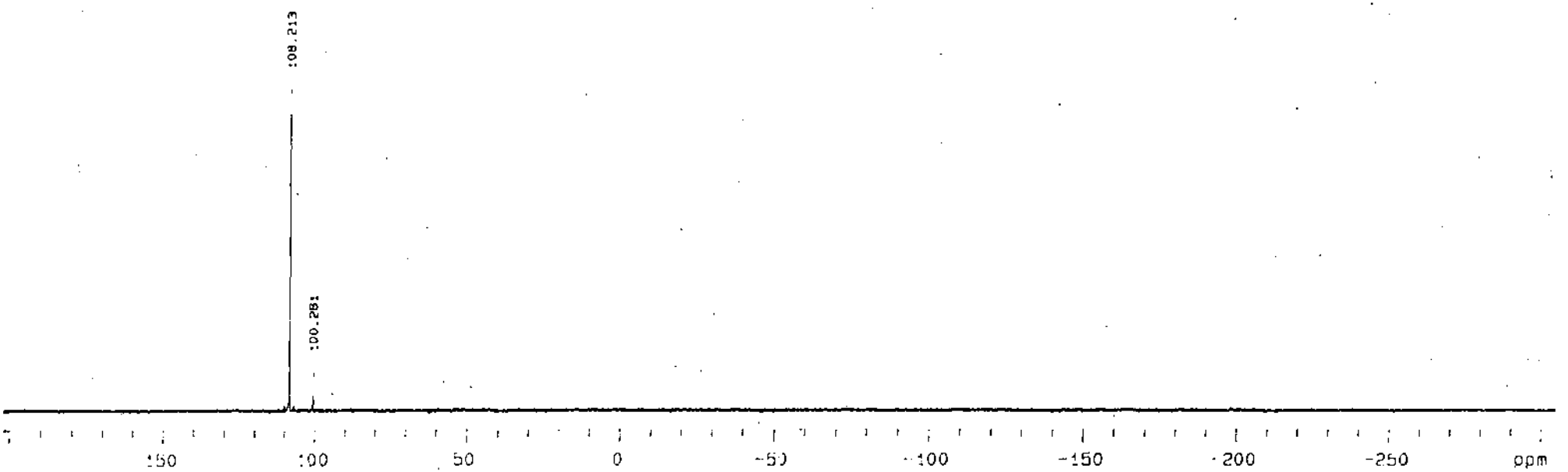
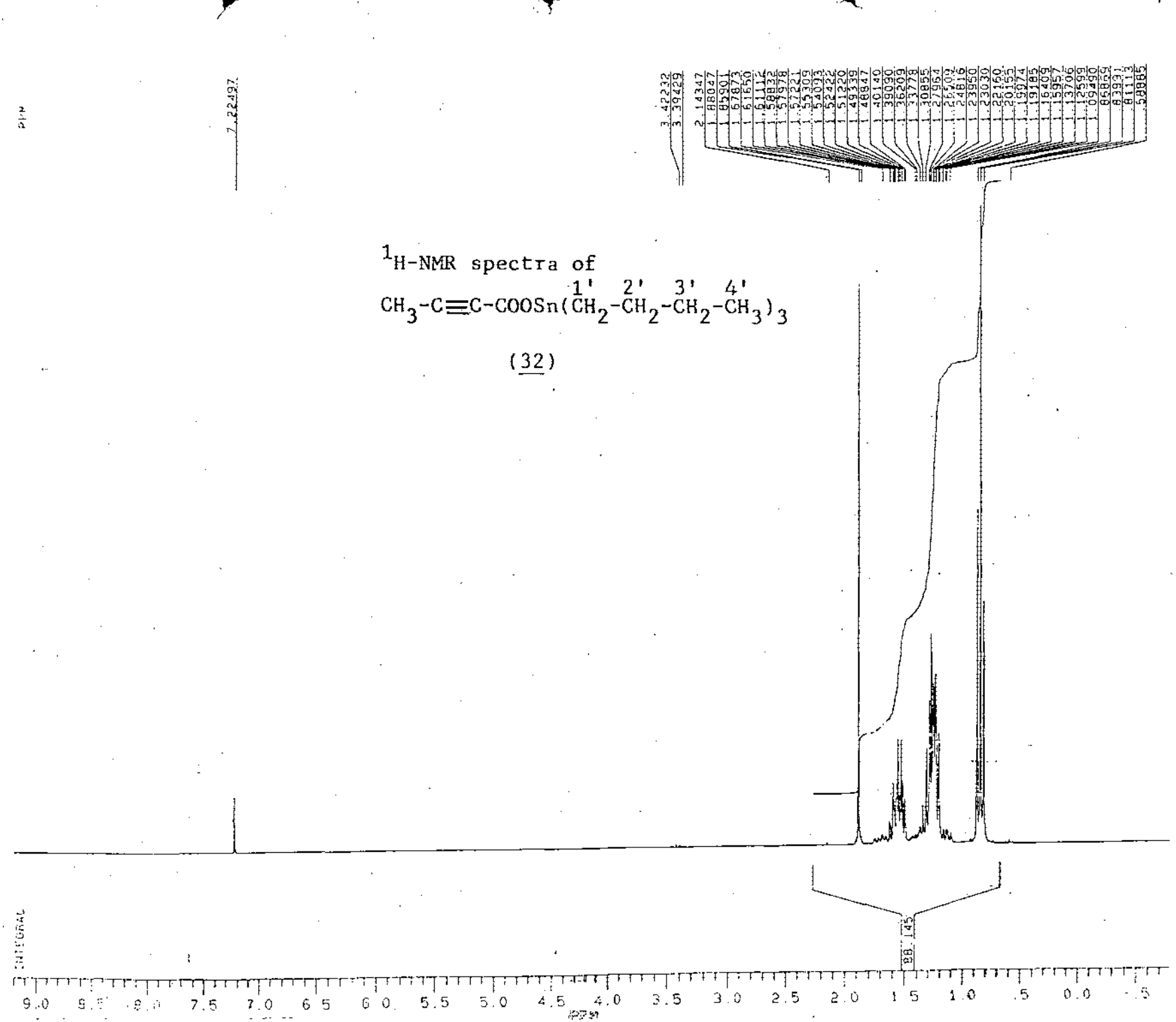


^{1}H-NMR spectra of

$CH_3-C\equiv C-COOSn(\overset{1'}{C}H_2-\overset{2'}{C}H_2-\overset{3'}{C}H_2-\overset{4'}{C}H_3)_3$

(32)



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DATE 9-10-92
TIME 11:01

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SF2 250.133
O1 4311.814
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

AQ 3.277
NS 16

O2 2714.499
DP 63L PO

LB .100
CX 23.50
CY 12.50
F1 9.201P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
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RD 0.0
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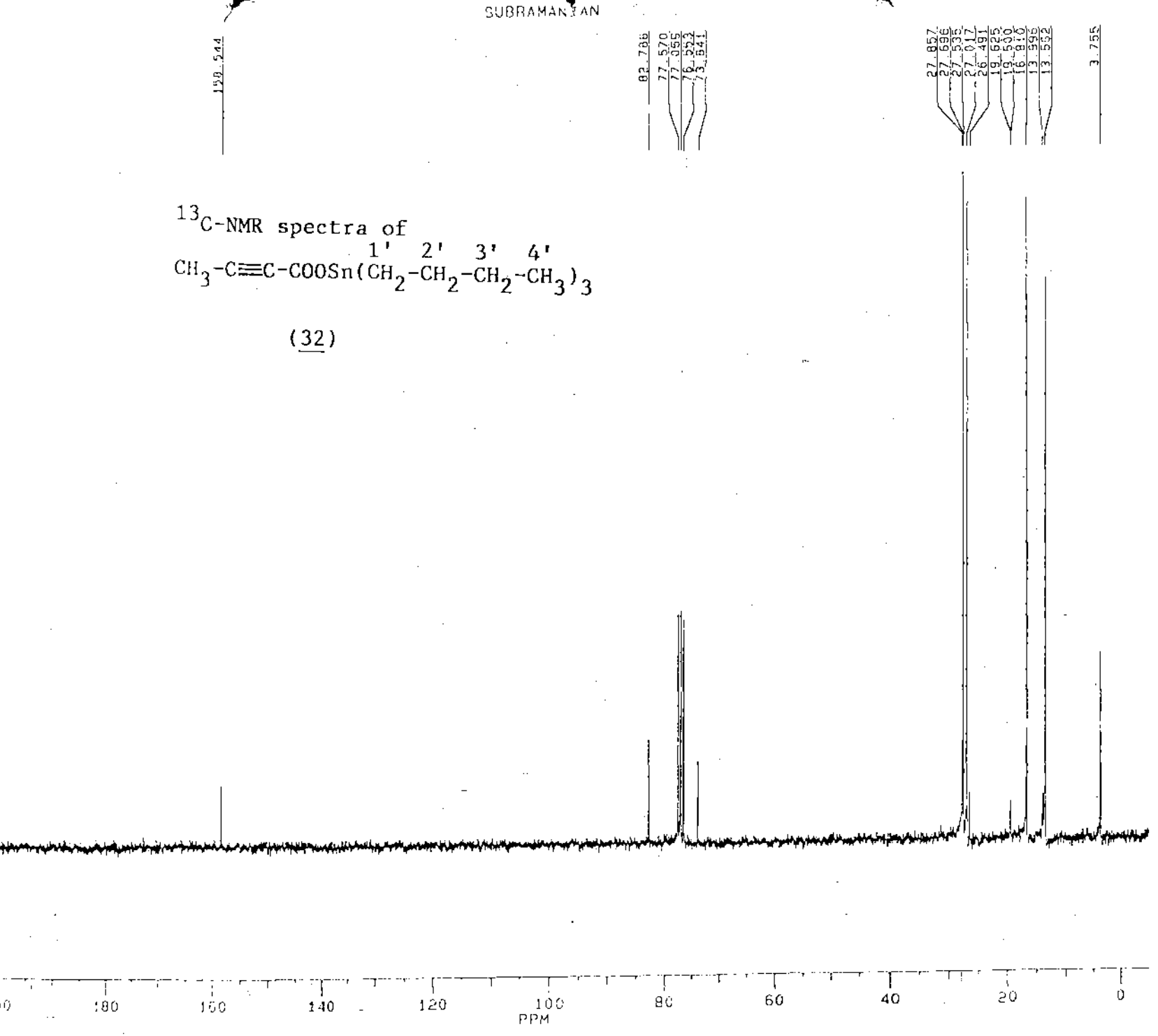
NS 16
DS 2

SUBRAMANIAN



^{13}C-NMR spectra of

$CH_3-C\equiv C-COOSn(\overset{1'}{CH_2}-\overset{2'}{CH_2}-\overset{3'}{CH_2}-\overset{4'}{CH_3})_3$

(32)

BRUKER

GK090S.109
AU PROG:
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DATE 9-10-92
TIME 10:37

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SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 256

O2 3871.265
OP 20H DO

LB 1.500
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
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PO 2.30
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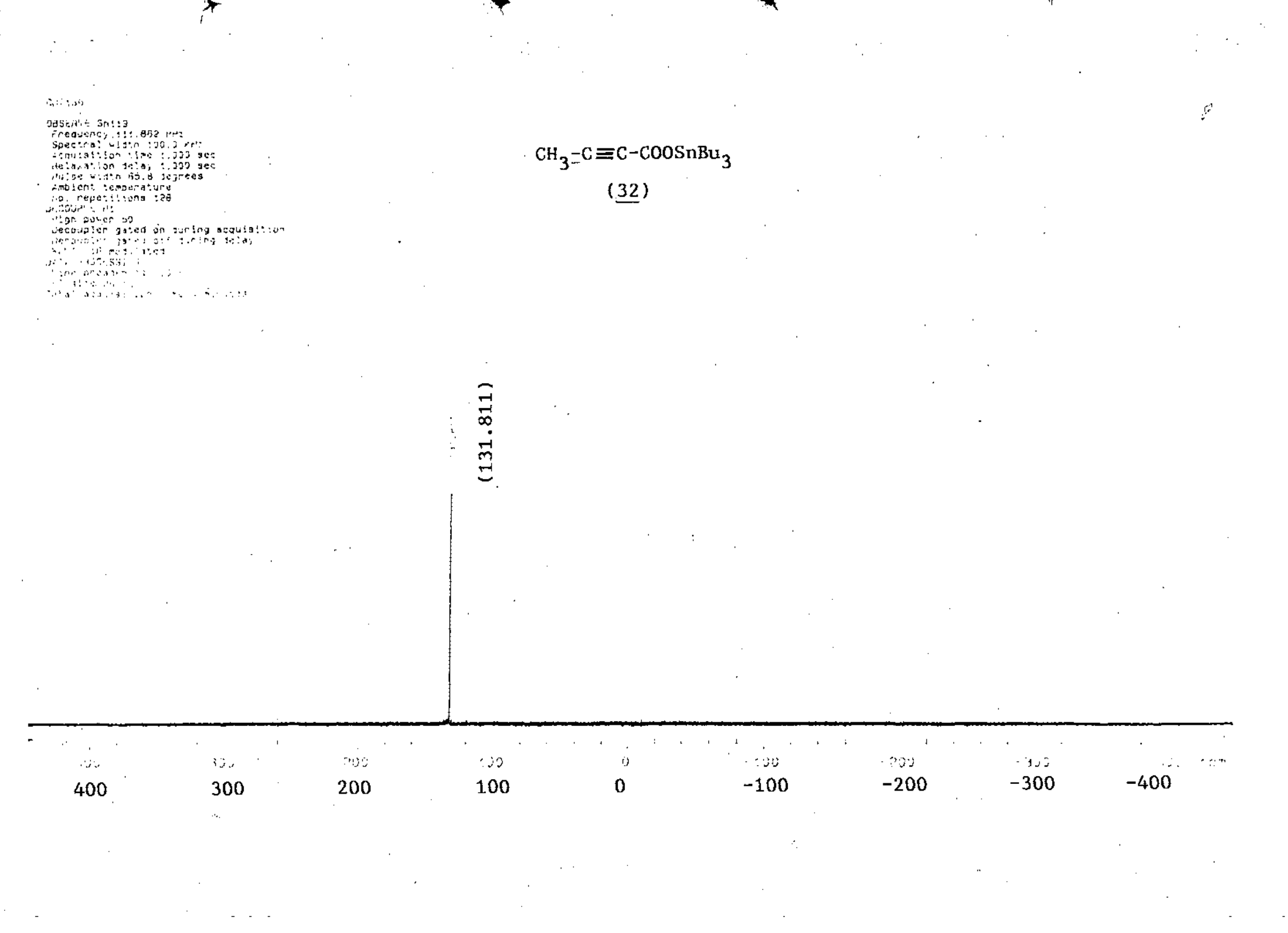
OS 2
O2 3871.265

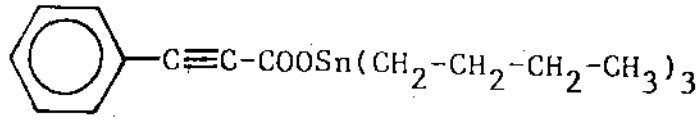


$CH_3-C\equiv C-COOSnBu_3$

(32)

SUBRAMANIAN

^{1}H-NMR spectra of



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DATE 28-4-93
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SF2 250.133
SY 100.0
O1 4311.614
SI 32768
TD 32768
SW 5000.000
SW2 5000.000
HZ/PT .305

RD 0.0
AQ 3.277
RG 2
NS 16
TE 297

DE 125.0
FW 6300
O2 2714.499
DP 63L PO

LB .100
GB 0.0
NC -1
CX 23.50
CY 12.50
F1 9.201P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2855.82

D1 1.0000000
PO 3.30
RGA
RD 0.0
PW 0.0
DE 125.00
NS 16
DS 2

INTEGRAL
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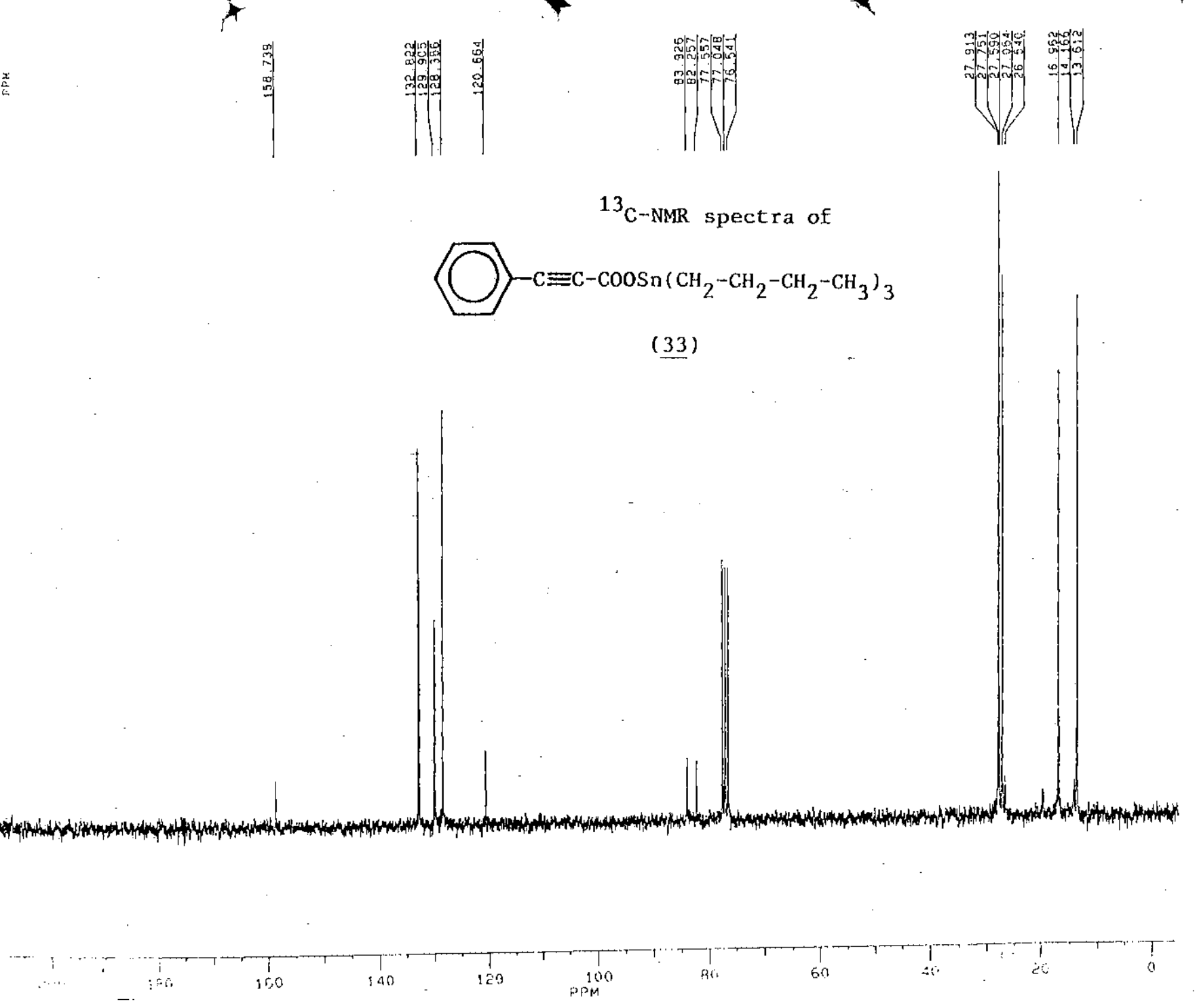
392.56
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0 -.5
PPM



^{13}C-NMR spectra of

(33)

BRUKER

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DATE 28-4-93
TIME 12:06

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SF2 62.896
SY 62.0
O1 2268.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 256
TE 297

DE 40.0
PW 19600
O2 3871.265
OP 20H DO

LB 1.600
GB 0.0
NC 4
CX 63.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.142
SR -4045.28

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SI 16K
D5 .0010000
SF 20M
PO 2.30
PCS
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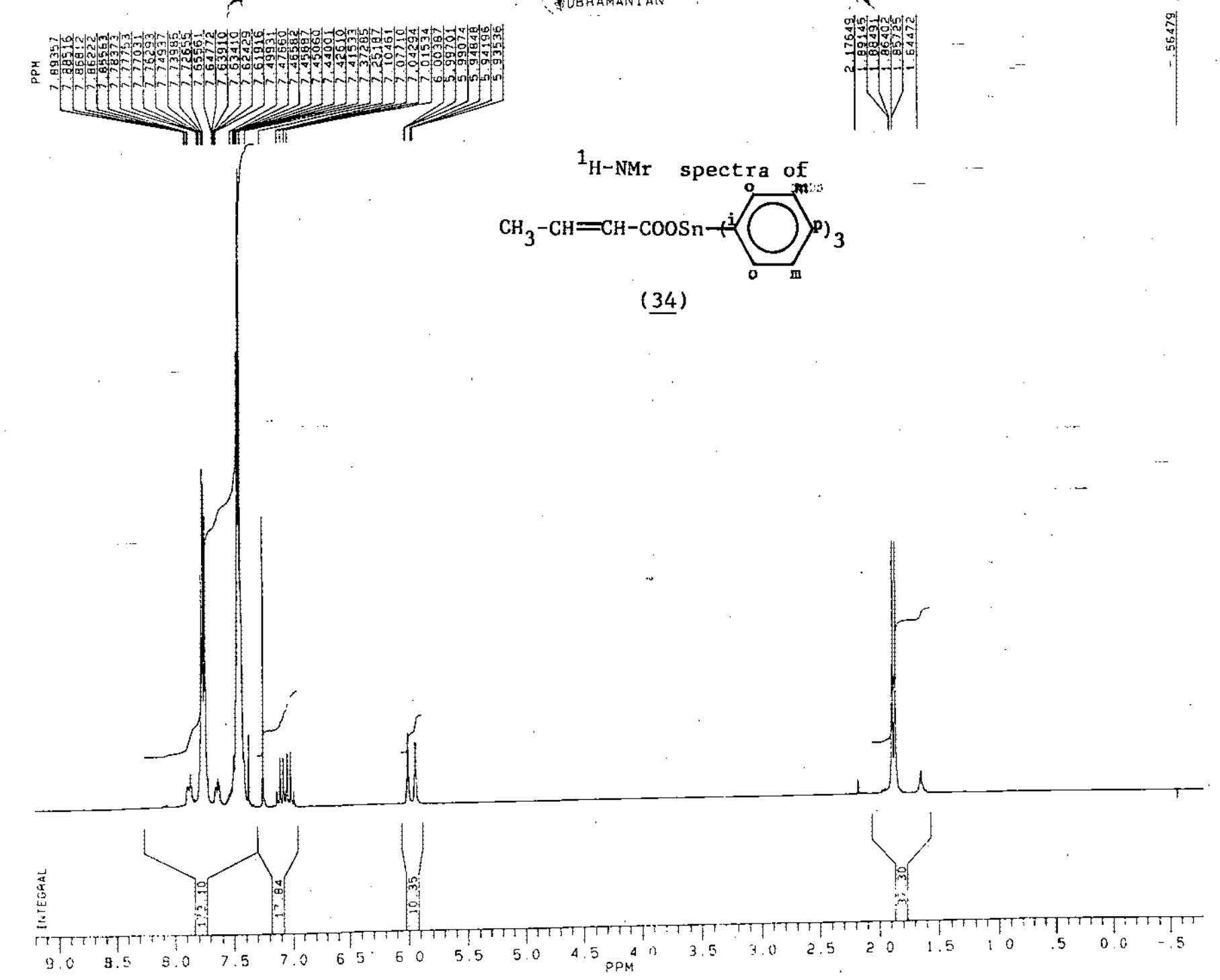
PW
DE 40.00
NS 256
DS 2



^{1}H-NMr spectra of

(34)

BRUKER

JA120S.126
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DATE 12-1-93
TIME 20:01

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SA.NO JA12 126
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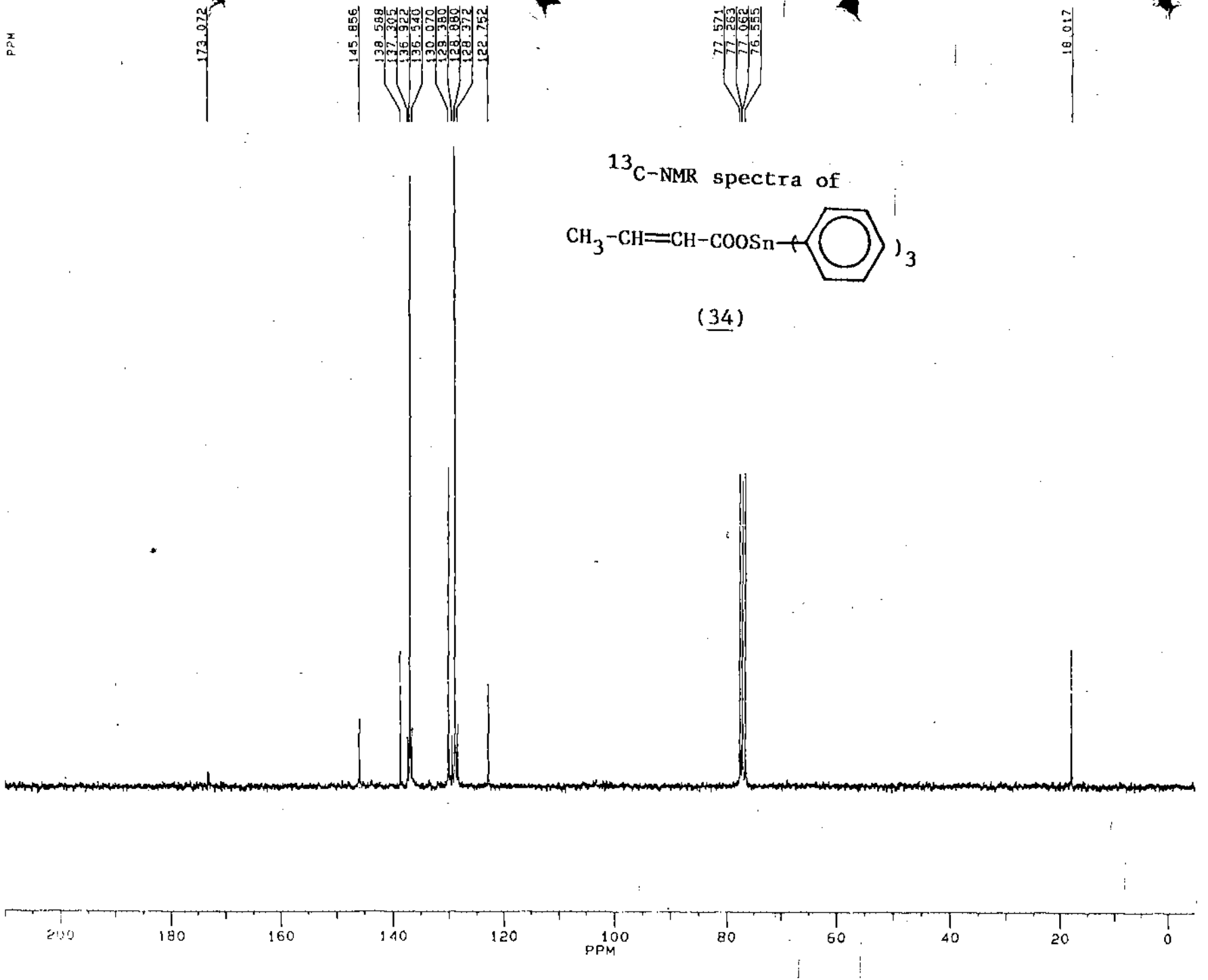
SF2 250.133
SY 100.0
O1 4311.814
SI 32768
TD 32768
SW 5000.000
SW2 5000.000
HZ/PT .305

RD 0.0
AQ 3.277
RG 10
NS 16
TE 297

DE 125.0
FW 6300
O2 2714.499
DP 63L PO

LB .100
GB 0.0
NC 1
CX 23.50
CY 12.50
F1 9.200P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2555.82

D1 1.0000000
PO 3.30
RGA
RD C 0
PW 0.0
DE 125.00
NS 16
DS 2



^{13}C-NMR spectra of

$CH_3-CH=CH-COOSn-(C_6H_5)_3$

(34)

BRUKER

JA121S.126
AU PROG:
X02.AU
DATE 12-1-93
TIME 20:56

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SFO2 0.0
SF2 62.896
SY 62.0
O1 2269.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 1024
TE 297

DE 40.0
FW 19600
O2 3871.265
OP 20H DO

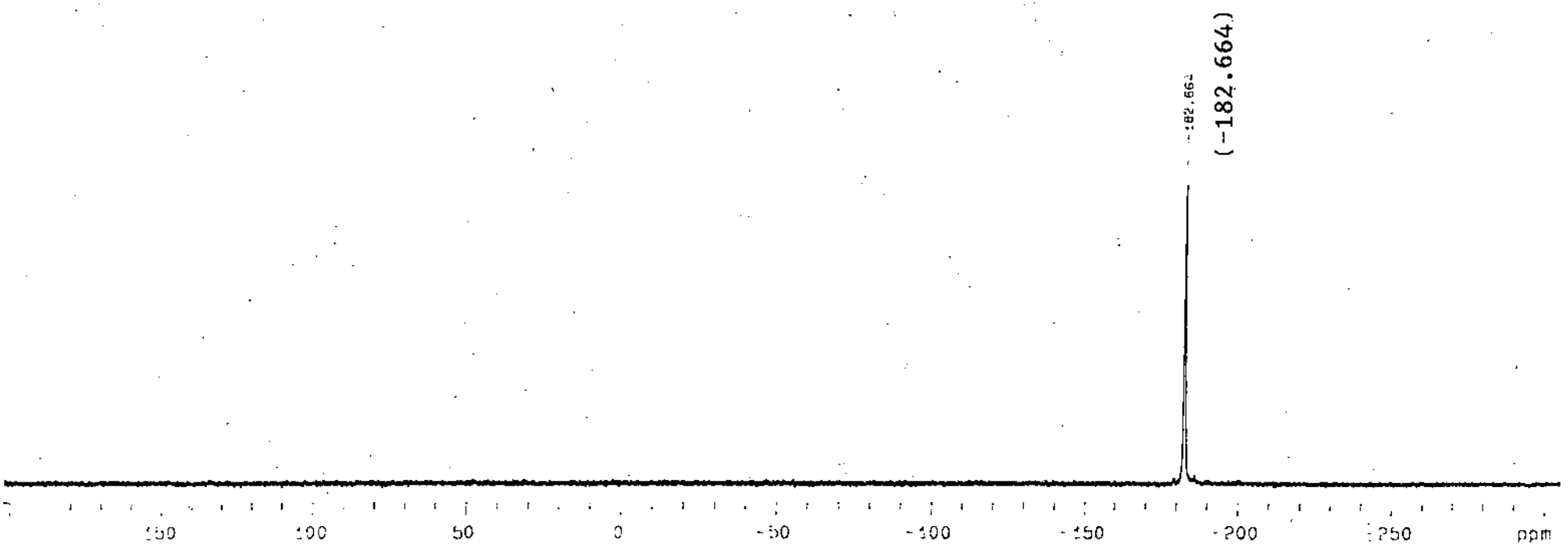
LB 1.600
GB 0.0
NC 5
CX 23.56
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.2P

D1 2.0000000
S1 16H
D5 .0010000
S2 20H
PO 2.30
BGA
RD 0 0 .
PW 0.0
DE 40.00
NS 1024
DS 2

OBSERVE Sn119
Frequency 111.862 MHz
Spectral width 100.0 KHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 2656
DECOUPLE H1
High power 59
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 4.0 Hz
FT size 262144
Total acquisition time 88 minutes

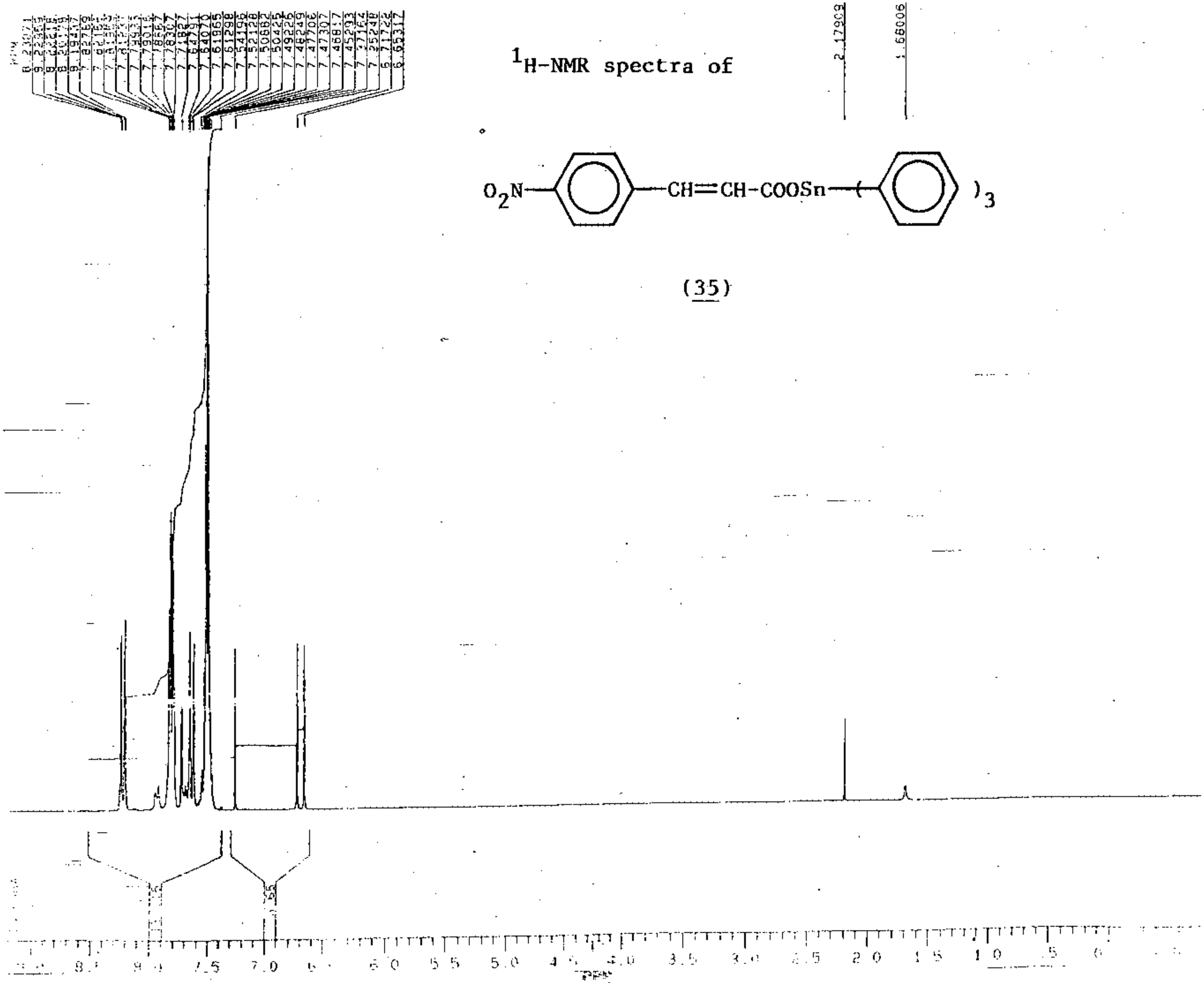
$CH_3-CH=CH-COOSnPh_3$

(34)



^{1}H-NMR spectra of

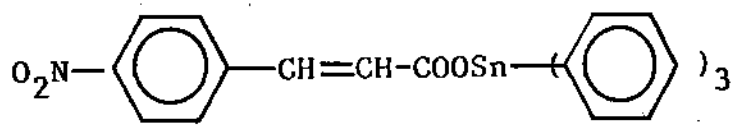
(35)



SUBRAMANIAN

171.989
148.399
142.376
140.959
138.040
137.317
136.533
136.549
130.369
129.569
129.063
128.587
124.151
123.138
77.613
77.104
76.597

^{13}C-NMR spectra of



(35)

BRUKER

OK090S.111
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SF2 62.896
O1 2268.997
SI 32768
TD 32768
SW 15625.000
HZ/PT .954

AQ 1.049
NS 256

O2 3871.265
DP 20H D0

LB 1.600
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

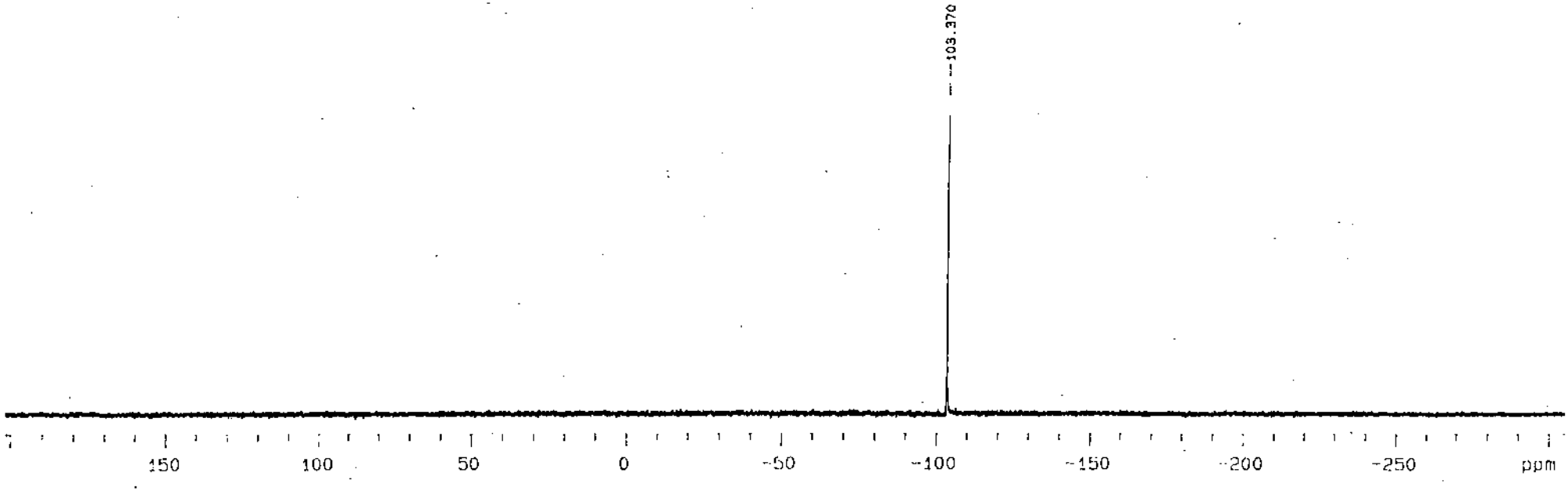
D1 2.0000000
P1 16H
D5 .0010000
S2 20H
P0 2.30
RGA
AD 0.0
PW 0.0
DE 40.00
NS 256
DS 2
D2 .0034500

CD 1?2

OBSERVE Sn119
 Frequency 111.862 MHz
 Spectral width 100.0 kHz
 Acquisition time 1.000 sec
 Relaxation delay 1.000 sec
 Pulse width 65.8 degrees
 Ambient temperature
 No. repetitions 240
DECOUPLE H1
 High power 50
 Decoupler gated on during acquisition
 Decoupler gated off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 4.0 Hz
 FT size 262144
Total acquisition time 8 minutes

$p\text{-}NO_2\text{-}PhCH{=}CH\text{-}COOSnPh_3$

(35)



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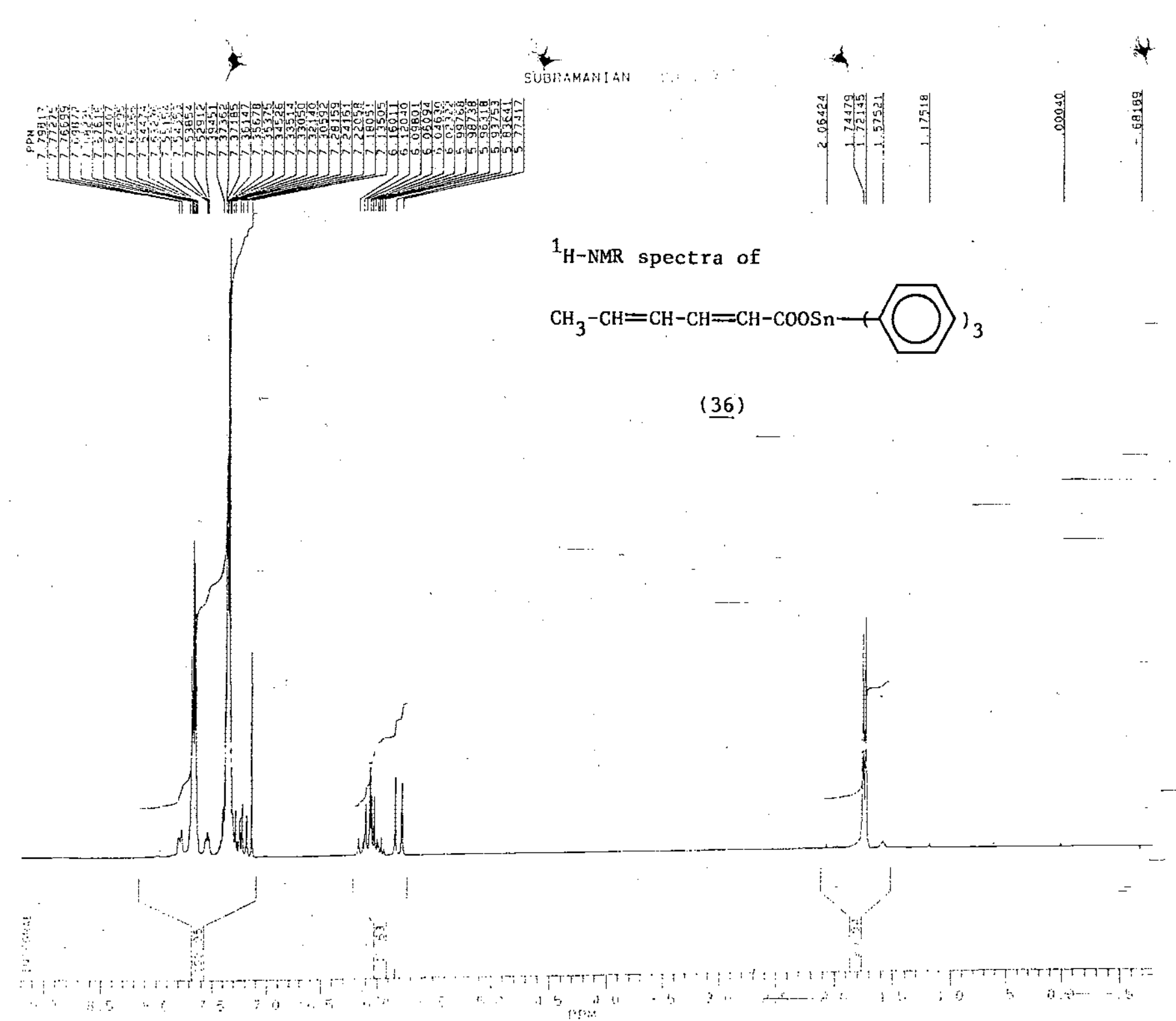
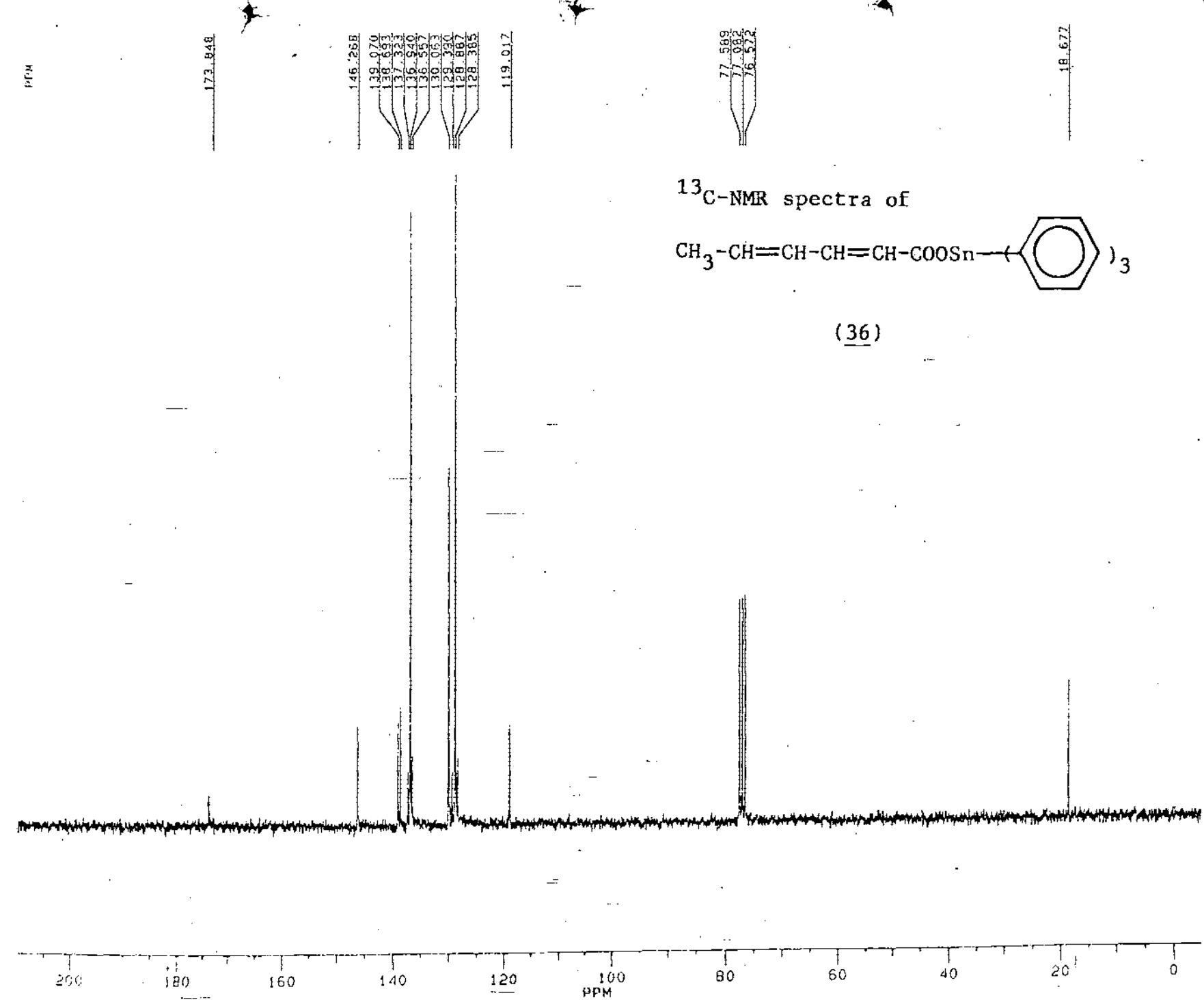


^{1}H-NMR spectra of

(36)



^{13}C-NMR spectra of

CH_3-CH=CH-CH=CH-COOSn-(C$_6$H$_5$)$_3$

(36)


```
OK091S.110
AU PROG:
 X02.AU
DATE 9-10-92
TIME 11:24

SA.NA SUB439
SA.NO OK09  110
SOLVENT CDCl3
SF       62.896
SF02      0.0
SF2      62.896
O1     2268.997
SI    32768
TD    32768
SW    15625.000
HZ/PT      .954

AQ        1.049
NS      256

O2     3871.265
DP    20H 00

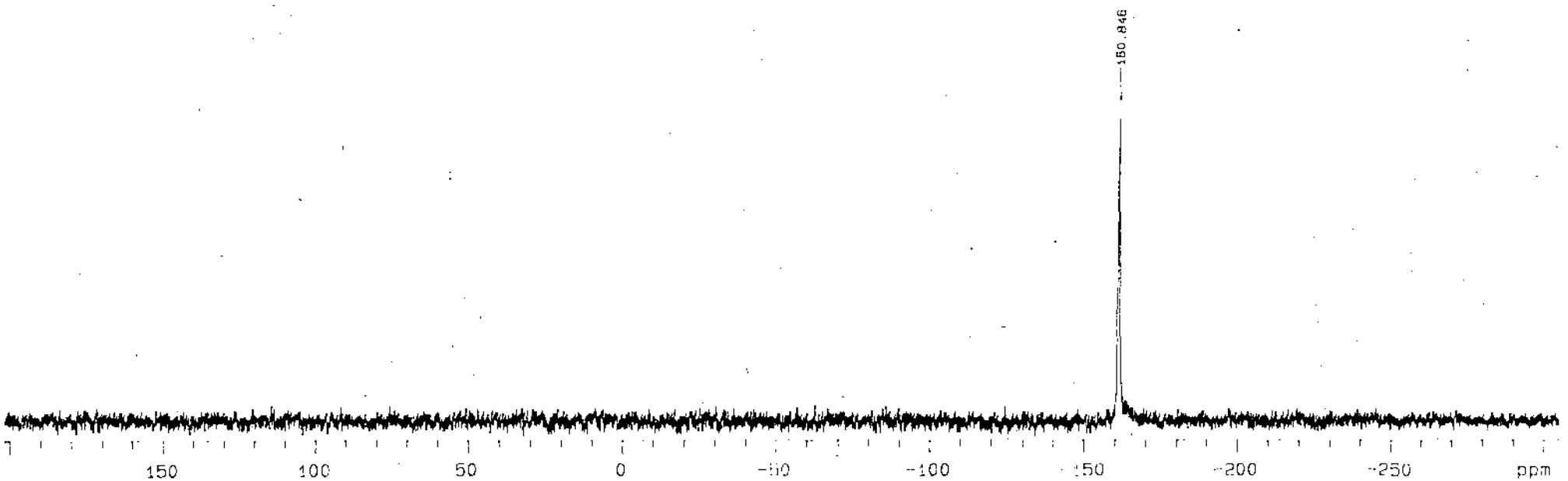
LB        1.600
CX       23.50
CY       12.50
F1      210.015P
F2       -4.977P
HZ/CM  575.411
PPM/CM   9.149
SR    -4045.28

D1     2.0000000
D5      .0010000
S2    20H
P0        2.30
RGA
RD     0.0
PW        0.0
DE       40.00
NS       256
DS         2
D2      0.34500
```

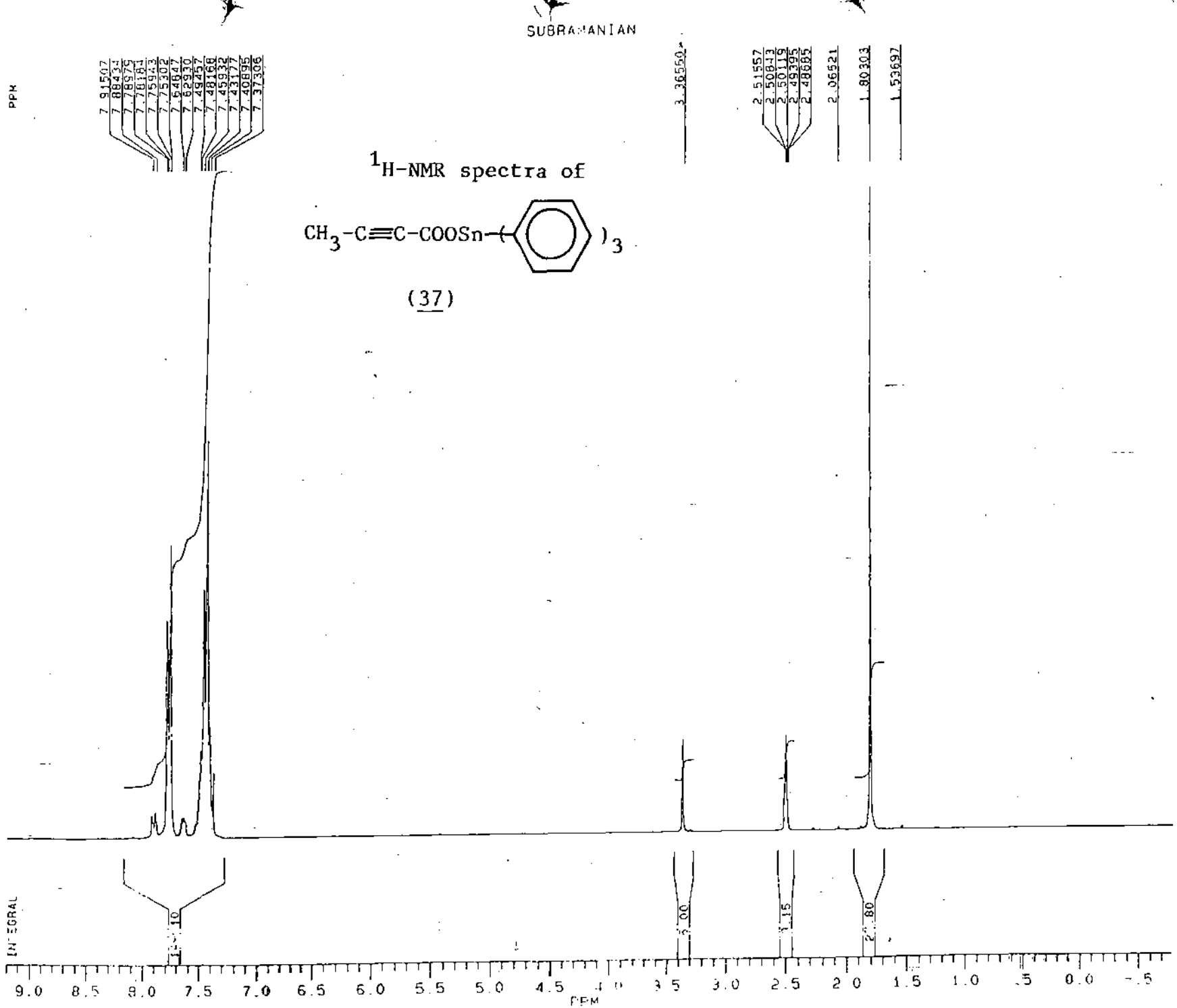
OBSERVE Sn119
 Frequency 111.862 MHz
 Spectral width 100.0 kHz
 Acquisition time 1.000 sec
 Relaxation delay 1.000 sec
 Pulse width 65.0 degrees
 Ambient temperature
 No. repetitions 1168
DECOUPLE H1
 High power 50
 Decoupler gated on during acquisition
 Decoupler gated off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 10.0 Hz
 FT size 262144
Total acquisition time 36 minutes

$CH_3-CH=CH-CH=CH-CO_2SnPh_3$

(36)



SUBRAMANIAN



^{1}H-NMR spectra of

(37)

BRUKER

OK080F.114
AU PROG:
XOO.AU
DATE 8-10-92
TIME 14:10

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SA.NO OK08 114
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SFO2 0.000
SF2 250.134
O1 5487.59
SI 32768
TD 32768
SW 5000.000
HZ/PT .305

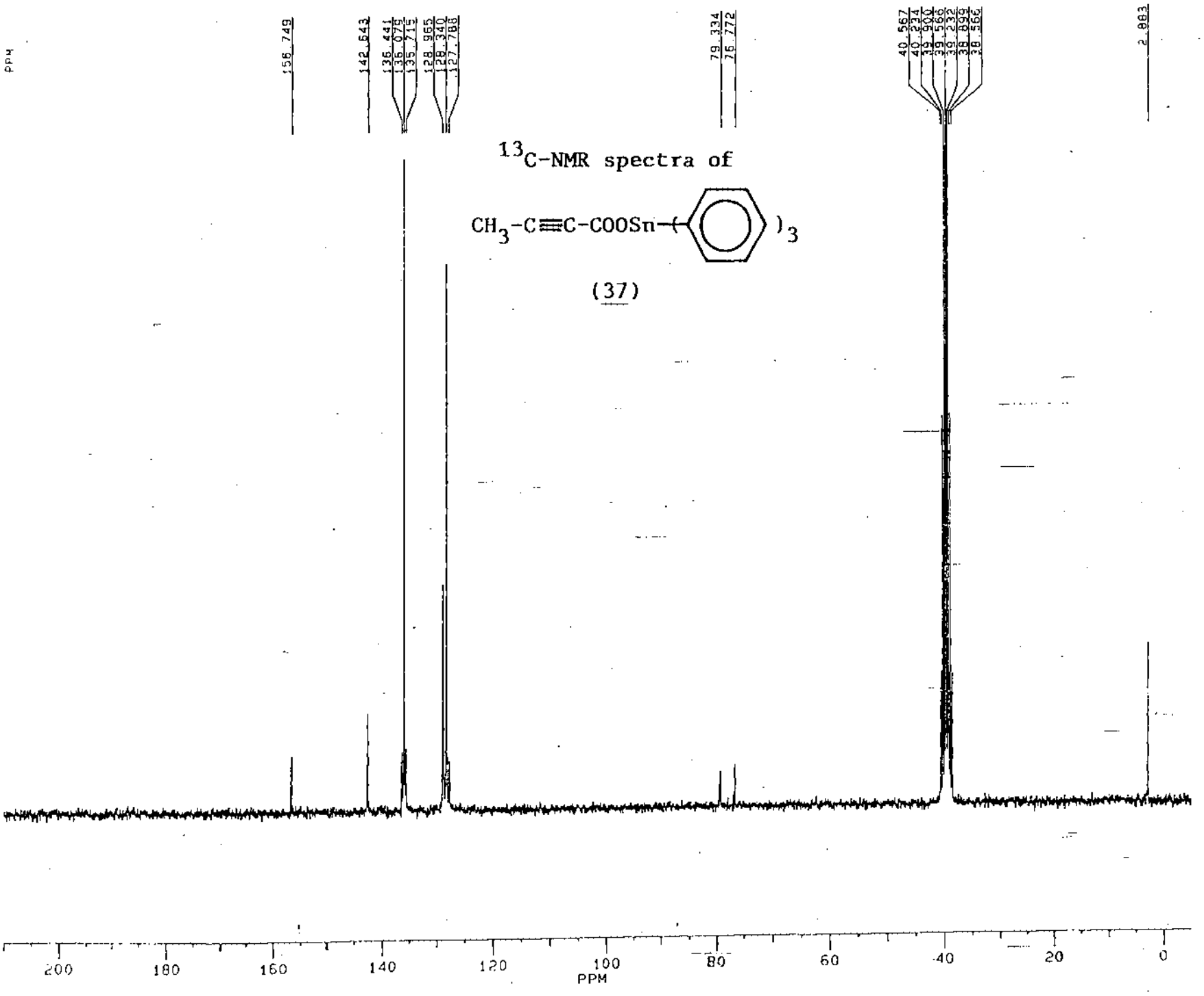
AQ 3.277
NS 16

O2 2714.499
DP 63L PO

LB .100
CX 23.60
CY 12.56
F1 9.2000P
F2 -.7999P
HZ/CM 106.435
PPM/CM .426
SR 4037.99

D1 1.00000000
[illegible]
RGA
RD 0.0
PW 0
DE 125.00
NS 16
OS 0

SUBRAMANIAN



^{13}C-NMR spectra of

(37)

BRUKER

```
OK080S.128
AU PROG:
 XO2.AU
DATE 8-10-92
TIME 16:54

SA.NA SU407
SA.NO OK08  128
SOLVENT DMSO
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SFO2     0.0
SF2     62.896
O1    2596.808
SI   32768
TD   32768
SW  15625.000
HZ/PT    .954

AG      1.049
NS    800

O2    5039.700
OP  20H DO

LB      1.600
CX     23.50
CY     12.50
F1    210.0102
F2     -4.9819
HZ/CM 575.411
PPM/CM  9.142
SR  -3717.47

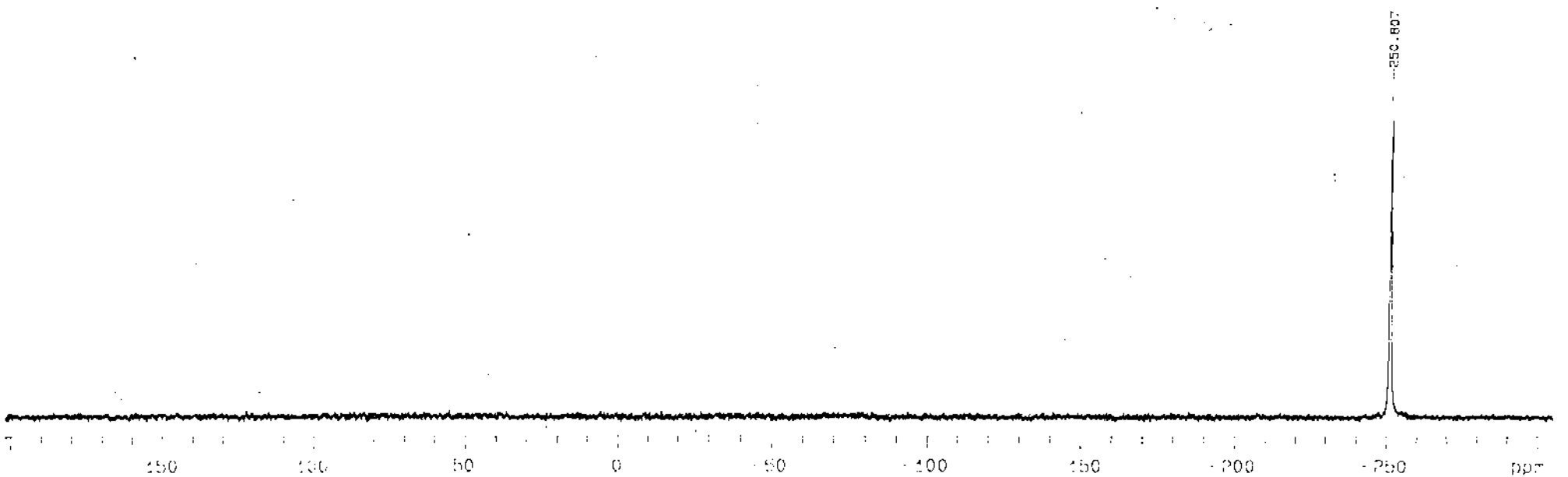
D1    4.0000000
[illegible]
D5     .0010000
S2    20H
PO       2 30.
RGA
BD    0.0
PW       0.0
DE      40.00
NS       800
DS         2
D2     .0034500
```

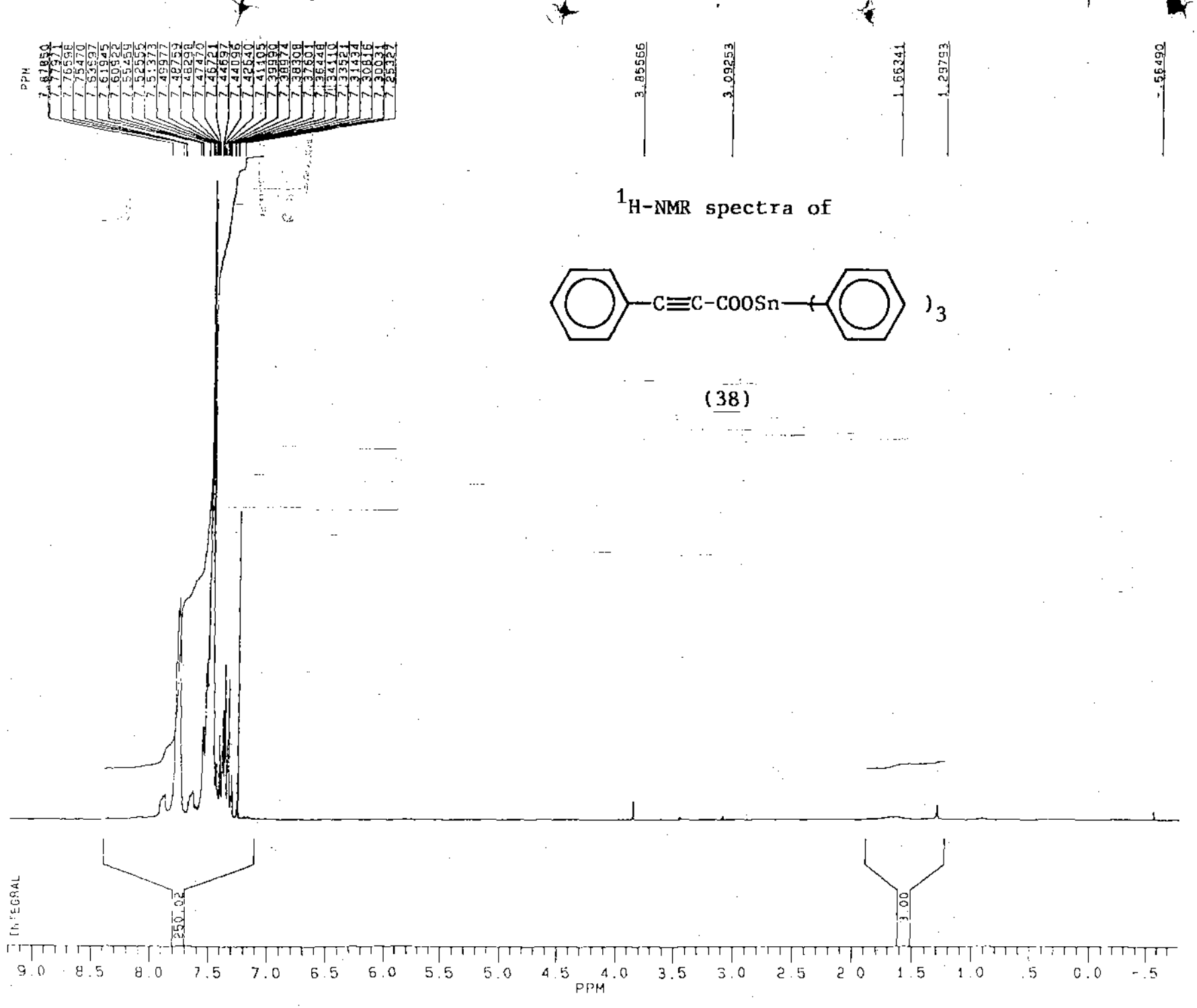
CU 1?5(14)

OBSERVE Sn119
Frequency 111.862 MHz
Spectral width 100.0 kHz
Acquisition time 1.000 sec
Relaxation delay 1.000 sec
Pulse width 65.8 degrees
Ambient temperature
No. repetitions 1840
DECOUPLE H1
High power 50
Decoupler gated on during acquisition
Decoupler gated off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 10.0 Hz
FT size 262144
Total acquisition time 61 minutes

$$CH_3-C\equiv C-CO_2SnPh_3$$

(37)





^{1}H-NMR spectra of

(38)

BRUKER

AP281F.113
AU PROG:
XOO.AU
DATE 28-4-93
TIME 12:28

SA.NA SUB225
SA.NO AP28 113
SOLVENT CDC13
SF 250.133
SF02 0.0
SF2 250.133
SY 100.0
O1 4311.814
SI 32768
TD 32768
SW 5000.000
SW2 5000.000
HZ/PT .305

RD 0.0
AG 3.277
RG 4
NS 16
TE 297

DE 125.0
PW 6300
O2 2714.499
OP 63L PO

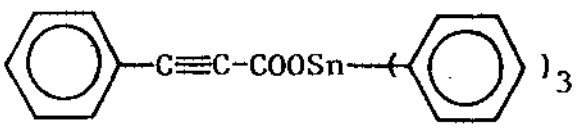
LB .100
GB 0.0
NC 0
CX 23.50
CY 12.50
F1 9.201P
F2 -.799P
HZ/CM 106.435
PPM/CM .426
SR 2855.82

D1 1.0000000
PO 3.30
RGA
RD 0.0
PW 0.0
DE 125.00
NS 16
DS 2

SUBRAMANIAN

159.766
137.577
137.331
136.948
136.565
132.942
130.453
130.274
129.568
129.080
128.494
120.301
86.209
81.487
77.606
77.304
77.099
76.590

^{13}C-NMR spectra of



(38)

BRUKER

AP280S.113
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X02.AU
DATE 28-4-93
TIME 12:24

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SA.NO AP28 113
SOLVENT CDC13
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SFO2 0.0
SF2 62.896
SY 62.0
O1 2268.997
SI 32768
TD 32768
SW 15625.000
SW2 15625.000
HZ/PT .954

RD 0.0
AQ 1.049
RG 400
NS 256
TE 297

DE 40.0
FW 19600
O2 3871.265
DP 20H 00

LB 1.600
GB 0.0
NC 5
CX 23.50
CY 12.50
F1 210.015P
F2 -4.977P
HZ/CM 575.411
PPM/CM 9.149
SR -4045.28

D1 2.0000000
S1 16H
D5 .0010000
S2 20H
PO 2.30
RGA
RD 0.0
PW 0.0
DE 40.00
NS 256.
DS 2

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