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The Syntheses and Characterization of New Dithiophosphonates derived from Novel 2,4-Bis(methoxytolyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfides and Their Ni(II) Complexes

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Abstract: Two novel perthiophosphonic acid anhydrides, 2,4-bis($R^{x,y}$)-1,3-dithia-2,4-diphosphetane 2,4-disulfide $[(R^{x,y}\text{-}P(S)S)_2$; R^x=3-methoxytolyl (**SAV-B1**) and R^y=2-methoxytolyl (**SAV-B2**)] were synthesized. From the reaction of **SAV-B1** and **SAV-B2** with alcohols, four new dithiophosphonic acids $[HS_2P(R^{x,y})(ORn)]$ (Rn; R1=ethyl R2=2-propyl) were prepared. These acids were converted to corresponding ammonium salts, $[NH_4][S_2P(R^{x,y})(ORn)]$. The ammonium salts were further reacted with $NiCl_2.6H_2O$ to prepare four new dithiophosphonato nickel(II) complexes, $[Ni(S_2P(R^{x,y})(ORn))_2]$. The ligands and complexes were characterized by elemental analyses, IR, ESI-MS, 1D ^1H, ^{13}C, ^{31}P NMR and 2D HSQC techniques. Complementary structural information was provided by the HSQC spectrum of the $[NH_4][S_2P(R^{x,y})(OR2)]$. The structure of the perthiophosphonic acid anhydrides was deduced from the structures of dithiophosphonates thereof.

Keywords:2,4-Diorganyl-1,3,2,4-dithiadiphosphetan-2,4-disulfide, Dithiadiphosphetanes, Perthiophosphonic acid anhydrides, Dithiophosphonic acid, Dithiophosphonato complexes.

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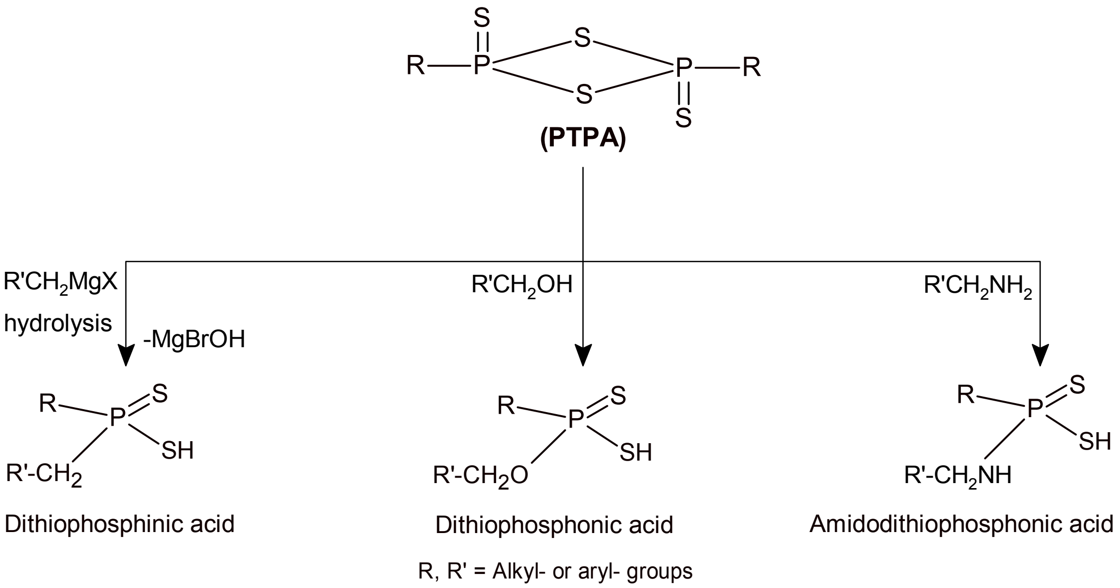
INTRODUCTION

Perthiophosphonic acid anhydrides (PTPA) are called as 2,4-diorganyl-1,3,2,4-dithiadiphosphetane-2,4-disulfides and known to be the starting materials in the synthesis of phosphorus-1,1-dithiolates. For example, dithiophosphonates, dithiophosphinates, and amidodithiophoshonates were obtained through the reactions of PTPAs with alcohols (1), Grignard compounds (2,3), and amines (4), respectively (Scheme 1).



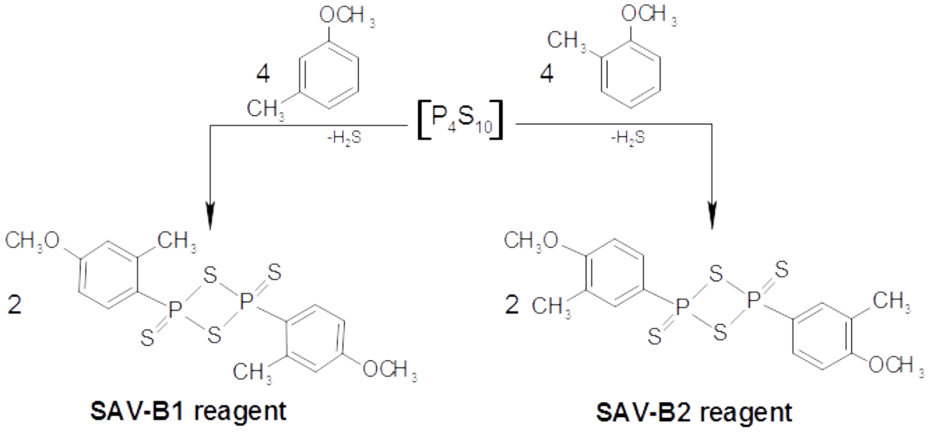
Scheme 1. Synthesis pathways through the reaction of perthiophosphonic acid anhydrides and nucleophiles to obtain phosphorus-1,1-dithiolates.

The first example of PTPA-type compounds was cyclohexyl-PTPA reported by Fay and co-workers (5). They reacted P_4S_{10} and cyclohexane directly. This procedure has been used ever since with various aromatic and aliphatic hydrocarbons instead of cyclohexane (6). In fact, there are two other routes to prepare PTPA compounds (7,8), but they are relatively more difficult and tiresome, not to mention a number of side-products.

Among commercially available PTPAs [R=-PhOPh (Belleu's reagent), $-SCH_3$ (Davy's reagent), -SPh (Yokoyama's reagent), etc.] (9), Lawesson's reagent ($R=-PhOCH_3$) (LR) has proven to be the most widely used (10). Ferrocenyl group can also be linked to the phosphorus-1,1-dithiolate group, and the resultant, so-called Ferrocenyl-Lawesson reagent (Fc-LR), 2,4-diferrocenyl-1,3-dithiadiphosphetane 2,4-disulfide is known for three decades, although not commercially available (11).

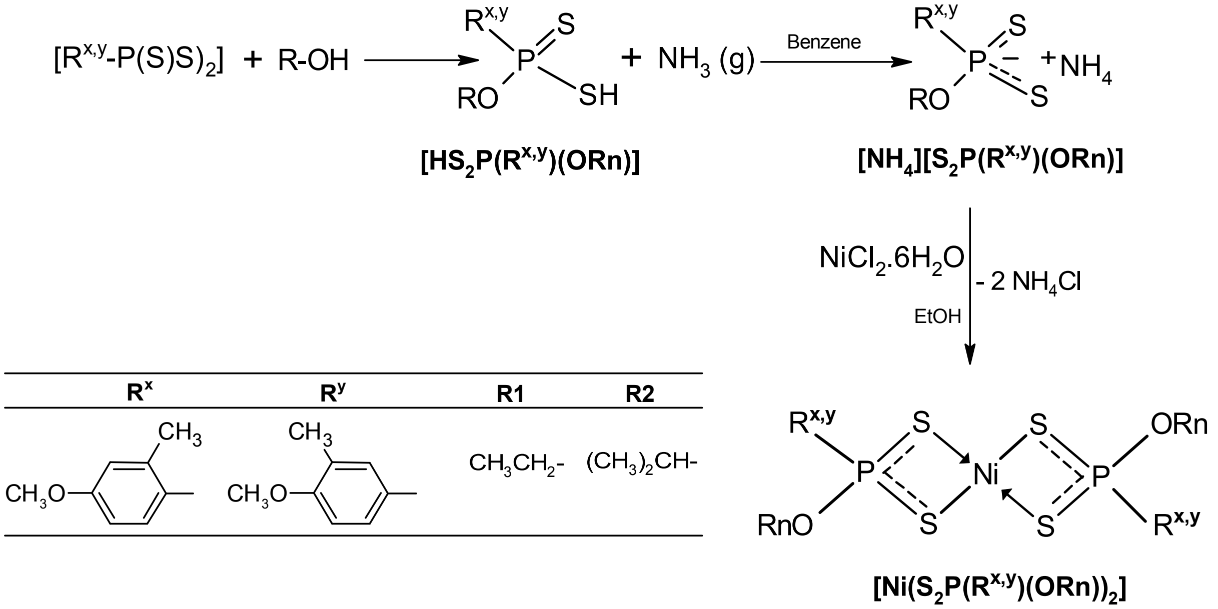
Phosphorus-1,1-dithiolates obtained from a PTPA and a nucleophile are soft base-type, bidentate ligands, and they find some use in industry (12, 13), agriculture (14), biochemistry (15), and metallurgy (16). The metal-complexing ability of phosphorus-1,1-dithiolates are based on sulfur donor groups that form four-membered chelate rings with metal cations (17). Dithiohosphonic acids, in particular, were reported to form complexes with transition metal cations like Ni(II), Cu(II), Zn(II), Cd(II), etc. (18,19). Among these, dithiohosphonato Ni(II) complexes possessing four-coordinate square-planar geometry (20).

In this work, first of all, we have prepared two novel PTPAs $[R^{x,y}\text{-}P(S)S)_2]$, that is, 2,4-bis(3-methoxytolyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide $[(R^{x}\text{-}P(S)S)_2]$ (**SAV-B1** reagent) and 2,4-bis(2-methoxytolyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide $[(R^{x}\text{-}P(S)S)_2]$ (**SAV-B2** reagent) (Scheme 2).



Scheme 2. Synthesis of novel PTPAs $[R^{x,y}\text{-}P(S)S)_2]$ (**SAV-B1** and **SAV-B2**).

The reaction of **SAV-B1** and **SAV-B2** reagents with ethanol and 2-propanol and then dry ammonia gas furnished the four new alkyl dithiophosphonate ligands, O-ethyl-(3-methoxytolyl)dithiophosphonate, O-2-propyl-(3-methoxytolyl)dithiophosphonate, O-ethyl-(2-methoxytolyl)dithiophosphonate, and O-2-propyl-(2-methoxytolyl)dithiophosphonate in the form of their ammonium salts $[NH_4][S_2P(R^{x,y})(ORn)]$. The ligands were reacted with $NiCl_2.6H_2O$ to produce the complexes $[Ni(S_2P(R^{x,y})(ORn))_2]$, *trans*-bis-[O-ethyl-(3-methoxytolyl)]nickel(II), *trans*-bis-[O-propyl-(3-methoxytolyl)]nickel(II), *trans*-bis-[O-ethyl-(2-methoxytolyl)]nickel(II), *trans*-bis-[O-propyl-(2-methoxytolyl)]nickel(II) (Scheme 3). The ligands and their Ni(II) complexes were elucidated by elemental analyses, IR, ESI-MS, 1D ^{1}H, ^{13}C, ^{31}P NMR, and 2D HSQC techniques.



Scheme 3. Syntheses of the ligands and Ni(II) complexes.

EXPERIMENTAL

Materials and Instruments

Methanol, ethanol, 2-propanol, benzene, chloroform, 3-methoxytoluene, 2-methoxytoluene, P_4S_{10}, and $NiCl_2.6H_2O$ were purchased from Sigma-Aldrich and used without further purification. Diethyl ether was also provided by Sigma-Aldrich but re-distilled and then dried with sodium wire.

Microanalyses were carried out on a LECO CHNS-932 CHNS-O elemental analyzer. Melting points were measured with an Electrothermal 9200 apparatus. IR spectra were run on a Perkin Elmer Spectrum Two Model FT-IR instrument (ATR method) with a wavenumber range of 200–4000 cm^{-1}. The MS spectra were run on a Waters Micromass ZQ, with an ESI(+) ionizer.

^{1}H (500 MHz), ^{13}C (125 MHz), and ^{31}P NMR (202.4 MHz) spectra were recorded on a Bruker FT spectrometer at 298 K. ^{1}H and ^{13}C NMR chemical shifts (δ) are given in ppm and referenced to the internal signal of TMS. 85% H_3PO_4 was used as the external standard for ^{31}P NMR. D_2O was the solvent of choice for the ligand-ammonium salts and $CDCl_3$ for Ni(II) complexes. Diagnostic correlations which are based on Heteronuclear Single Quantum Coherence (HSQC) experiments were also performed on a Bruker FT spectrometer at 298 K.

Preparation of SAV-B1 $[(R^x\text{-}P(S)S)_2]$ and SAV-B2 $[(R^y\text{-}P(S)S)_2]$

In a fume hood with an inert (argon) atmosphere, 4.00 g (9.0 mmol) of P_4S_{10} and an excess (90 mmol, 11.00 g) of either 3-methylanisole or 2-methylanisole (the same molar mass) were mixed in a three-necked, round-bottomed flask mounted to a dropping funnel in one neck. Our experience proved that 2-methylanisole should be added dropwise. Adding in one batch leads to side reactions and low yield. 3-methylanisole, however, does not appear to be as reactive and could be added in one portion. The mixture was heated to 165°C (with 3-methylanisole) or 130°C (with 2-methylanisole), and kept as such for three hours. The PTPA derivative of 3-methylanisole precipitated in the third hour whereas the 2-methylanisole analog appeared to have formed within the first hour. The mixture was left to cool down to ambient temperature, then poured into 30 mL of dry ether, filtered, washed with ether, dried and kept in water-tight, amber-colored bottles under argon atmosphere. The PTPA compounds are stable for weeks if handled like this.

Characteristics:

SAV-B1

Yield: 4.3 g (55%). Yellow. m.p. 257-260°C. Anal. Calcd. for: $C_{16}H_{18}O_2P_2S_4$ (432.52 g.mol^{-1}): C, 44.43; H, 4.19; S, 29.65; found: C, 44.53; H, 4.23; S, 29.72 %.

SAV-B2

Yield: 5.7 g (73%). Yellow. m.p. 230-232°C. Anal. Calcd. for: $C_{16}H_{18}O_2P_2S_4$ (432.52 g.mol^{-1}): C, 44.43; H, 4.19; S, 29.65; found: C, 44.49; H, 4.20; S, 29.75 %.

General Procedure for the ammonium salts of dithiophosphonic acids [NH$_4$][S$_2$P(R^{x,y})(ORn)]

1.00 g (2.3 mmol) of the PTPA reagent [(R^{x,y}-P(S)S)$_2$] was taken into a three-necked flask, and onto it, a 4.6 mmol of one of the alcohols (0.21 g of ethanol; 0.28 g of 2-propanol) was added dropwise. The mixture was heated to 50-60^{0}C, kept at this temperature range until complete dissolution, and then left aside to cool. The crude dithiophosphonic acid (an oily, viscous mixture), was poured into 50-60 mL of benzene. The benzene solution was filtered (filter paper) and cooled to 0^{0}C. Through this solution, dry gaseous ammonia was bubbled at a rate of 20 mL/min until the precipitation was complete. The white, amorphous precipitate was filtered (filter paper), washed with benzene, and dried in a vacuum desiccator.

General Procedure for the synthesis of the complexes [Ni(S$_2$P(R^{x,y})(ORn))$_2$]

A 2 mmol sample of the ammonium salt of interest (0.56 g [NH$_4$][S$_2$P(R^x)(OR1)] or [NH$_4$][S$_2$P(R^y)(OR1)] and 0.59 g [NH$_4$][S$_2$P(R^x)(OR2)] or [NH$_4$][S$_2$P(R^y)(OR2)]) was dissolved in 20-30 mL ethanol. Onto this, a solution of 1 mmol (2.4 g) $NiCl_2.6H_2O$ in the same solvent was added dropwise. The mixture was heated to 50-60^{0}C; kept as such for 5-10 min and filtered through filter paper without letting excess cooling. Tiny, violet crystals formed upon cooling. This compound was recrystallized from ethanol.

Characteristics:

[NH$_4$][S$_2$P(R^x)(OR1)]

Yield: 0.89 g (69%). White. m.p. 102-105°C, (decomposition). LC/MS: m/z 261.65 ([M-NH$_4$]$^+$, 100%). Anal. Calcd. for: $C_{10}H_{18}NO_2PS_2$ (279.36 g.mol^{-1}): C, 43.00; H, 6.49; N, 5.01; S, 24.35; found: C, 43.13; H, 6.62; N, 5.05; S, 24.75 %.

[NH$_4$][S$_2$P(R^x)(OR2)]

Yield: 1.19 g (87%). White. m.p. 195-198°C, (decomposition). LC/MS: m/z 275.69 ([M-NH$_4$]$^+$, 100%). Anal. Calcd. for: $C_{11}H_{20}NO_2PS_2$ (293.38 g.mol^{-1}): C, 45.03; H, 6.82; N, 4.77; S, 21.86; found: C, 45.15; H, 6.98; N, 4.85; S, 21.98 %.

[NH$_4$][S$_2$P(R^y)(OR1)]

Yield: 1.11 g (85%). White. m.p. 158-160°C. LC/MS: m/z 261.72 ([M-NH$_4$]$^+$, 100%). Anal. Calcd. for: $C_{10}H_{18}NO_2PS_2$ (279.36 g.mol^{-1}): C, 43.00; H, 6.49; N, 5.01; S, 24.35; found: C, 43.20; H, 6.55; N, 5.10; S, 24.38%.

[NH$_4$][S$_2$P(R^y)(OR2)]

Yield: 1.11 g (82%). White. m.p. 153-155°C. LC/MS: m/z 275.68 ([M-NH$_4$]$^+$, 100%). Anal. Calcd. for: $C_{11}H_{20}NO_2PS_2$ (293.38 g.mol^{-1}): C, 45.03; H, 6.82; N, 4.77; S, 21.86; found: C, 45.23; H, 7.01; N, 4.92; S, 21.89 %.

[Ni(S$_2$P(R^x)(OR1))$_2$]

Yield: 4,9 g (84%). Violet. m.p. 190-193°C, (decomposition). LC/MS: m/z 581.93 ([M-H]$^+$, 100%). Anal. Calcd. for: $C_{20}H_{28}NiO_4P_2S_4$ (581.34 g.mol^{-1}): C, 41.31; H, 4.85; S, 22.06; found: C, 41.52; H, 5.01; S, 22.15 %.

[Ni(S$_2$P(R^x)(OR2))$_2$]

Yield: 4,7 g (77%). Violet. m.p. 205-207°C. LC/MS: m/z 151.98 ([P(C$_6$H$_3$-(CH$_3$)(OCH$_3$)]$^+$, 100%), 610.04 ([M]$^+$, 93%). Anal. Calcd. for: $C_{22}H_{32}NiO_4P_2S_4$ (609.39 g.mol^{-1}): C, 43.35; H, 5.25; S, 21.04; found: C, 43.42; H, 5.45; S, 21.18 %.

[Ni(S$_2$P(R^y)(OR1))$_2$]

Yield: 5,1 g (87%). Violet. m.p. 165-168°C. LC/MS: m/z 151.98 ([P(C$_6$H$_3$-(CH$_3$)(OCH$_3$)]$^+$, 100%), 610.04 ([M]$^+$, 32%). Anal. Calcd. for: $C_{20}H_{28}NiO_4P_2S_4$ (581.34 g.mol^{-1}): C, 41.31; H, 4.85; S, 22.06; found: C, 41.40; H, 4.93; S, 22.13%.

[Ni(S$_2$P(R^y)(OR2))$_2$]

Yield: 5,1 g (88%). Violet. m.p. 128-130°C. LC/MS: m/z 610.00 ([M]$^+$, 100%). Anal. Calcd. for: $C_{22}H_{32}NiO_4P_2S_4$ (609.39 g.mol^{-1}): C, 43.35; H, 5.25; S, 21.04; found: C, 43.48; H, 5.38; S, 21.11 %.

RESULTS AND DISCUSSION

Spectroscopic studies

IR spectra

IR spectra were inspected to find evidence about the existence of PS and Ni-S bonds. The modes $\nu(PS)_{asym}$ and $\nu(PS)_{sym}$ as well as a couple of bands relating to the Ni-S coordination namely, $\nu(Ni\text{-}S)_{asym}$ and $\nu(Ni\text{-}S)_{sym}$ are visible as listed in Table 1.

Table 1: Selected IR data (ν, cm^{-1}) assignment of vibrational bands for the compounds.

Compounds	$\nu(Ni\text{-}S)_{sym}$	$\nu(Ni\text{-}S)_{asym}$	$\nu(PS)_{sym}$	$\nu(PS)_{asym}$	$\nu(N\text{-}H)$
$[(R^x\text{-}P(S)S)_2]$	-	-	583	663	-
$[(R^y\text{-}P(S)S)_2]$	-	-	577	687	-
$[NH_4][S_2P(R^X)(OR1)]$	-	-	540	747	2945
$[NH_4][S_2P(R^X)(OR2)]$	-	-	556;544	743	2973
$[NH_4][S_2P(R^y)(OR1)]$	-	-	559	752	2977
$[NH_4][S_2P(R^y)(OR2)]$	-	-	584;567	738	2970
$[Ni(S_2P(R^X)(OR1))_2]$	275	325	553	670	-
$[Ni(S_2P(R^X)(OR2))_2]$	271	322	553	666	-
$[Ni(S_2P(R^y)(OR1))_2]$	277	327	573	665	-
$[Ni(S_2P(R^y)(OR2))_2]$	283	329	557	663	-

The N-H stretching signal, ν(N-H), observed in the spectra of the ammonium salts at 2945 and 2977 cm^{-1} disappears in the spectra of the complexes. IR data reported for similar compounds agree well with the signals (19-22).

Mass Spectra

The structure of the peaks in the mass spectra reflects the natural abundance of nickel and sulfur isotopes. The molecular ion peaks are clearly visible and in fact, they are either the main peak or comparable in intensity for the mass spectra of the complexes. Mass spectral data reported for similar compounds agree well (23-26) with the signals we observed.

NMR Spectroscopy

The PTPA acids are insoluble in the NMR solvents available, so no NMR data were provided for them. The numbering scheme for carbon and hydrogen atoms is given in Figure 1.

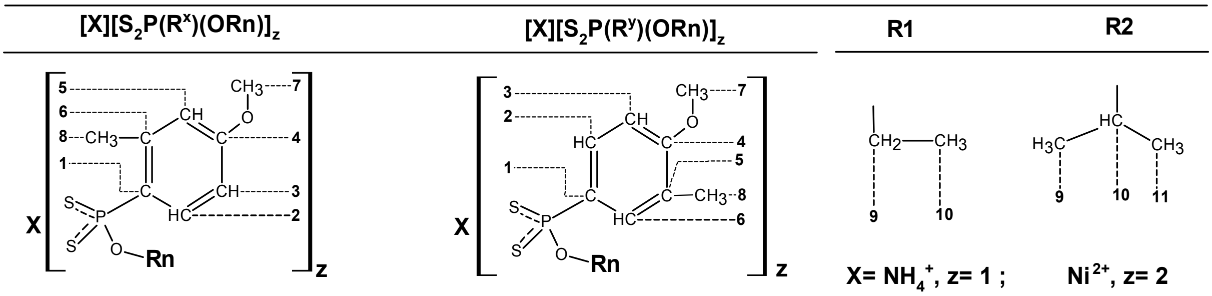


Figure 1. Numbering scheme for the ligands $[NH_4][S_2P(R^{x,y})(ORn)]$ and complexes $[Ni(S_2P(R^{x,y})(ORn))_2]$.

The ^{31}P NMR data of the ligands and complexes are presented in Table 2. No general relation was observed between the ^{31}P chemical shifts of the complexes and of the ligands. All these values are in agreement with the literature (3,19,20).

Table 2: ^{31}P NMR data of the ligands and the corresponding complexes.

$[NH_4][S_2P(R^{x,y})(ORn)]$	δ (ppm)		$[Ni(S_2P(R^{x,y})(ORn))_2]$
$[NH_4][S_2P(R^X)(OR1)]$	102.6	102.0	$[Ni(S_2P(R^X)(OR1))_2]$
$[NH_4][S_2P(R^X)(OR2)]$	100.2	99.2	$[Ni(S_2P(R^X)(OR2))_2]$
$[NH_4][S_2P(R^y)(OR1)]$	67.5	101.7	$[Ni(S_2P(R^y)(OR1))_2]$
$[NH_4][S_2P(R^y)(OR2)]$	103.8	98.6	$[Ni(S_2P(R^y)(OR2))_2]$

The ^{13}C NMR data are listed in Table 3 and 4. Remarkably, the strong, single-bond P-C coupling constants in the complexes is somewhat greater (~112.5 Hz) than those in the ligands (109.6 Hz). In the spectra of the ligands ($[NH_4][S_2P(R^x)(ORn)]$), the signals of the neighboring carbons $\boldsymbol{C}_2$ and $\boldsymbol{C}_3$ give rise to the *doublets* with two ($^2J_{PC}$) and three ($^3J_{PC}$) bond couplings to the P-atom of *ca*. 11 and

14.5 Hz, respectively. These values compare well with the literature reports for similar structures (19,20). Interestingly, the three-bond coupling of the phosphorus atom to **C_8** is not observable whereas, again, the three-bond coupling to **C_5** (7.4 Hz) and the four-bond coupling to **C_4** are (2.9 Hz). Presumably, the electron delocalization in the aromatic ring facilitates somewhat stronger coupling relative to aliphatic carbons. As a general trend, the ^{13}C NMR signals of all the complexes show up at higher fields relative to the corresponding signals in the spectra of the ligands. Similar trends were reported for structurally related compounds (26-32).

As to the ^{13}C NMR spectra of ligand $[NH_4][S_2P(R^y)(ORn)]$, two-bond P-C couplings to C2$_{ar}$ and C6$_{ar}$ are the same with $^{2}J_{PC}$= 12.0 Hz. It is noteworthy to state that P-C three-bond coupling constants ($^{3}J_{PC}$) are 15.6 Hz for **C_3** and 14.7 Hz for **C_5**. In addition, the P-C two- and three-bond coupling constants can be put into order as; $^{3}J_{PC}$>$^{2}J_{PC}$. This observation has been reported in the literature for similar structures (19,20). No general trend was observed in the ^{13}C NMR spectral data of the complexes with respect to these ligands.

Table 3: ^{13}C NMR data of $[NH_4][S_2P(R^x)(ORn)]$ (D_2O) and $[Ni(S_2P(R^x)(ORn))_2]$ ($CDCl_3$) (δ in ppm, J in Hz).

	$[NH_4][S_2P(R^x)(OR1)]$	**$[NH_4][S_2P(R^x)(OR2)]$**	**$[Ni(S_2P(R^x)(OR1))_2]$**	**$[Ni(S_2P(R^x)(OR2))_2]$**
C_1	127.8, $^{1}J_{PC}$=109.4	128.4, $^{1}J_{PC}$=109.7	120.8, $^{1}J_{PC}$= 112.0	121.0, $^{1}J_{PC}$=113.2
C_2	135.8, $^{2}J_{PC}$=11.3	136.0, $^{2}J_{PC}$=11.8	132.4, $^{2}J_{PC}$=13.5	132.5, $^{2}J_{PC}$=13.3
C_3	123.5, $^{3}J_{PC}$=14.5	123.2, $^{3}J_{PC}$=14.5	121.1, $^{3}J_{PC}$=16.2	120.9, $^{3}J_{PC}$=16.0
C_4	162.0, $^{4}J_{PC}$=2.9	162.2, $^{4}J_{PC}$=2.8	160.5	160.4
C_5	115.8, $^{3}J_{PC}$=7.4	115.6, $^{3}J_{PC}$=7.4	112.6, $^{3}J_{PC}$=7.2	112.5, $^{3}J_{PC}$=7.4
C_6	147.5, $^{2}J_{PC}$=2.5	147.4, $^{2}J_{PC}$=2.5	145.4	145.4
C_7	58.2	57.9	55.9	55.7
C_8	23.5	23.5	21.9	21.9
C_9	64.3, $^{2}J_{PC}$=7.4	-	62.5, $^{2}J_{PC}$=5.6	-
C_{10}	18.3, $^{3}J_{PC}$=8.7	73.7, $^{2}J_{PC}$=7.4	16.3, $^{3}J_{PC}$=7.1	71.7, $^{2}J_{PC}$=6.0
$C_{9,11}$	-	26.1, $^{3}J_{PC}$=4.1	-	24.1, $^{3}J_{PC}$=3.7

Table 4: ^{13}C NMR data of $[NH_4][S_2P(R^y)(ORn)]$ (D_2O) and $[Ni(S_2P(R^y)(ORn))_2]$ ($CDCl_3$) (δ in ppm, J in Hz).

	$[NH_4][S_2P(R^y)(OR1)]$	**$[NH_4][S_2P(R^y)(OR2)]$**	**$[Ni(S_2P(R^y)(OR1))_2]$**	**$[Ni(S_2P(R^y)(OR2))_2]$**
C_1	129.7, $^{1}J_{PC}$=144.8	133.8, $^{1}J_{PC}$=114.4	128.0, $^{1}J_{PC}$=115.6	128.2, $^{1}J_{PC}$=116.5
C_2	129.7, $^{2}J_{PC}$=12.0	129.3, $^{2}J_{PC}$=13.2	129.4, $^{2}J_{PC}$=14.6	129.4, $^{2}J_{PC}$=14.5
C_3	110.2, $^{3}J_{PC}$=15.6	109.9, $^{3}J_{PC}$=15.7	109.4, $^{3}J_{PC}$=17.4	109.4, $^{3}J_{PC}$=17.4
C_4	159.4, $^{4}J_{PC}$=3.5	159.3, $^{4}J_{PC}$=3.0	161.2, $^{4}J_{PC}$=1.4	161.1
C_5	126.4, $^{3}J_{PC}$=14.7	126.1, $^{3}J_{PC}$=14.6	127.2, $^{3}J_{PC}$=15.7	127.1, $^{3}J_{PC}$=15.7
C_6	132.3, $^{2}J_{PC}$=12.1	132.0, $^{2}J_{PC}$=13.0	131.6, $^{2}J_{PC}$=14.1	131.6, $^{2}J_{PC}$=14.2
C_7	55.5	55.6,	55.6	55.6
C_8	15.5	15.5	16.3	24.3
C_9	61.4, $^{2}J_{PC}$=6.2	-	62.6, $^{2}J_{PC}$=5.9	-
C_{10}	15.6, $^{3}J_{PC}$=7.3	70.7, $^{2}J_{PC}$=7.3	16.2, $^{3}J_{PC}$=3.7	72.1, $^{2}J_{PC}$=5.5
$C_{9,11}$	-	23.4, $^{3}J_{PC}$=3.8	-	16.3

The ^{1}H NMR data of the ligands $[NH_4][S_2P(R^x)(OR1)]$, $[NH_4][S_2P(R^x)(OR2)]$, $[Ni(S_2P(R^x)(OR1))_2]$ and $[Ni(S_2P(R^x)(OR2))_2]$ are given in Table 5. As seen in the Table 5, the signals of the aromatic protons are virtually the same for the ligand salts $[NH_4][S_2P(R^x)(OR1)]$ and $[NH_4][S_2P(R^x)(OR2)]$. The proton C$_2$-***H*** appears at about 8 ppm as *doublet of doublets* with $^3J_{HH}$= 7.8 Hz and $^3J_{PH}$= ~17.1 Hz. On the other hand, C$_3$-***H*** appears at 6.9 ppm with $^3J_{HH}$= 7.8 Hz. The four-bond coupling to phosphorus is barely appreciable as the *doublet* is slightly broadened. Phosphorus does not also split the signal of the C$_8$-C***H***$_3$ protons that show up at 2.4 ppm. However, the four-bond coupling between phosphorus and C$_5$-***H*** is notable with a $^4J_{PH}$ of 6.0 Hz.

Similar trends in the coupling patterns of the aromatic protons are observed in the ^{1}H NMR spectra of $[Ni(S_2P(R^x)(OR1))_2]$ and $[Ni(S_2P(R^x)(OR2))_2]$.

The ^{1}H NMR data of $[NH_4][S_2P(R^y)(OR1)]$ and $[NH_4][S_2P(R^y)(OR2)]$ ligands and $[Ni(S_2P(R^y)(OR1))_2]$ and $[Ni(S_2P(R^y)(OR2))_2]$ complexes are listed in Table 6. The signals of the aromatic protons are again, almost the same for the two ligands, $[NH_4][S_2P(R^y)(OR1)]$ and $[NH_4][S_2P(R^y)(OR2)]$. Here the proton C$_2$-***H*** appears at about 8 ppm as a *doublet of doublets* with $^3J_{HH}$= 8.4 Hz and $^3J_{PH}$= 12.8 Hz (for $[NH_4][S_2P(R^y)(OR1)]$) and $^3J_{PH}$= 14.1 Hz (for $[NH_4][S_2P(R^y)(OR2)]$). In these compounds, the four-bond couplings between phosphorus and C$_3$-***H*** is read as $^4J_{PH}$= ~3 Hz. On the other hand, phosphorus splits C$_2$-***H*** (δ= 7.6 ppm) and C$_6$-***H*** (δ= 7.5 ppm) by $^3J_{HH}$= 12.8 Hz (for $[NH_4][S_2P(R^y)(OR1)]$) and $^3J_{HH}$= 14.0 Hz (for $[NH_4][S_2P(R^y)(OR2)]$). All the ^{1}H NMR shifts are in agreement with findings in the literature for similar compounds (3,19,20).

Similar trends are also observed in the coupling patterns of the aromatic protons of the ^{1}H NMR spectra of $[Ni(S_2P(R^y)(OR1))_2]$ and $[Ni(S_2P(R^y)(OR2))_2]$.

Table 5: ^{1}H NMR data of $[NH_4][S_2P(R^x)(ORn)]$ (D_2O) and $[Ni(S_2P(R^x)(ORn))_2]$ ($CDCl_3$) (*δ* in ppm, *J* in Hz, s: *singlet*, d: *doublet*, dd: *doublet of doublets*, t: *triplet*, and m: *multiplet*).

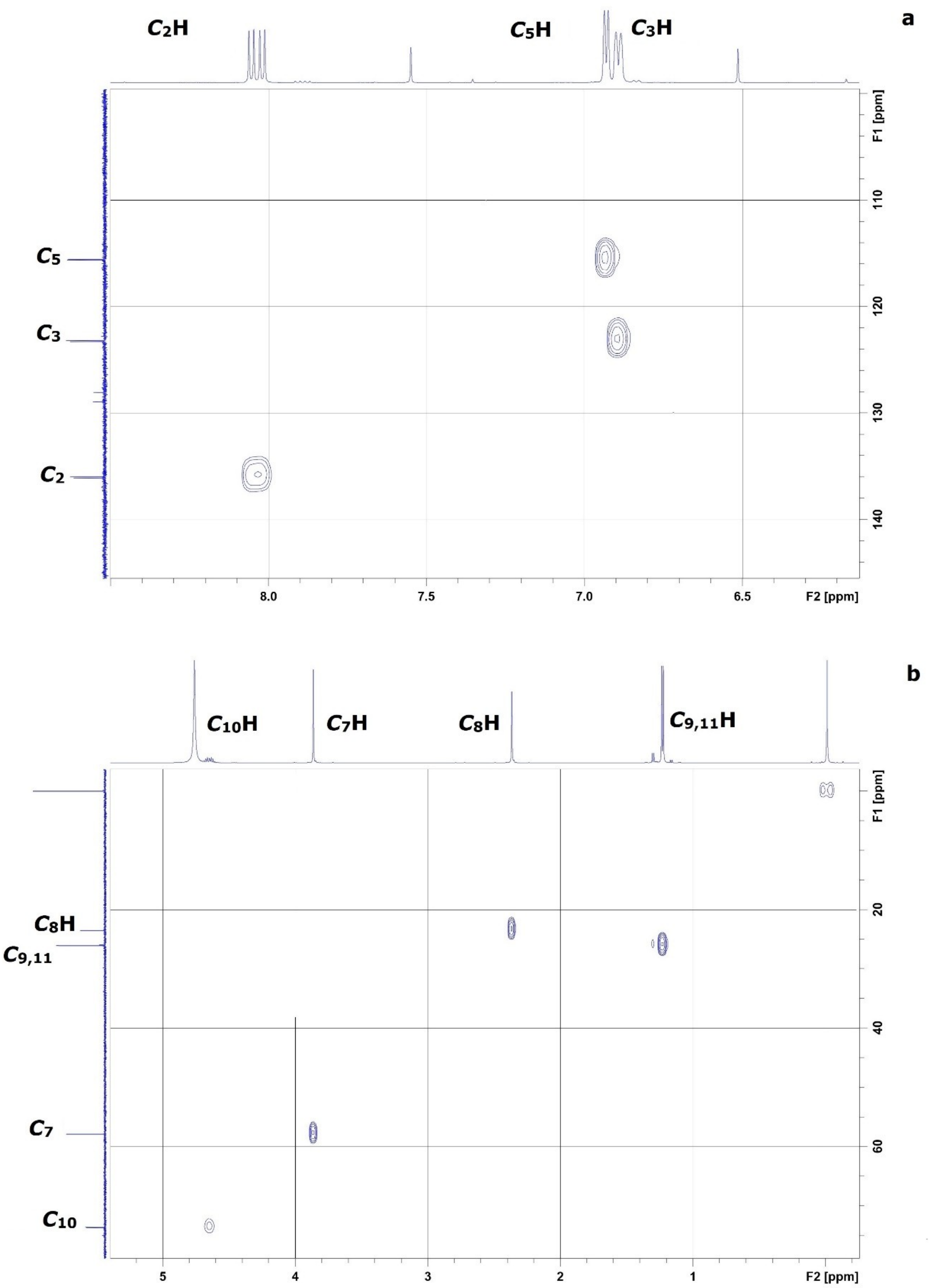
	$[NH_4][S_2P(R^x)(OR1)]$	**$[NH_4][S_2P(R^x)(OR2)]$**	**$[Ni(S_2P(R^x)(OR1))_2]$**	**$[Ni(S_2P(R^x)(OR2))_2]$**
*C$_2$-**H***	8.0 (dd,1H) $^3J_{PH}$=17.0 $^3J_{HH}$=7.8	8.1 (dd,1H) $^3J_{PH}$=17.3 $^3J_{HH}$=7.8	7.9 (dd,2H) $^3J_{PH}$=18.1 $^3J_{HH}$=7.5	7.9 (dd,2H) $^3J_{PH}$=18.3 $^3J_{HH}$=7.7
C$_7$-***H***	3.9(s,3H)	3.9 (s,3H)	3.9 (s,6H)	3.9 (s,6H)
C$_3$-***H***	6.9 (d,1H) $^3J_{HH}$=7.8	6.9 (d,1H) $^3J_{HH}$=7.8	6.8 (d,2H) $^3J_{HH}$=5.1	6.7 (d, 2H) $^3J_{PH}$=5.8
C$_8$-***H***	2.4 (s,3H)	2.4 (s, 3H)	2.4 (s,6H)	2.4 (s,6H)
C$_5$-***H***	7.0 (d,1H) $^4J_{PH}$=6.0	7.0 (d,1H) $^4J_{PH}$=6.0	6.9 (d,2H) $^4J_{PH}$=6.5	6.9 (d,2H) $^4J_{PH}$=7.7
C$_9$-***H***	δ= 3.9 (m,2H)	-	4.4 (m,4H)	-
*C$_{10}$-**H***	1.3 (t,3H) $^3J_{HH}$=7.1	4.7 (m,1H)	1.4 (t,6H) $^3J_{HH}$=6.9	5.1(m,2H)
C$_{9,11}$-***H***	-	1.2 (d,6H) $^3J_{HH}$=6.2	-	1.3 (d,12H) $^3J_{HH}$=6.2

Table 6: ^{1}H NMR data of $[NH_4][S_2P(R^y)(ORn)]$ (D_2O) and $[Ni(S_2P(R^y)(ORn))_2]$ ($CDCl_3$) (*δ* in ppm, *J* in Hz, s: *singlet*, d: *doublet*, dd: *doublet of doublets*, t: *triplet*, and m: *multiplet*).

	$[NH_4][S_2P(R^y)(OR1)]$	**$[NH_4][S_2P(R^y)(OR2)]$**	**$[Ni(S_2P(R^y)(OR1))_2]$**	**$[Ni(S_2P(R^y)(OR2))_2]$**
C$_2$-***H***	7.6 (dd,H) $^3J_{PH}$=12.8 $^3J_{HH}$=8.4	7.8 (dd,1H) $^3J_{PH}$=14.1 $^3J_{HH}$=8.5	7.9 (dd,2H) $^3J_{PH}$=13.5 $^3J_{HH}$=9.4	7.9 (dd,2H) $^3J_{PH}$=12.8 $^3J_{HH}$=8.6
C$_7$-***H***	3.8 (s,3H)	3.8 (s,3H)	3.9 (s,6H)	3.9 (s,6H)
C$_3$-***H***	6.9 (dd,1H) $^4J_{PH}$=3.1 $^3J_{HH}$=8.4	7.0 (dd,H) $^4J_{PH}$=3.0 $^3J_{HH}$=8.5	6.9 (dd, 2H) $^4J_{PH}$=3.1 $^3J_{HH}$=8.4	6.9 (dd,2H) $^4J_{PH}$=3.0 $^3J_{HH}$=8.4
C$_8$-***H***	2.1 (s,3H)	2.2 (s,3H)	2.3 (s,6H)	2.3 (s, 6H)
C$_6$-***H***	δ=7.5 (d,1H)	7.8 (d,1H)	7.8 (d,2H)	7.8 (d,2H)

	$^3J_{PH}$=12.8	$^3J_{PH}$=14.0	$^3J_{PH}$=13.3	$^3J_{PH}$=13.5
C_9-***H***	3.8 (m,2H)	-	4.5 (m,4H)	-
C_{10}-***H***	1.1 (t,3H) $^3J_{HH}$=7.1	4.6 (m,1H)	1.5 (t,6H) $^3J_{HH}$=7.1	5.3 (m,2H)
$C_{9,11}$-***H***	**-**	1.2 (d,6H) $^3J_{HH}$=6.3	**-**	1.4 (d,12H) $^3J_{HH}$=6.2

The unambiguous assignments of ^{1}H and ^{13}C NMR data of the ligands and complexes are made by HSQC spectra. The HSQC spectra of the ligands $[NH_4][S_2P(R^x)(OR2)]$ and $[NH_4][S_2P(R^y)(OR2)]$ are given as examples in Figures 2 and 3, respectively. The HSQC spectra of $[NH_4][S_2P(R^{x,y})(OR2)]$ are also depicted in the Supplementary Material.



$[NH_4][S_2P(R^x)(OR2)]$

Figure 2. HSQC spectrum (**a**) for the aromatic region and (**b**) for the aliphatic region of $[NH_4][S_2P(R^x)(OR2)]$.

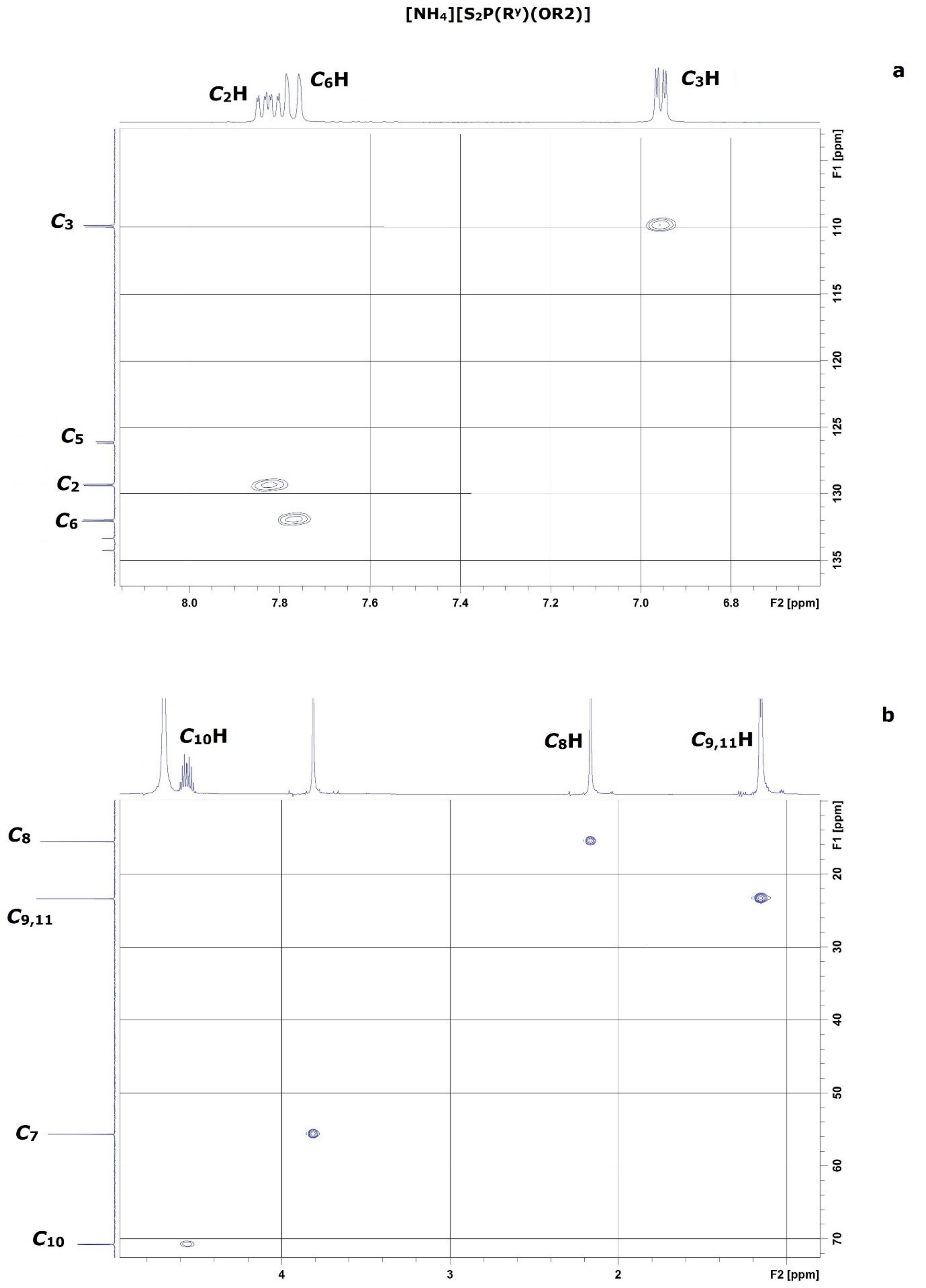


Figure 3. HSQC spectrum (**a**) for the aromatic region and (**b**) for the aliphatic region of $[NH_4][S_2P(R^y)(OR2)]$.

CONCLUSIONS

As an approach to create more alternatives to the well-known Lawesson's reagent, an easy procedure for the synthesis of two new perthiophosphonic acid anhydrides were described. These compounds were used in the synthesis of structurally different organo- dithiophosphonic acid ammonium salts, and the anions of these salts were used in the preparation of new dithiophosphonato Ni(II) complexes. The structures of the ligands and the complexes were determined by spectroscopic techniques. The ^{13}C NMR spectra of the aromatic parts of the compounds display interesting features. Three-bond P-C couplings, for example, are bigger than the two-bond P-C couplings.

ACKNOWLEDGEMENTS

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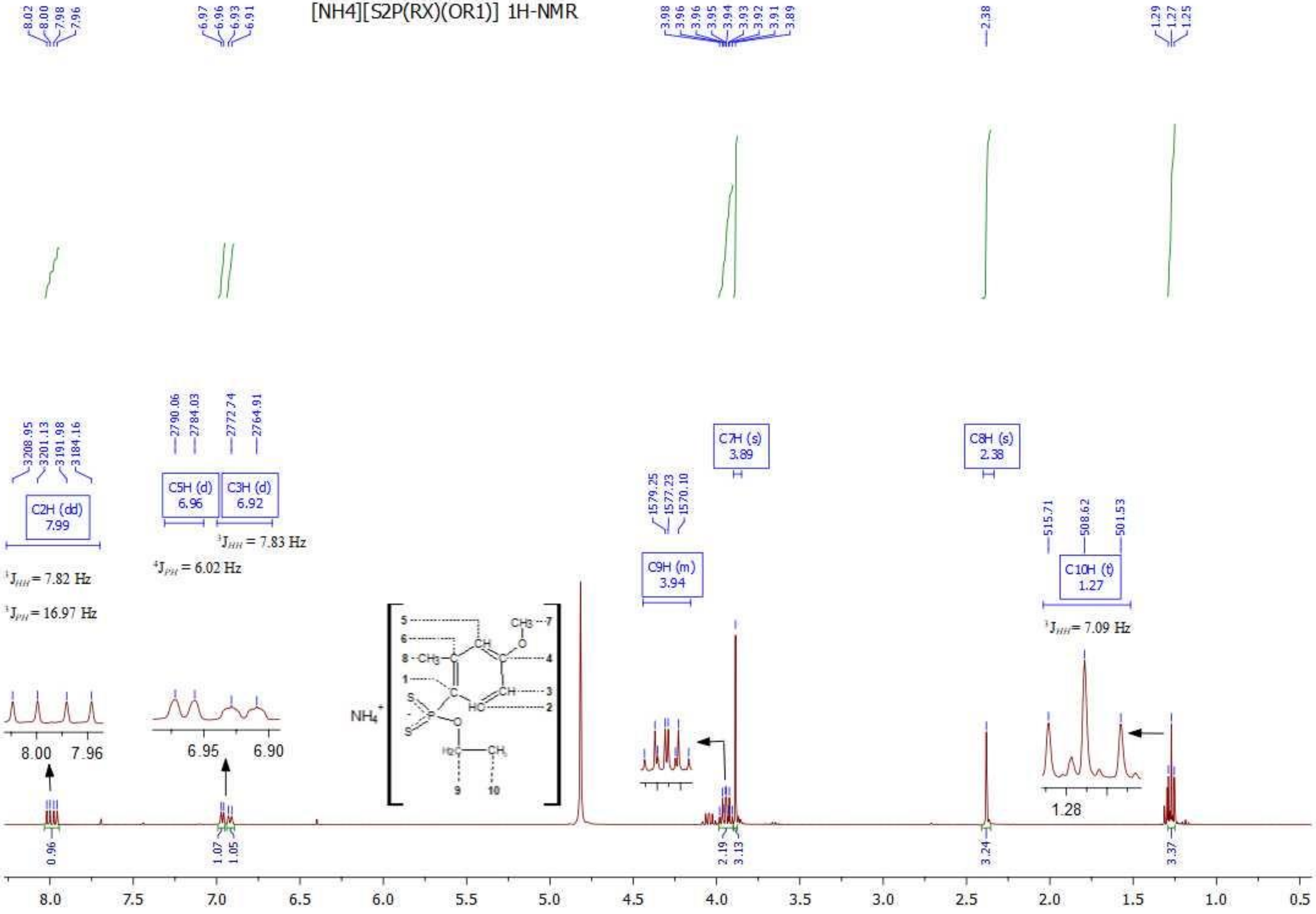
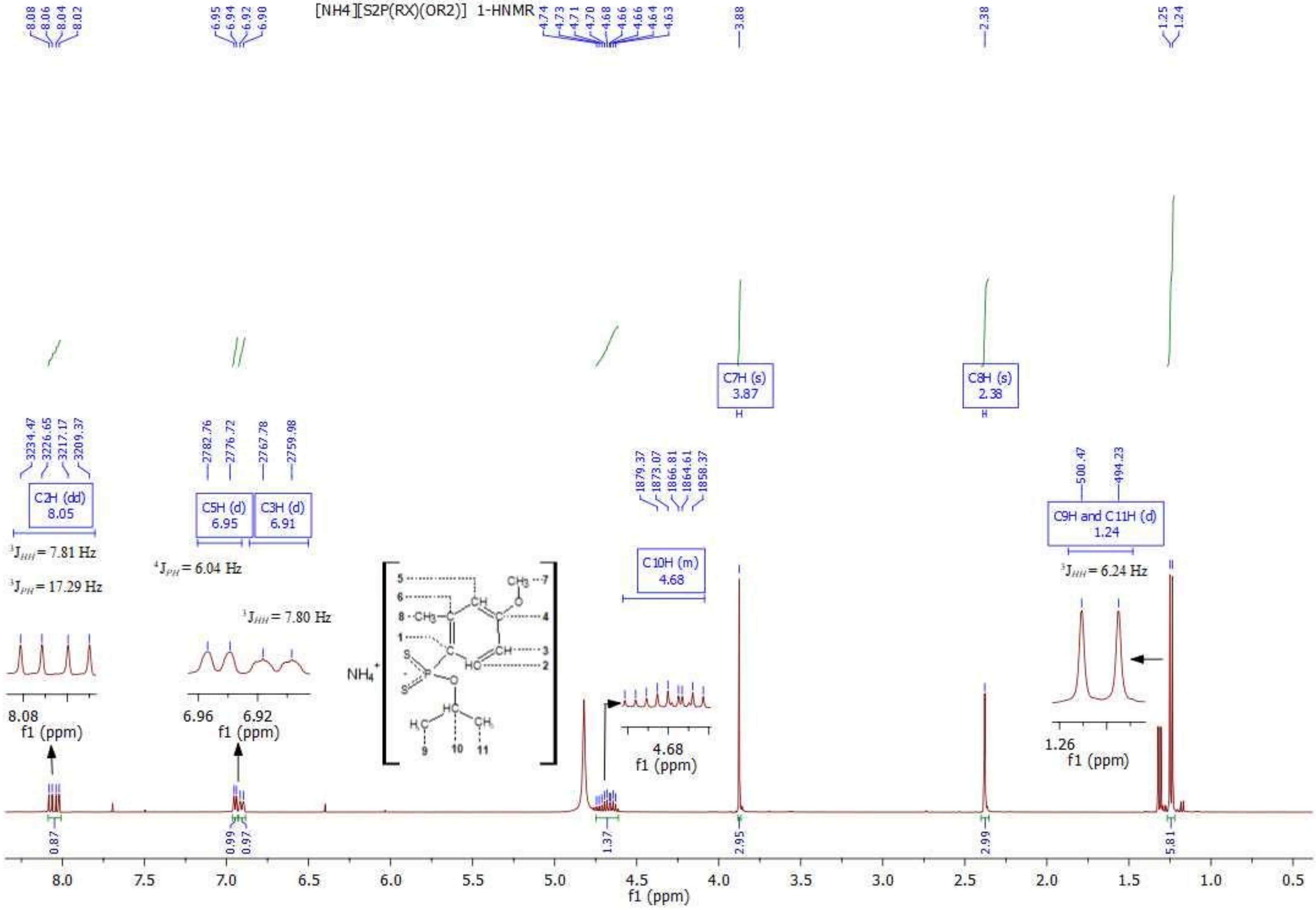
NMR (1H, 13C, 31P) HSQC SPECTRA of the LIGANDS and COMPLEXES

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8.08
8.06
8.04
8.02
6.95
6.94
6.92
6.90
4.74
4.73
4.71
4.70
4.68
4.66
4.66
4.64
4.63
3.88
2.38
1.25
1.24
C7H (s) 3.87
C8H (s) 2.38
3234.47
3226.65
3217.17
3209.37
C2H (dd) 8.05
$^3J_{HH}$ = 7.81 Hz
$^3J_{PH}$ = 17.29 Hz
2782.76
2776.72
2767.78
2759.98
C5H (d) 6.95
C3H (d) 6.91
$^4J_{PH}$ = 6.04 Hz
$^3J_{HH}$ = 7.80 Hz
1879.37
1873.07
1866.81
1864.61
1858.37
C10H (m) 4.68
500.47
494.23
C9H and C11H (d) 1.24
$^3J_{HH}$ = 6.24 Hz
8.08
f1 (ppm)
6.96
6.92
f1 (ppm)
4.68
f1 (ppm)
1.26
f1 (ppm)
NH$_4^+$
5
6
8
1
7
4
3
2
9
10
11
CH$_3$
CH
HC
C
P
S
O
0.87
0.99
0.97
1.37
2.95
2.99
5.81
8.0
7.5
7.0
6.5
6.0
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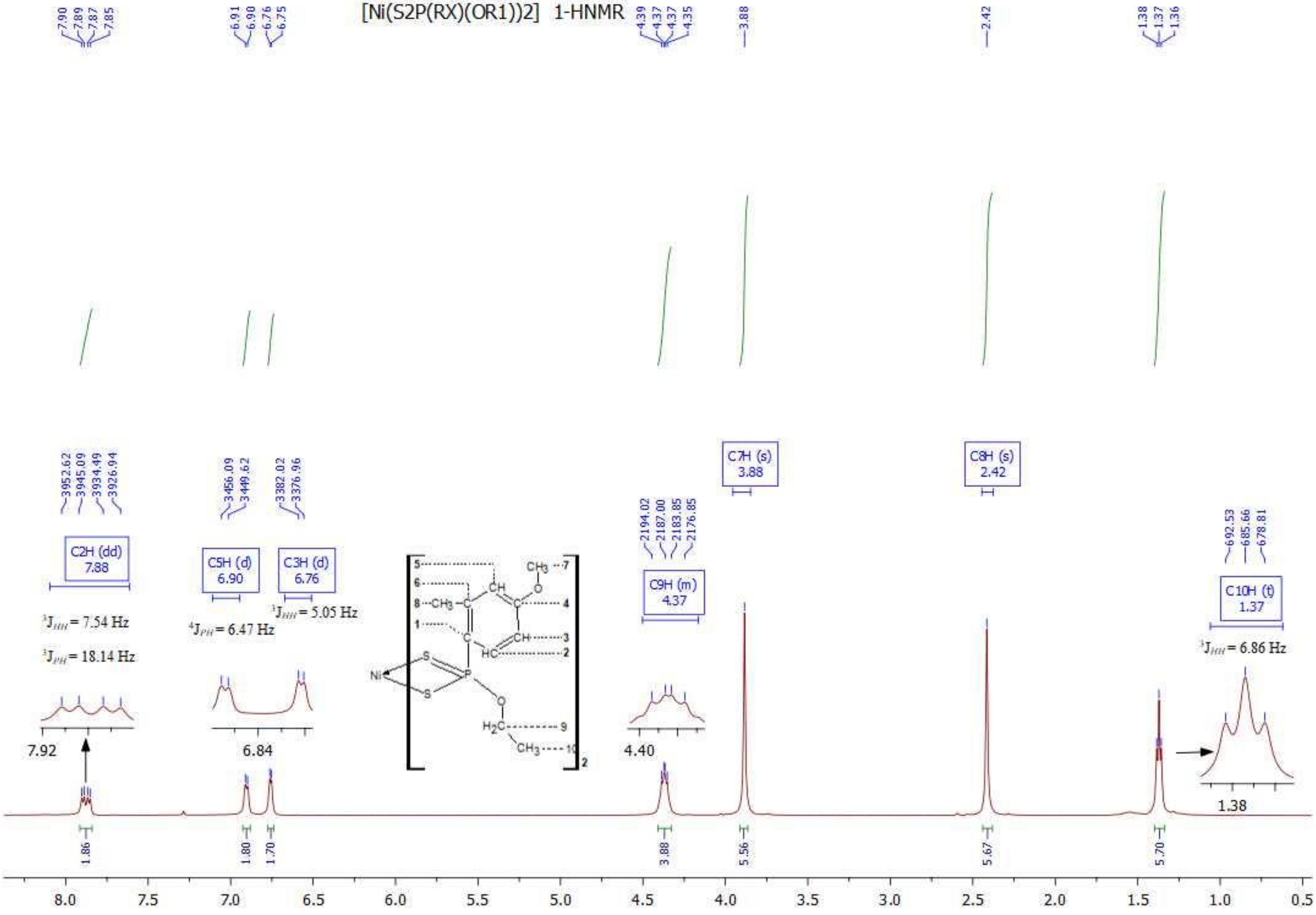
1.5
1.0
0.5
f1 (ppm)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6.90
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4.39
4.37
4.37
4.35
3.88
2.42
1.38
1.37
1.36
3952.62
3945.09
3934.49
3926.94
3456.09
3449.62
3382.02
3376.96
2194.02
2187.00
2183.85
2176.85
692.53
685.66
678.81
C2H (dd)
7.88
C5H (d)
6.90
C3H (d)
6.76
C9H (m)
4.37
C7H (s)
3.88
C8H (s)
2.42
C10H (t)
1.37
$^3J_{HH}$ = 7.54 Hz
$^3J_{PH}$ = 18.14 Hz
$^4J_{PH}$ = 6.47 Hz
$^3J_{HH}$ = 5.05 Hz
$^3J_{HH}$ = 6.86 Hz
7.92
6.84
4.40
1.38
1
2
3
4
5
6
7
8
9
10
Ni
S
S
P
O
O
CH
CH
HC
C
C
C
CH3
CH3
CH3
H2C
2
1.86
1.80
1.70
3.88
5.56
5.67
5.70
8.0
7.5
7.0
6.5
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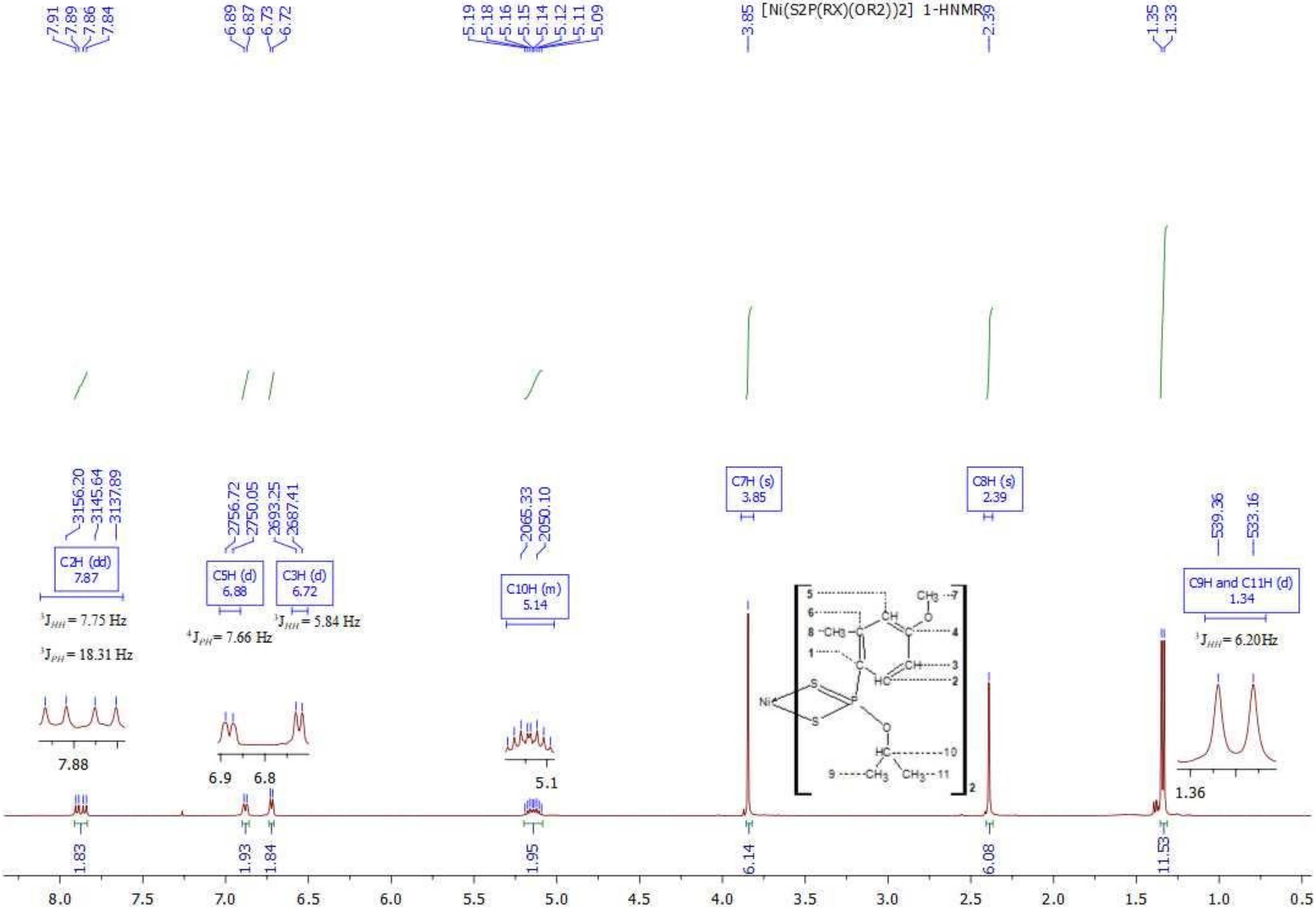
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7.89
7.86
7.84
6.89
6.87
6.73
6.72
5.19
5.18
5.16
5.15
5.14
5.12
5.11
5.09
3.85
2.39
1.35
1.33
3156.20
3145.64
3137.89
C2H (dd)
7.87
³J_HH = 7.75 Hz
³J_PH = 18.31 Hz
7.88
2756.72
2750.05
2693.25
2687.41
C5H (d)
6.88
⁴J_PH = 7.66 Hz
C3H (d)
6.72
³J_HH = 5.84 Hz
6.9
6.8
2065.33
2050.10
C10H (m)
5.14
5.1
C7H (s)
3.85
C8H (s)
2.39
539.36
533.16
C9H and C11H (d)
1.34
³J_HH = 6.20Hz
1.36
Ni
S
P
O
CH3
CH
HC
C
HC
CH3
CH3
1
2
3
4
5
6
7
8
9
10
11
2
1.83
1.93
1.84
1.95
6.14
6.08
11.53
8.0
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7.0
6.5
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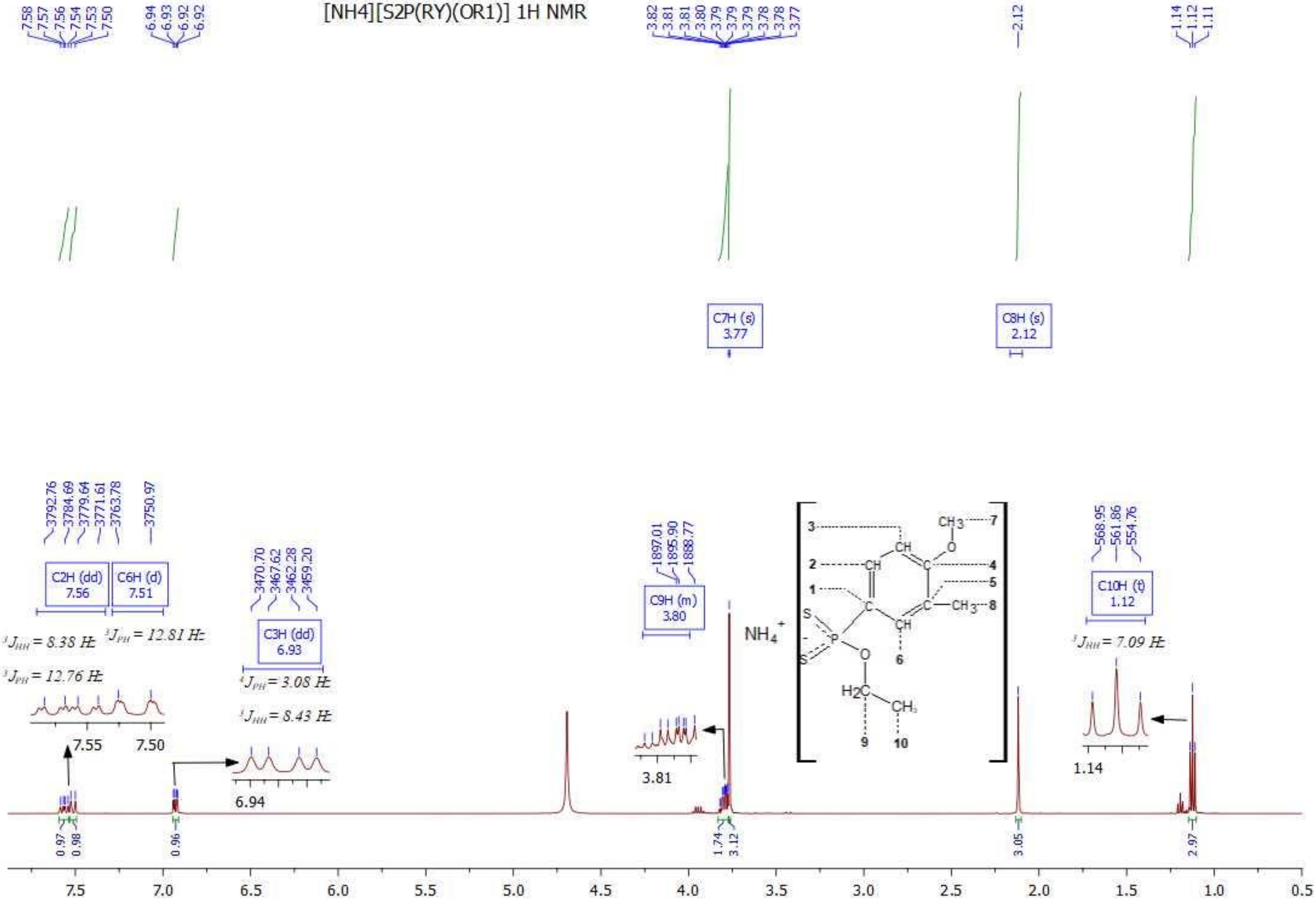
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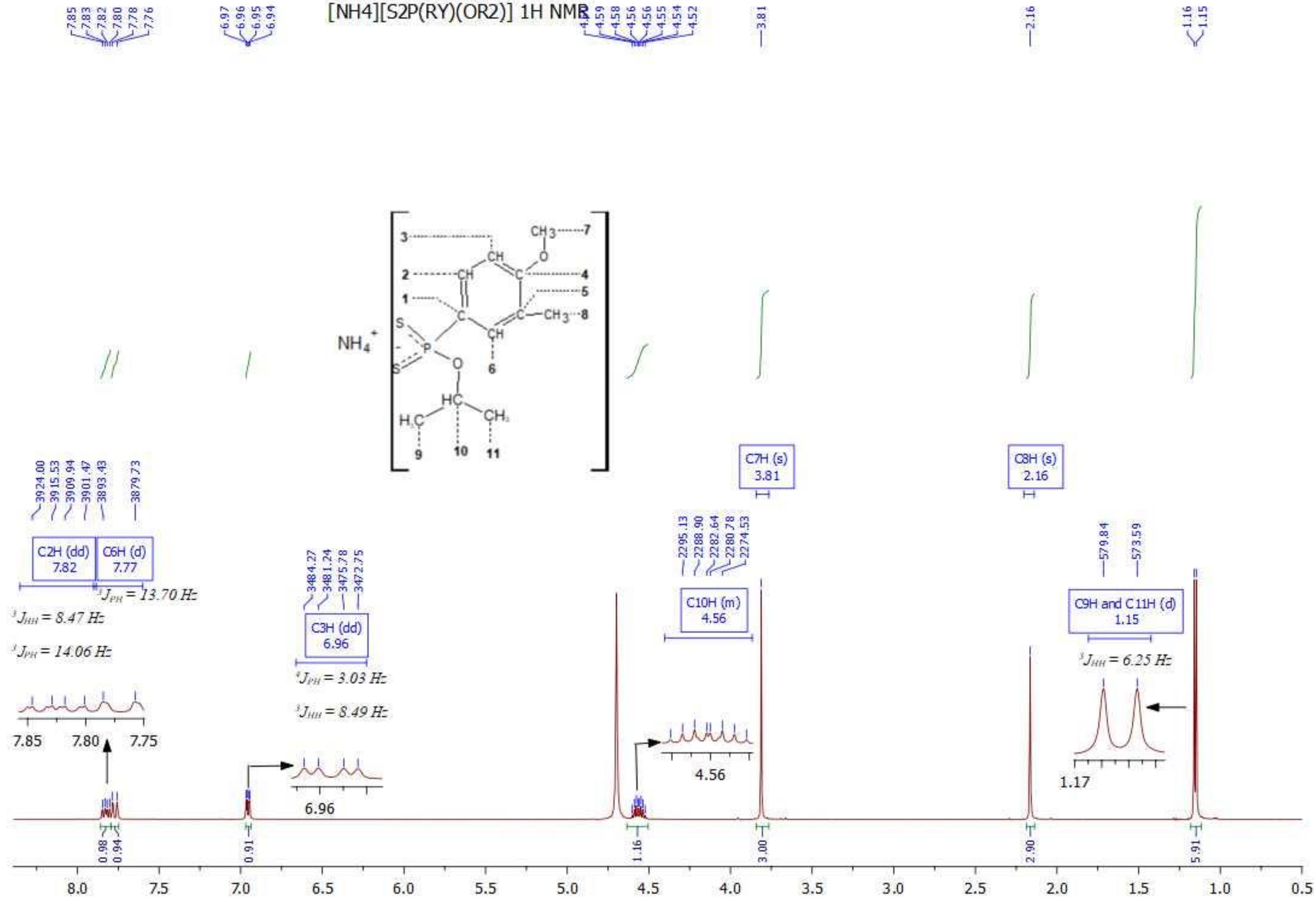
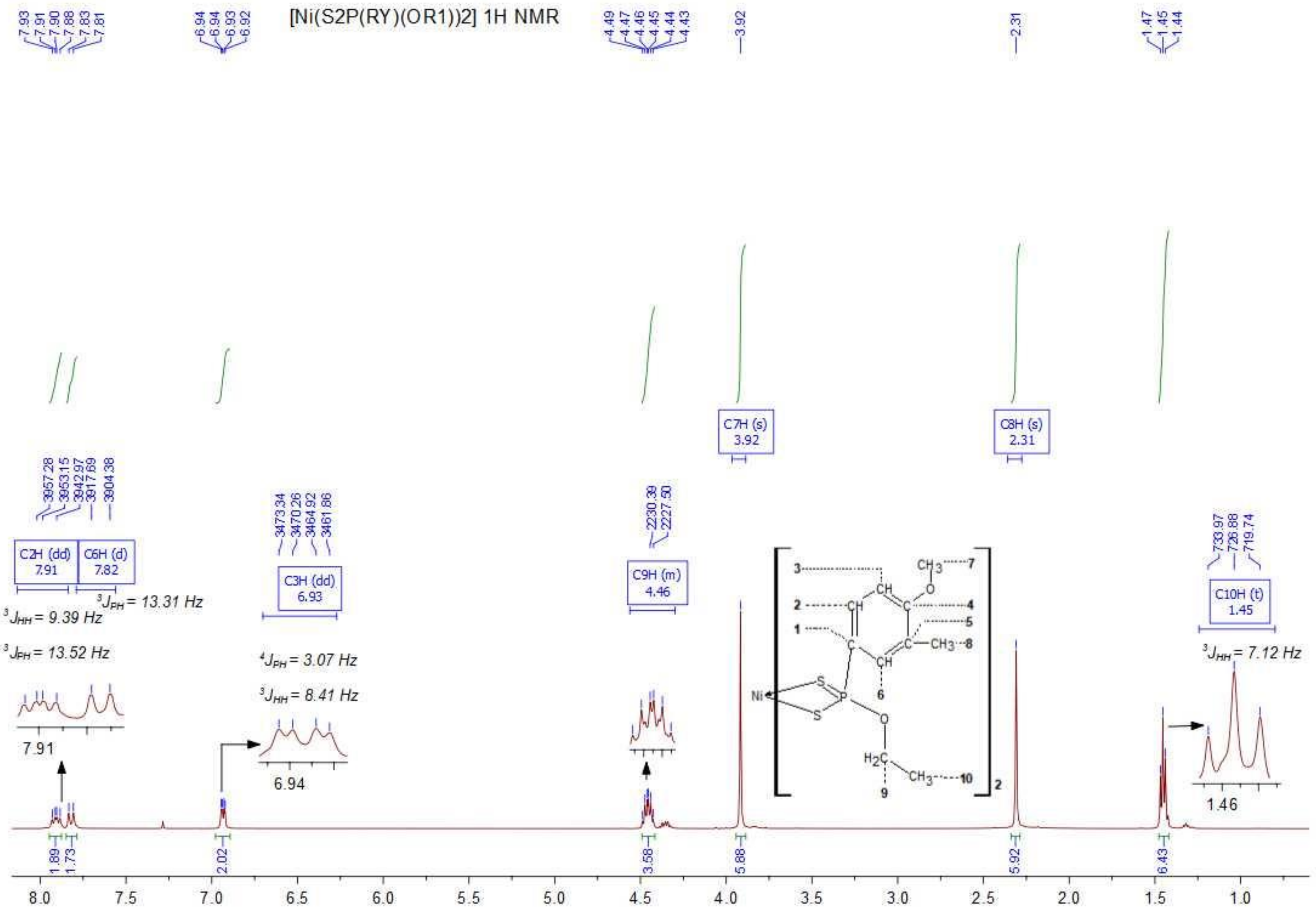
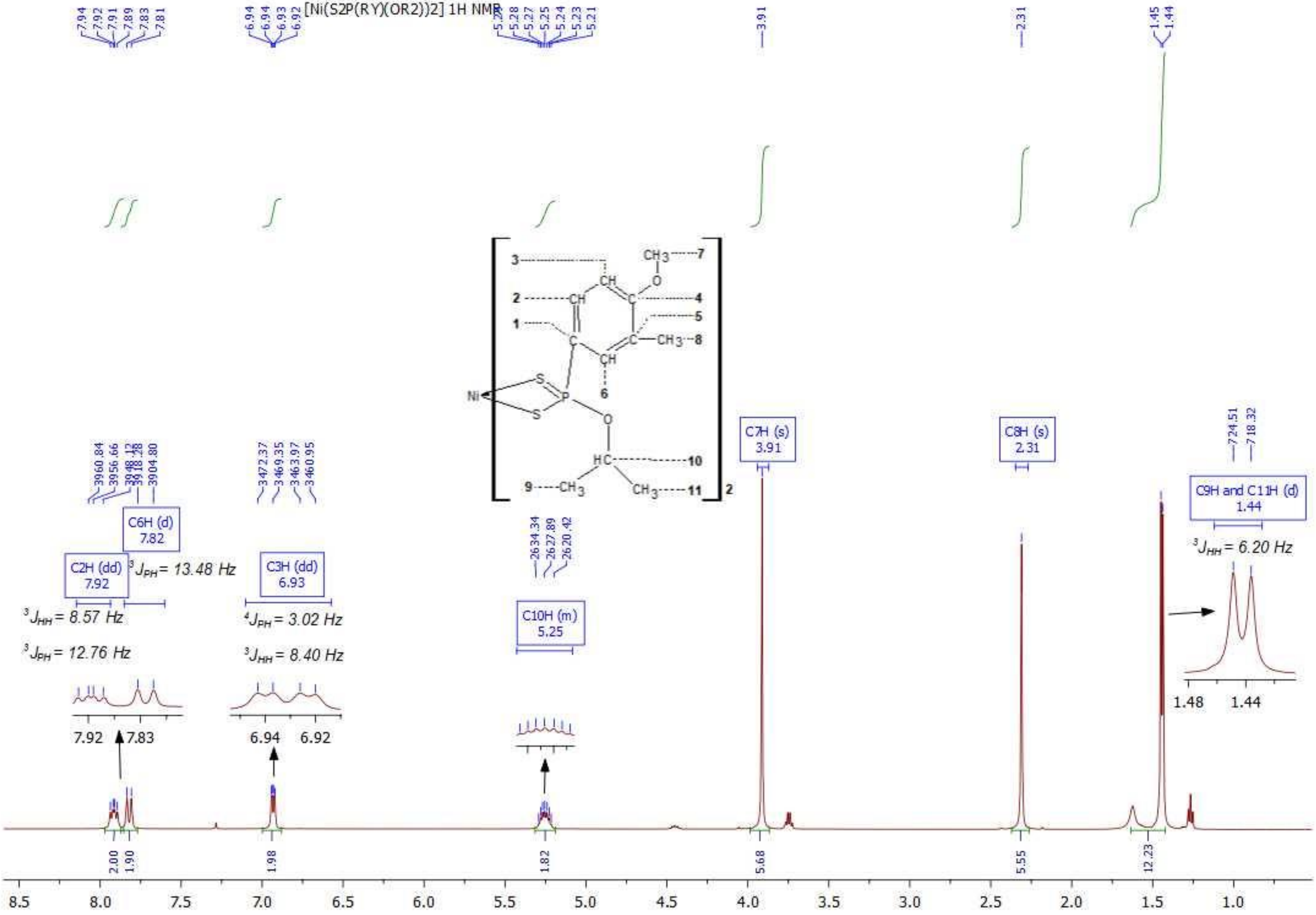
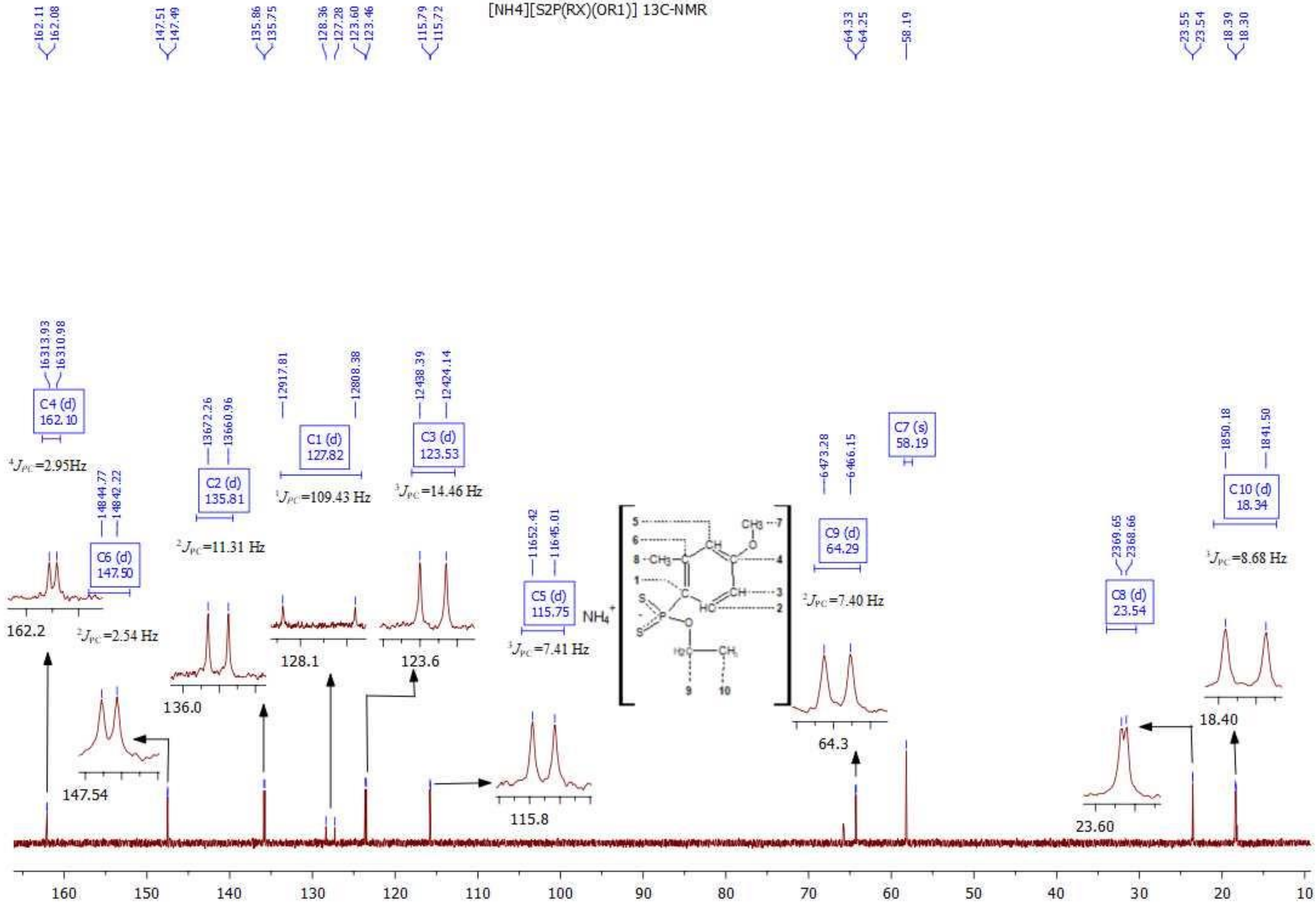


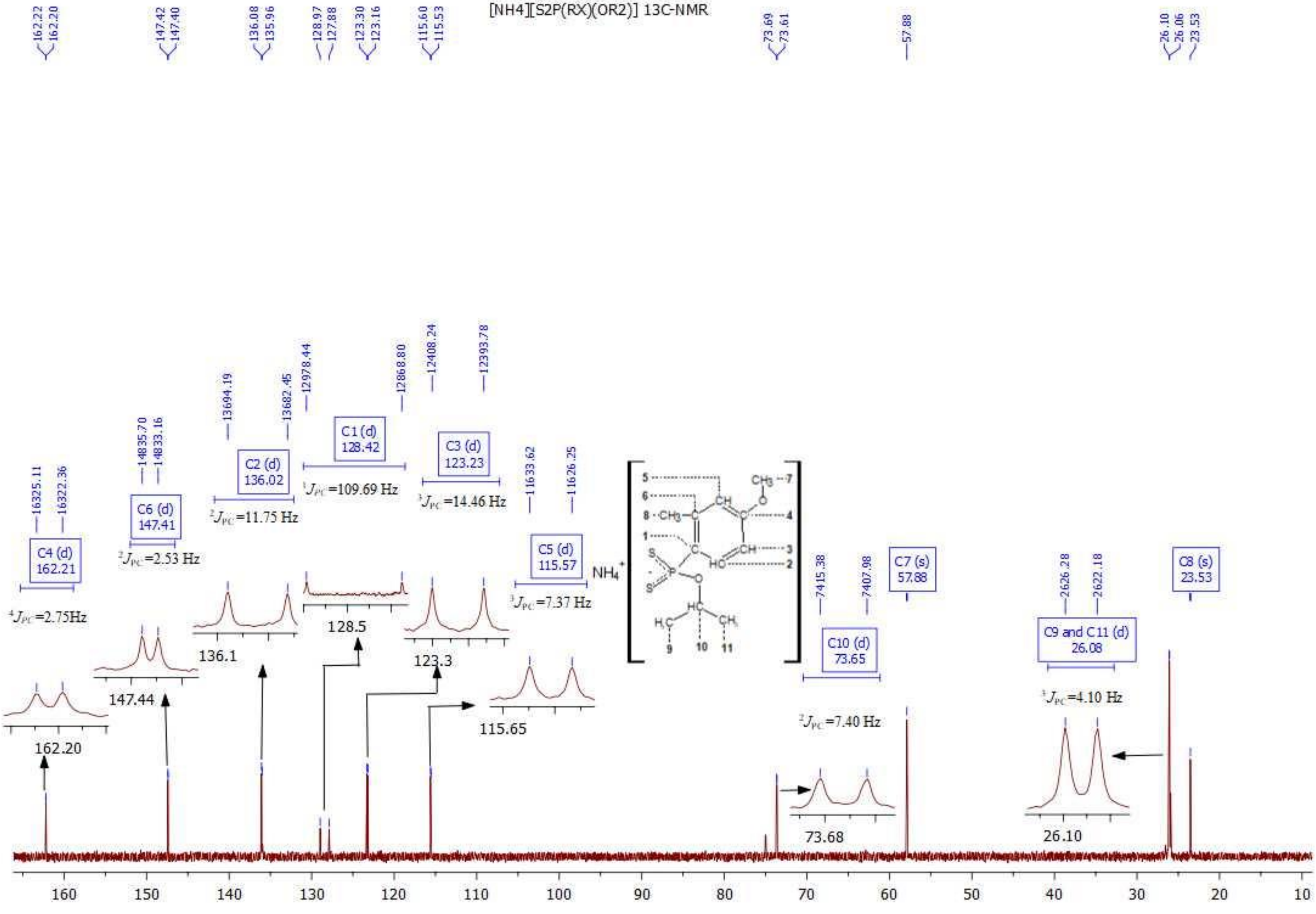
[NH4][S2P(RY)(OR2)] 1H NMR

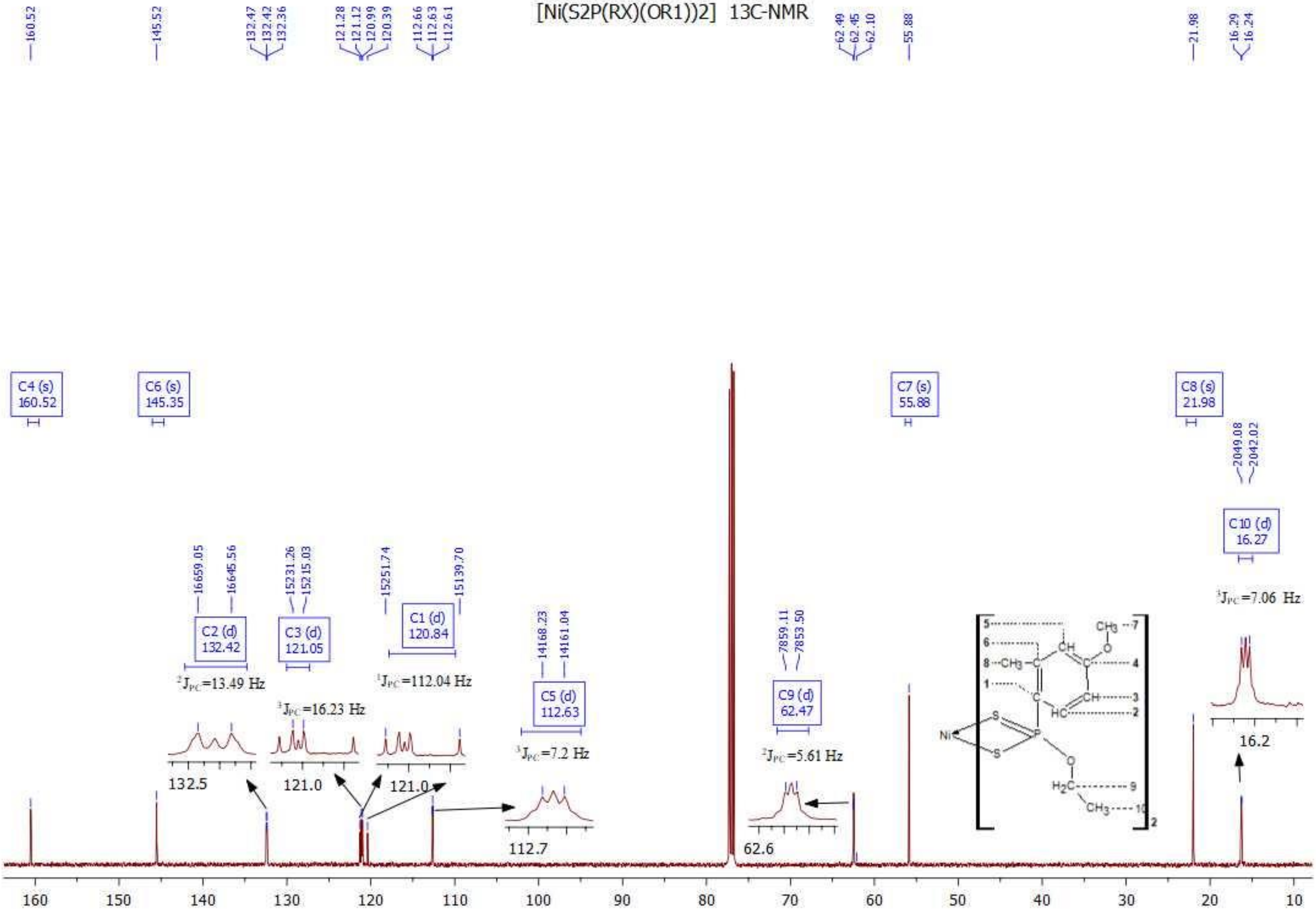


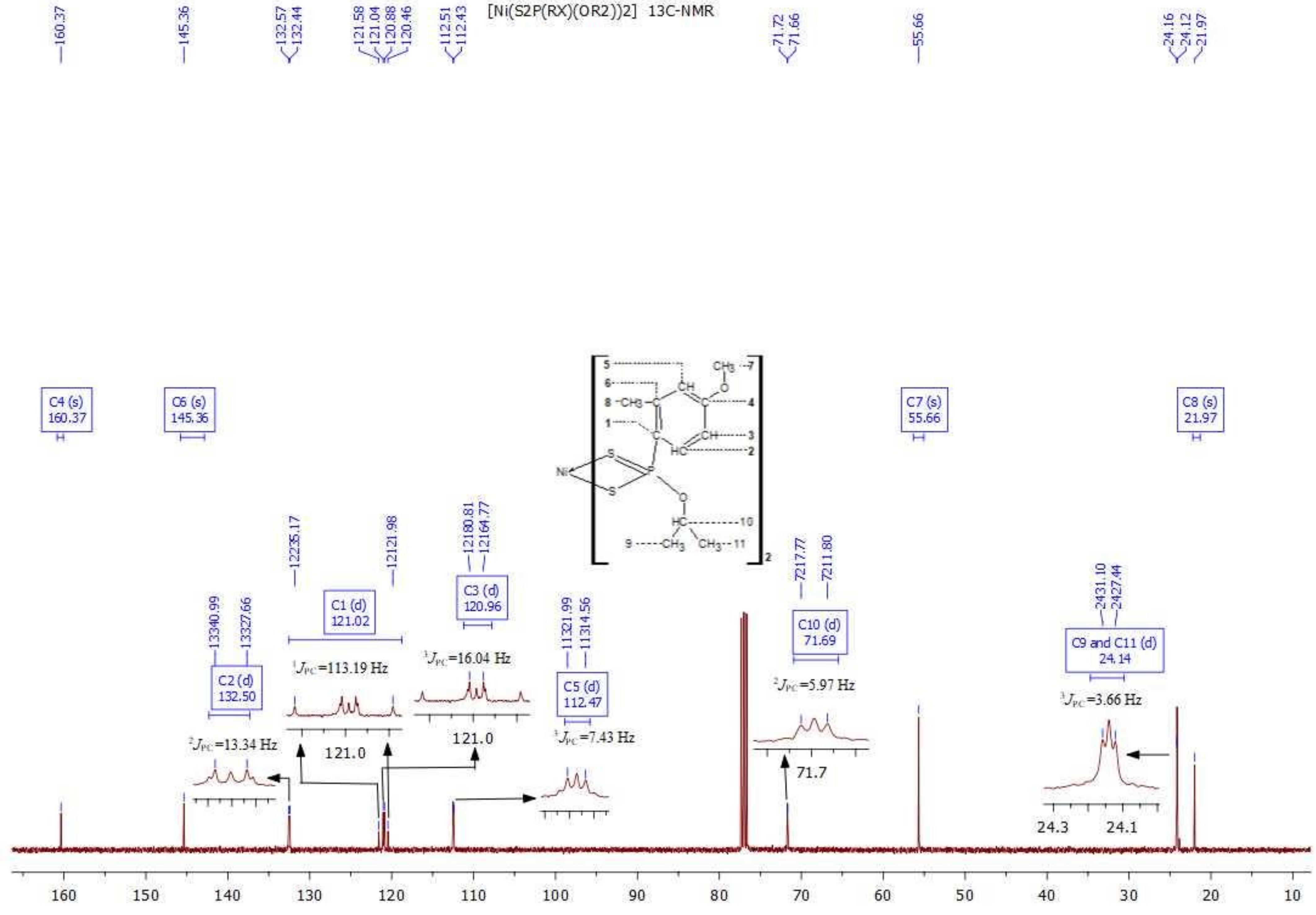
[Ni(S2P(RY)(OR1))2] 1H NMR

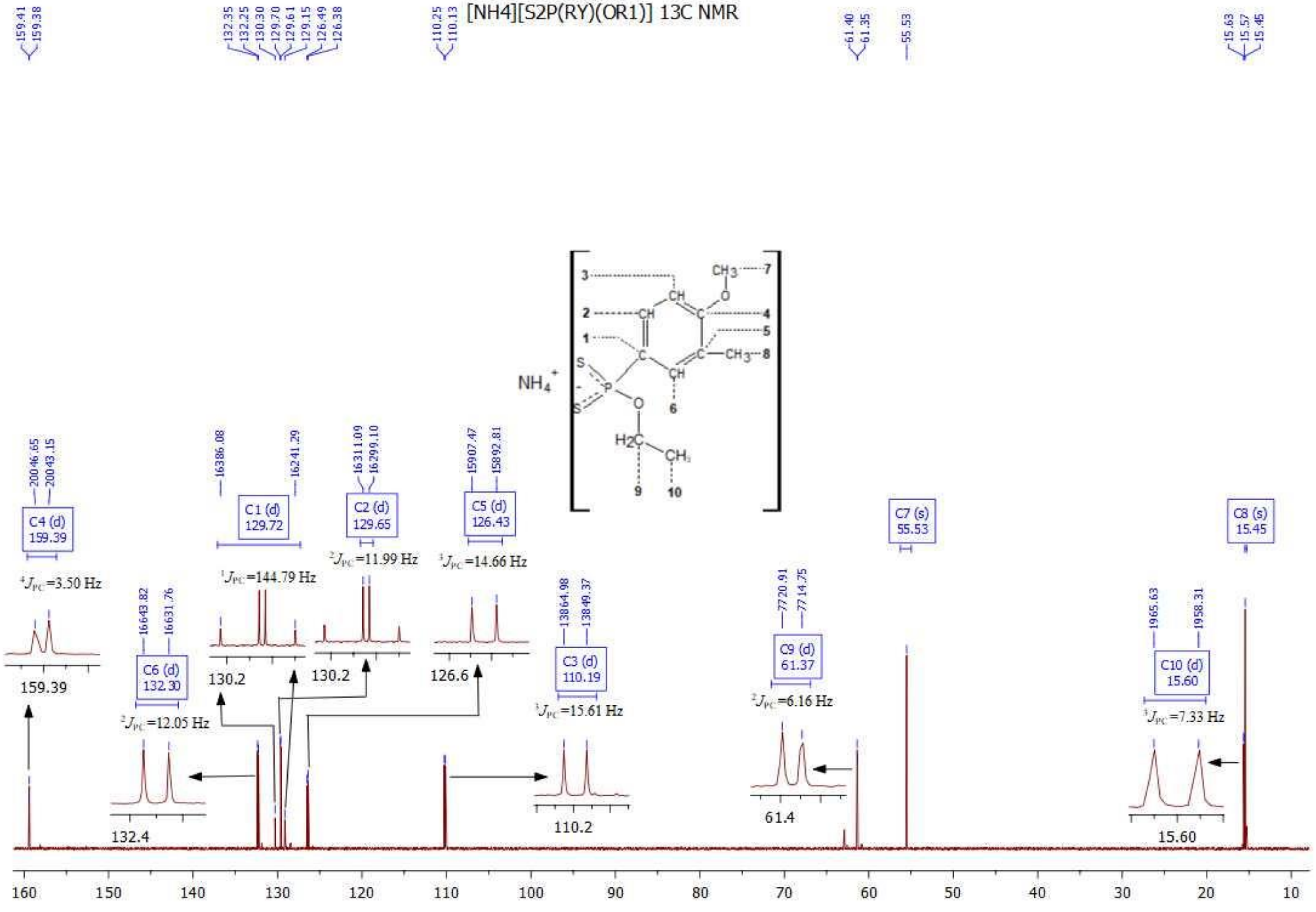

[Ni(S2P(RY)(OR2))2] 1H NMR
7.94
7.92
7.91
7.89
7.83
7.81
6.94
6.94
6.93
6.92
5.29
5.28
5.27
5.25
5.24
5.23
5.21
3.91
2.31
1.45
1.44
3
2
1
CH3
7
CH
O
CH
C
4
5
C
C
CH3
8
CH
6
Ni
S
P
S
O
HC
10
9
CH3
CH3
11
2
3960.84
3956.66
3948.12
3918.28
3904.80
3472.37
3469.35
3463.97
3460.95
2634.34
2627.89
2620.42
724.51
718.32
C6H (d)
7.82
C2H (dd)
7.92
$^3J_{PH}$ = 13.48 Hz
$^3J_{HH}$ = 8.57 Hz
$^3J_{PH}$ = 12.76 Hz
C3H (dd)
6.93
$^4J_{PH}$ = 3.02 Hz
$^3J_{HH}$ = 8.40 Hz
C10H (m)
5.25
C7H (s)
3.91
C8H (s)
2.31
C9H and C11H (d)
1.44
$^3J_{HH}$ = 6.20 Hz
7.92
7.83
6.94
6.92
1.48
1.44
2.00
1.90
1.98
1.82
5.68
5.55
12.23
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

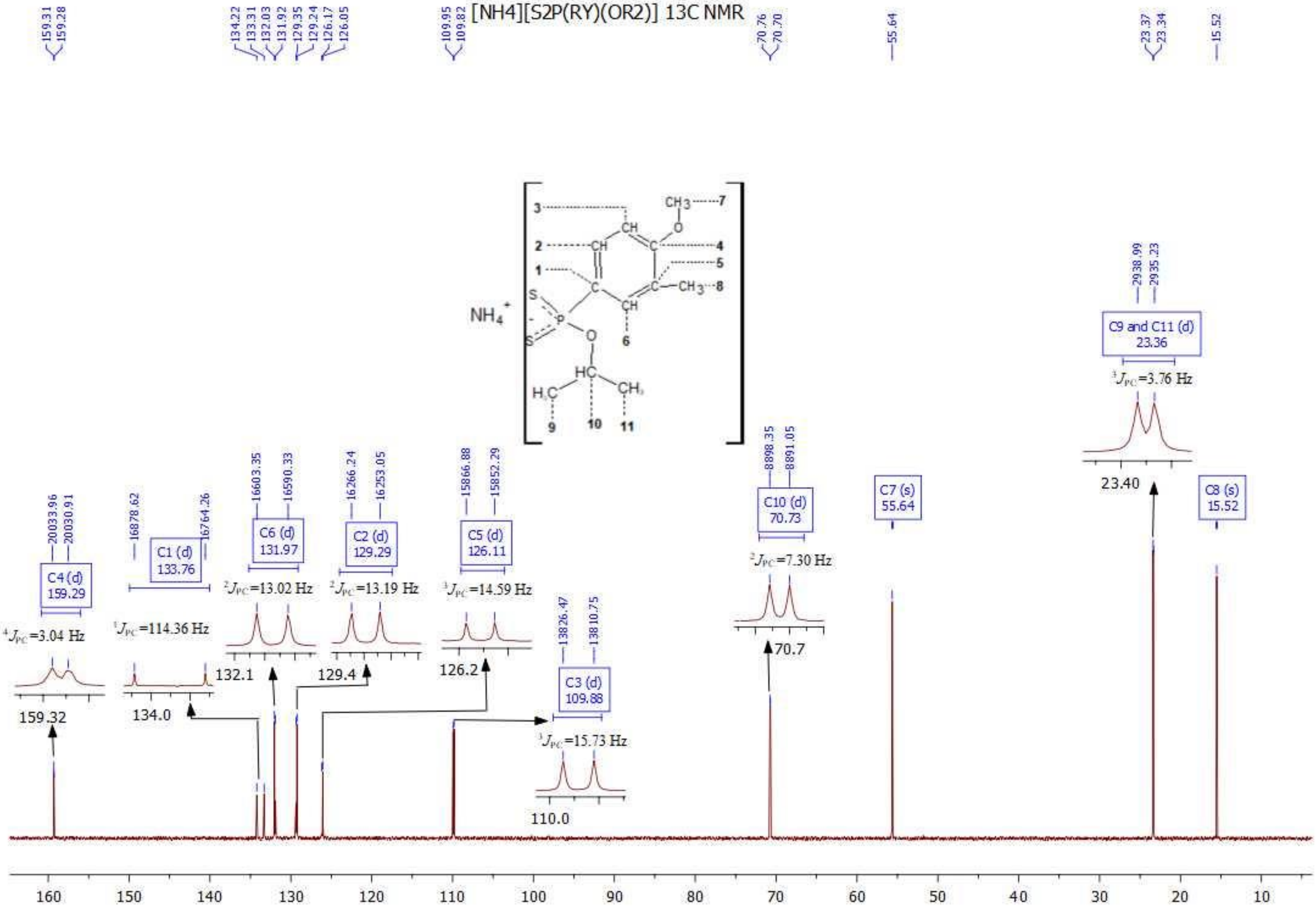

[NH4][S2P(RX)(OR1)] 13C-NMR
162.11
162.08
147.51
147.49
135.86
135.75
128.36
127.28
123.60
123.46
115.79
115.72
64.33
64.25
58.19
23.55
23.54
18.39
18.30
16313.93
16310.98
C4 (d)
162.10
$^4J_{PC}$=2.95Hz
162.2
14844.77
14842.22
C6 (d)
147.50
$^2J_{PC}$=2.54 Hz
147.54
13672.26
13660.96
C2 (d)
135.81
$^2J_{PC}$=11.31 Hz
136.0
12917.81
12808.38
C1 (d)
127.82
$^1J_{PC}$=109.43 Hz
128.1
12438.39
12424.14
C3 (d)
123.53
$^3J_{PC}$=14.46 Hz
123.6
11652.42
11645.01
C5 (d)
115.75
$^3J_{PC}$=7.41 Hz
115.8
NH_4^+
5
6
8
1
CH3
7
4
3
2
CH
C
O
HC
S
P
H_2C
CH_3
9
10
6473.28
6466.15
C9 (d)
64.29
$^2J_{PC}$=7.40 Hz
64.3
C7 (s)
58.19
2369.65
2368.66
C8 (d)
23.54
23.60
1850.18
1841.50
C10 (d)
18.34
$^3J_{PC}$=8.68 Hz
18.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

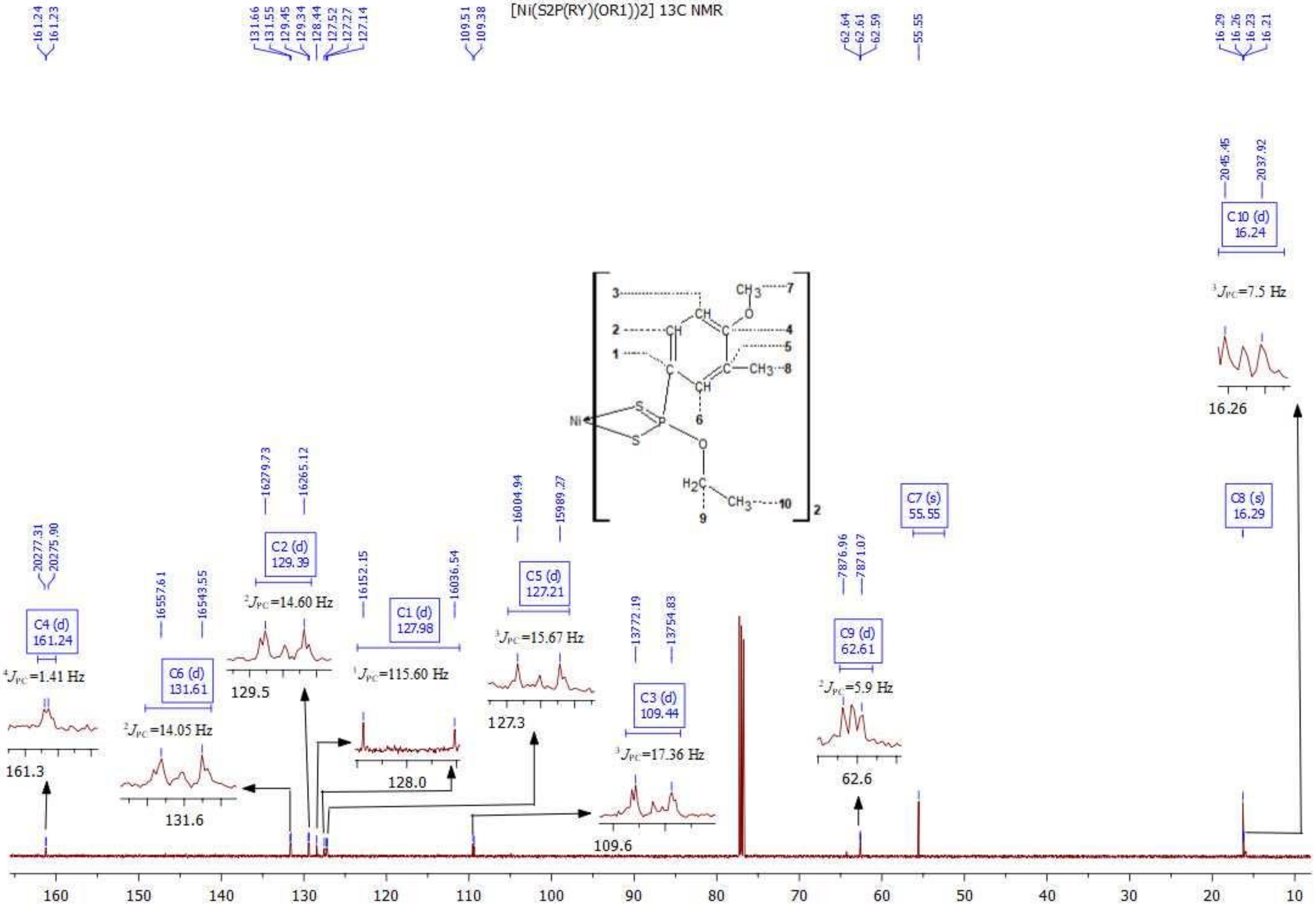

[NH4][S2P(RX)(OR2)] 13C-NMR
162.22
162.20
147.42
147.40
136.08
135.96
128.97
127.88
123.30
123.16
115.60
115.53
73.69
73.61
57.88
26.10
26.06
23.53
16325.11
16322.36
C4 (d)
162.21
$^4J_{PC}$=2.75Hz
162.20
14835.70
14833.16
C6 (d)
147.41
$^2J_{PC}$=2.53 Hz
147.44
13694.19
13682.45
C2 (d)
136.02
$^2J_{PC}$=11.75 Hz
136.1
12978.44
12868.80
C1 (d)
128.42
$^1J_{PC}$=109.69 Hz
128.5
12408.24
12393.78
C3 (d)
123.23
$^3J_{PC}$=14.46 Hz
123.3
11633.62
11626.25
C5 (d)
115.57
$^3J_{PC}$=7.37 Hz
115.65
NH_4^+
5
6
8
1
7
4
3
2
9
10
11
CH_3
C
CH
O
S
P
HC
7415.38
7407.98
C10 (d)
73.65
$^2J_{PC}$=7.40 Hz
73.68
C7 (s)
57.88
2626.28
2622.18
C9 and C11 (d)
26.08
$^3J_{PC}$=4.10 Hz
26.10
C8 (s)
23.53
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

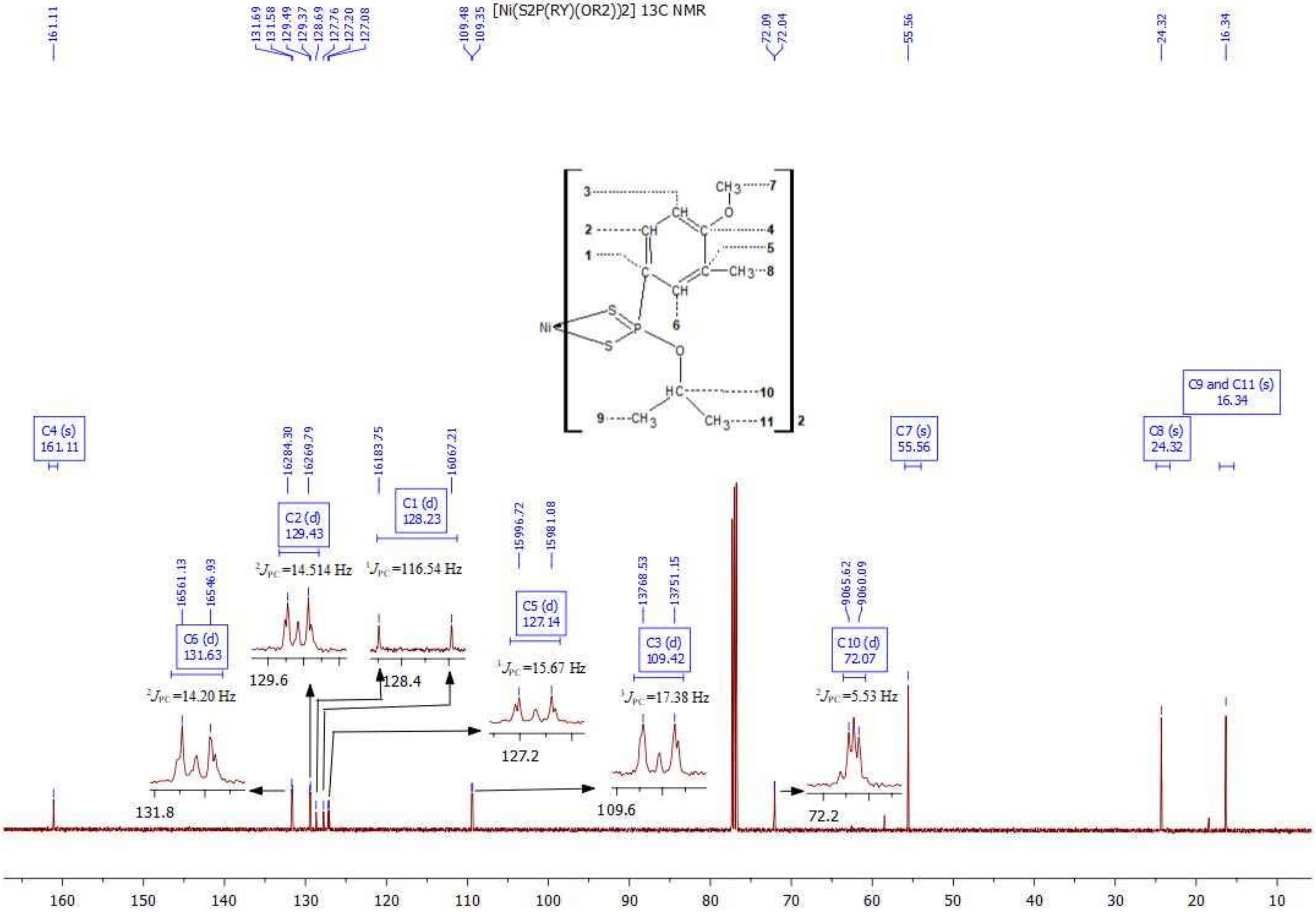

[Ni(S2P(RX)(OR1))2] 13C-NMR
160.52
145.52
132.47
132.42
132.36
121.28
121.12
120.99
120.39
112.66
112.63
112.61
62.49
62.45
62.10
55.88
21.98
16.29
16.24
C4 (s)
160.52
C6 (s)
145.35
C7 (s)
55.88
C8 (s)
21.98
2049.08
2042.02
C10 (d)
16.27
$^3J_{PC}$=7.06 Hz
16659.05
16645.56
C2 (d)
132.42
$^2J_{PC}$=13.49 Hz
15231.26
15215.03
C3 (d)
121.05
$^3J_{PC}$=16.23 Hz
15251.74
15139.70
C1 (d)
120.84
$^1J_{PC}$=112.04 Hz
14168.23
14161.04
C5 (d)
112.63
$^3J_{PC}$=7.2 Hz
7859.11
7853.50
C9 (d)
62.47
$^2J_{PC}$=5.61 Hz
132.5
121.0
121.0
112.7
62.6
16.2
5
6
8
1
CH
CH_3
O
C
CH
HC
S
S
Ni
P
O
H_2C
CH_3
7
4
3
2
9
10
2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


[Ni(S2P(RX)(OR2))2] 13C-NMR
160.37
145.36
132.57
132.44
121.58
121.04
120.88
120.46
112.51
112.43
71.72
71.66
55.66
24.16
24.12
21.97
C4 (s) 160.37
C6 (s) 145.36
C7 (s) 55.66
C8 (s) 21.97
13340.99
13327.66
C2 (d) 132.50
$^2J_{PC}$=13.34 Hz
12235.17
12121.98
C1 (d) 121.02
$^1J_{PC}$=113.19 Hz
121.0
12180.81
12164.77
C3 (d) 120.96
$^3J_{PC}$=16.04 Hz
121.0
11321.99
11314.56
C5 (d) 112.47
$^3J_{PC}$=7.43 Hz
7217.77
7211.80
C10 (d) 71.69
$^2J_{PC}$=5.97 Hz
71.7
2431.10
2427.44
C9 and C11 (d) 24.14
$^3J_{PC}$=3.66 Hz
24.3
24.1
5
6
8 CH3
1
CH
CH3 7
O
C 4
CH 3
HC 2
Ni
S
S
P
O
HC 10
9 CH3
CH3 11
2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

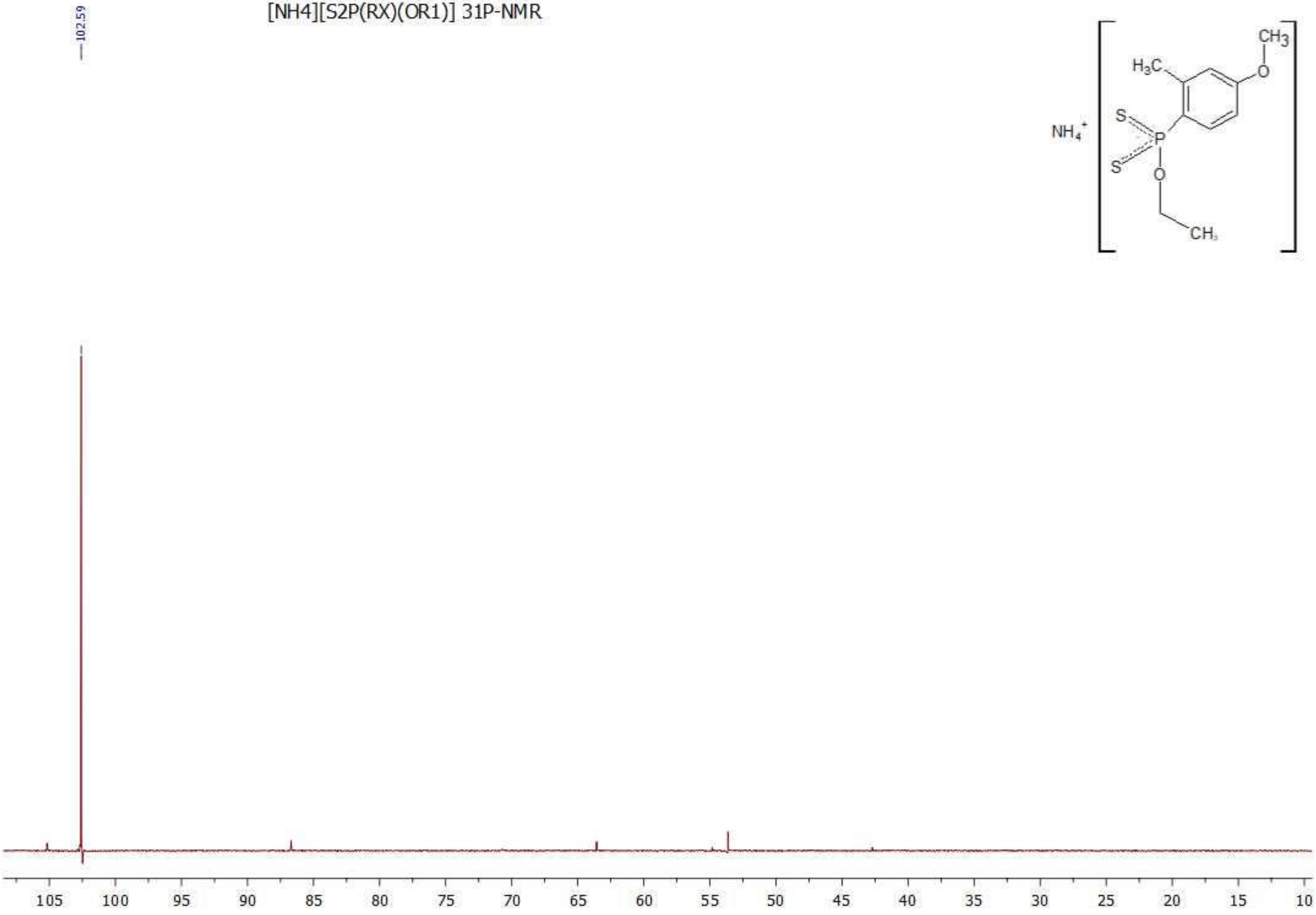

[NH4][S2P(RY)(OR1)] 13C NMR
159.41
159.38
132.35
132.25
130.30
129.70
129.61
129.15
126.49
126.38
110.25
110.13
61.40
61.35
55.53
15.63
15.57
15.45
NH4+
S
S
P
O
H2C
CH3
CH
C
O
CH3
1
2
3
4
5
6
7
8
9
10
20046.65
20043.15
C4 (d)
159.39
4JPC=3.50 Hz
159.39
16386.08
16241.29
C1 (d)
129.72
1JPC=144.79 Hz
130.2
16311.09
16299.10
C2 (d)
129.65
2JPC=11.99 Hz
130.2
15907.47
15892.81
C5 (d)
126.43
3JPC=14.66 Hz
126.6
16643.82
16631.76
C6 (d)
132.30
2JPC=12.05 Hz
132.4
13864.98
13849.37
C3 (d)
110.19
3JPC=15.61 Hz
110.2
C7 (s)
55.53
7720.91
7714.75
C9 (d)
61.37
2JPC=6.16 Hz
61.4
1965.63
1958.31
C10 (d)
15.60
3JPC=7.33 Hz
15.60
C8 (s)
15.45
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


[NH4][S2P(RY)(OR2)] 13C NMR

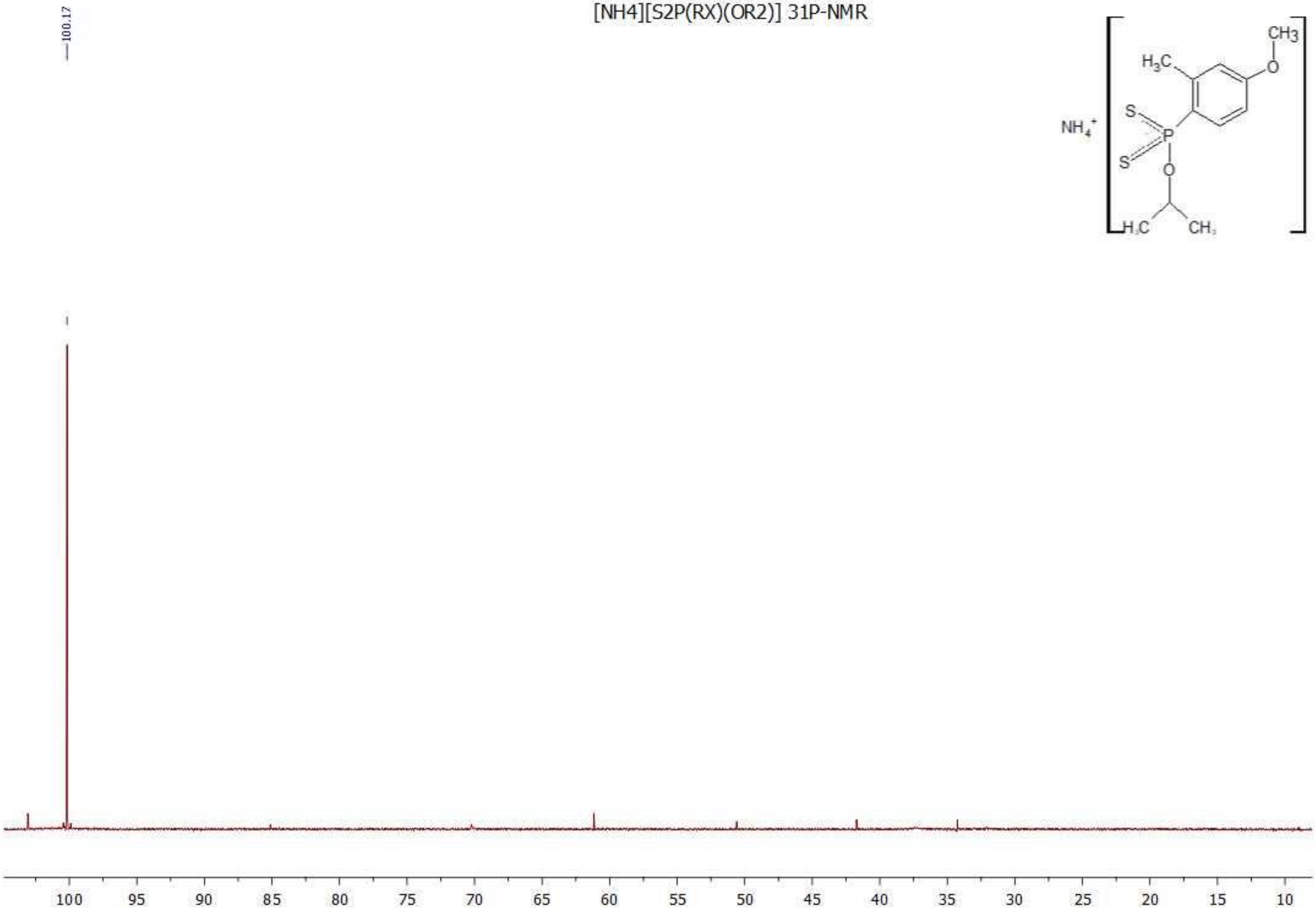

[Ni(S2P(RY)(OR1))2] 13C NMR
161.24
161.23
131.66
131.55
129.45
129.34
128.44
127.52
127.27
127.14
109.51
109.38
62.64
62.61
62.59
55.55
16.29
16.26
16.23
16.21
2045.45
2037.92
C10 (d)
16.24
$^3J_{PC}$=7.5 Hz
16.26
20277.31
20275.90
C4 (d)
161.24
$^4J_{PC}$=1.41 Hz
161.3
16557.61
16543.55
C6 (d)
131.61
$^2J_{PC}$=14.05 Hz
131.6
16279.73
16265.12
C2 (d)
129.39
$^2J_{PC}$=14.60 Hz
129.5
16152.15
16036.54
C1 (d)
127.98
$^1J_{PC}$=115.60 Hz
128.0
16004.94
15989.27
C5 (d)
127.21
$^3J_{PC}$=15.67 Hz
127.3
13772.19
13754.83
C3 (d)
109.44
$^3J_{PC}$=17.36 Hz
109.6
7876.96
7871.07
C9 (d)
62.61
$^2J_{PC}$=5.9 Hz
62.6
C7 (s)
55.55
C8 (s)
16.29
Ni
S
S
P
O
H_2C
CH_3
CH
CH
CH
C
C
C
O
CH_3
CH_3
1
2
3
4
5
6
7
8
9
10
2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


[Ni(S2P(RY)(OR2))2] 13C NMR
161.11
131.69
131.58
129.49
129.37
128.69
127.76
127.20
127.08
109.48
109.35
72.09
72.04
55.56
24.32
16.34
CH3 7
3 CH
O
2 CH
C 4
5
1 C
C CH3 8
CH
6
Ni
S
P
S
O
HC 10
9 CH3
CH3 11
2
C4 (s)
161.11
16284.30
16269.79
C2 (d)
129.43
$^2J_{PC}$=14.514 Hz
16183.75
16067.21
C1 (d)
128.23
$^1J_{PC}$=116.54 Hz
15996.72
15981.08
C5 (d)
127.14
$^1J_{PC}$=15.67 Hz
16561.13
16546.93
C6 (d)
131.63
$^2J_{PC}$=14.20 Hz
129.6
128.4
127.2
131.8
13768.53
13751.15
C3 (d)
109.42
$^1J_{PC}$=17.38 Hz
109.6
9065.62
9060.09
C10 (d)
72.07
$^2J_{PC}$=5.53 Hz
72.2
C7 (s)
55.56
C8 (s)
24.32
C9 and C11 (s)
16.34
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

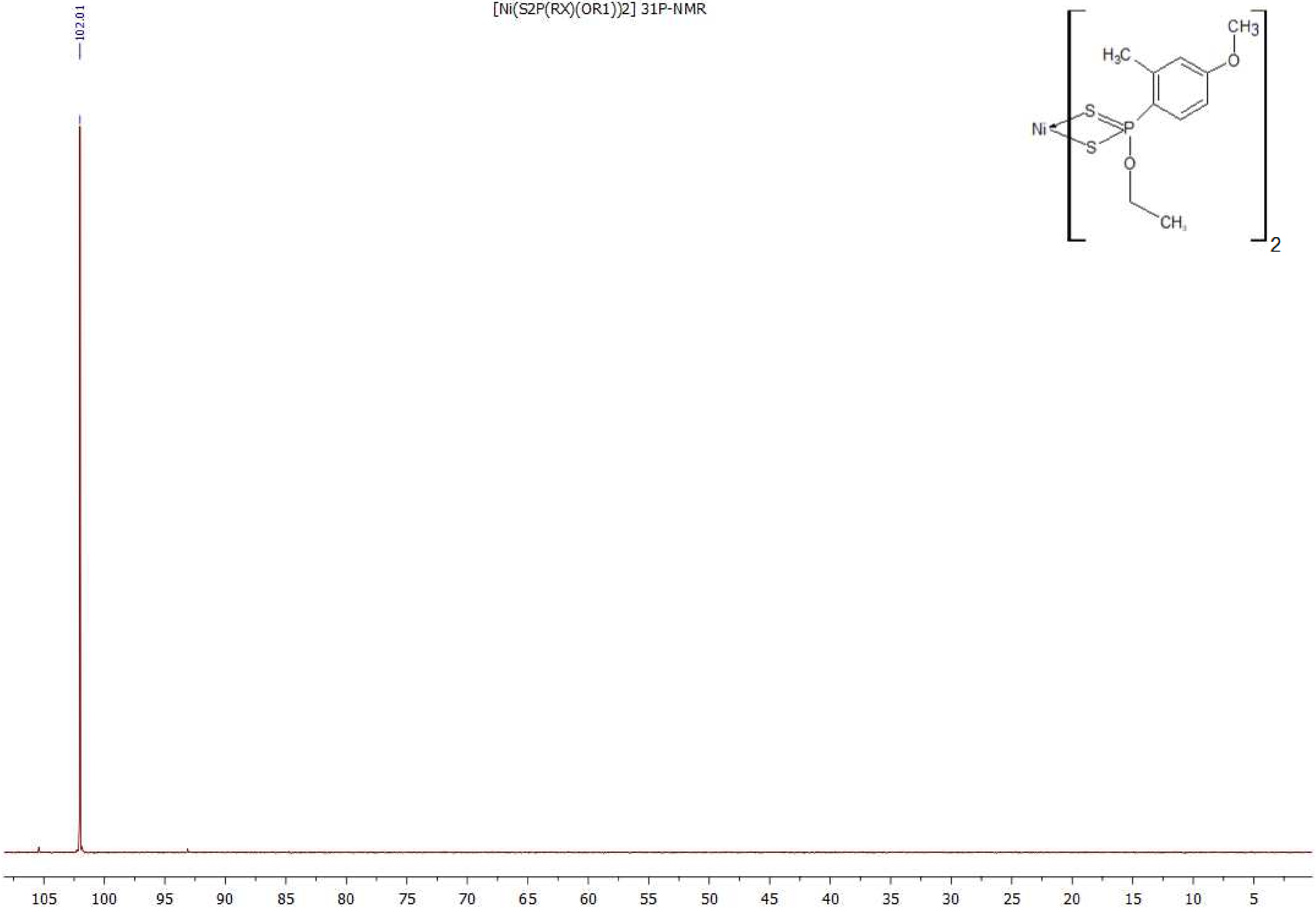
[NH4][S2P(RX)(OR1)] 31P-NMR



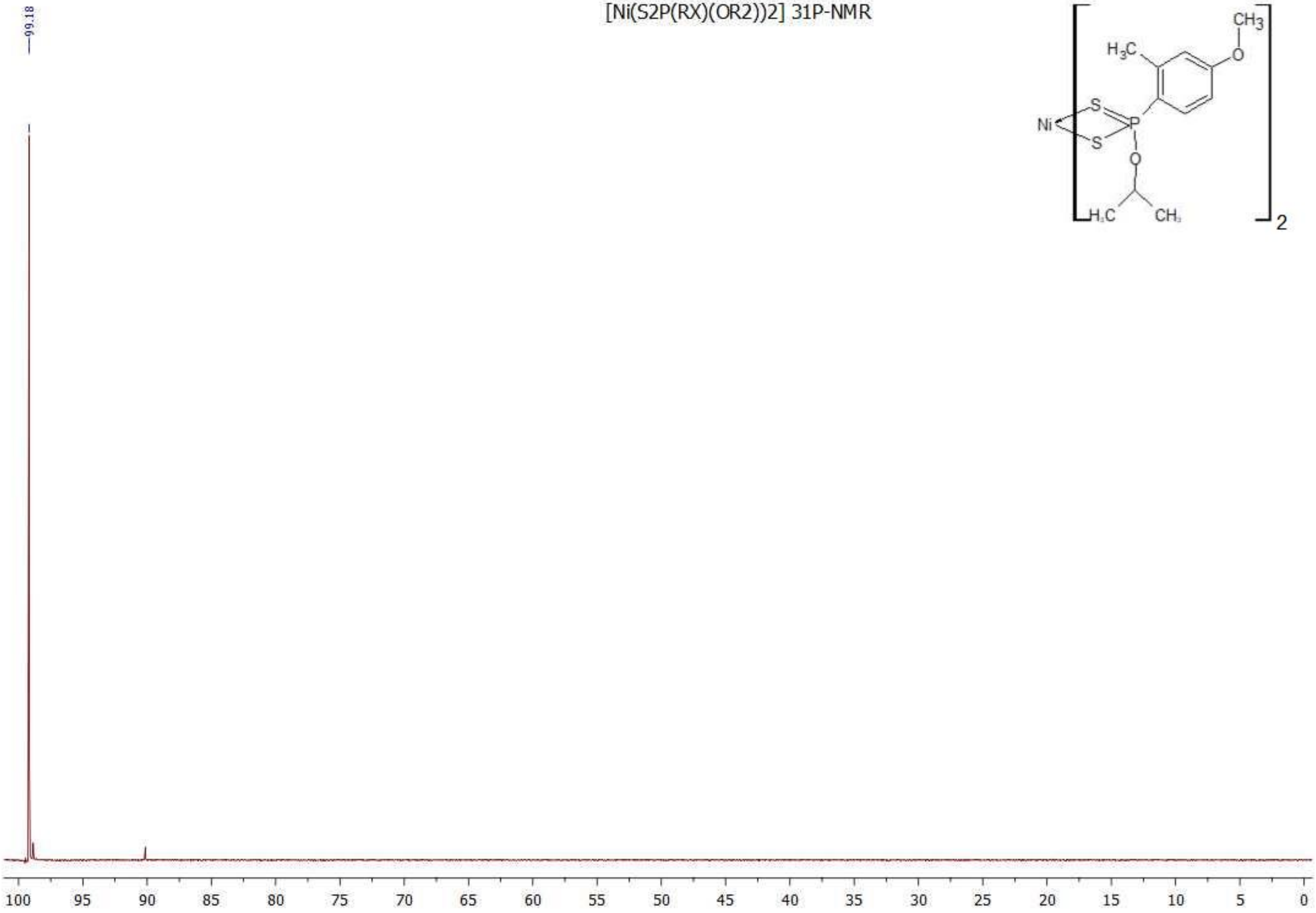
[NH4][S2P(RX)(OR2)] 31P-NMR



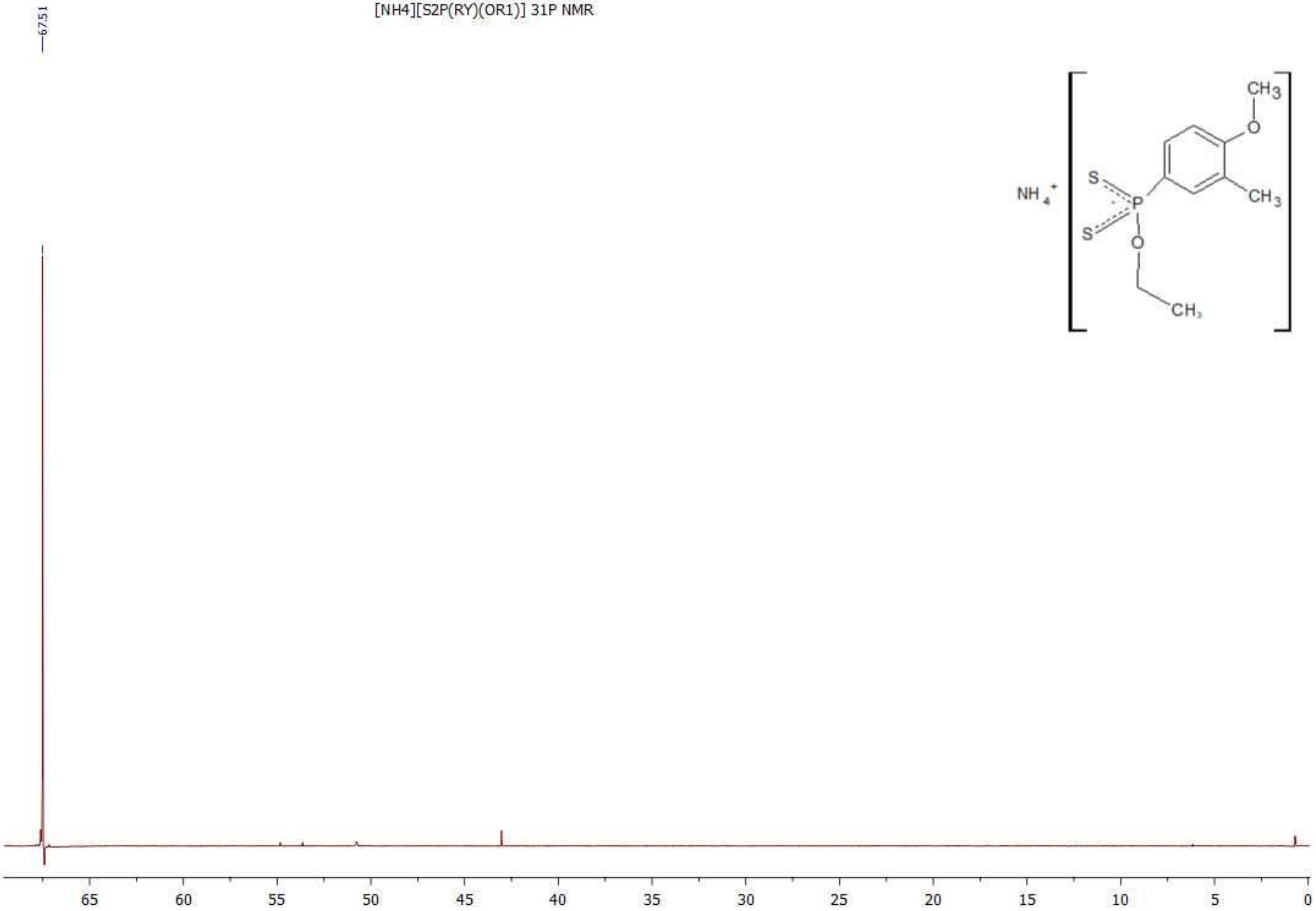
[Ni(S2P(RX)(OR1))2] 31P-NMR

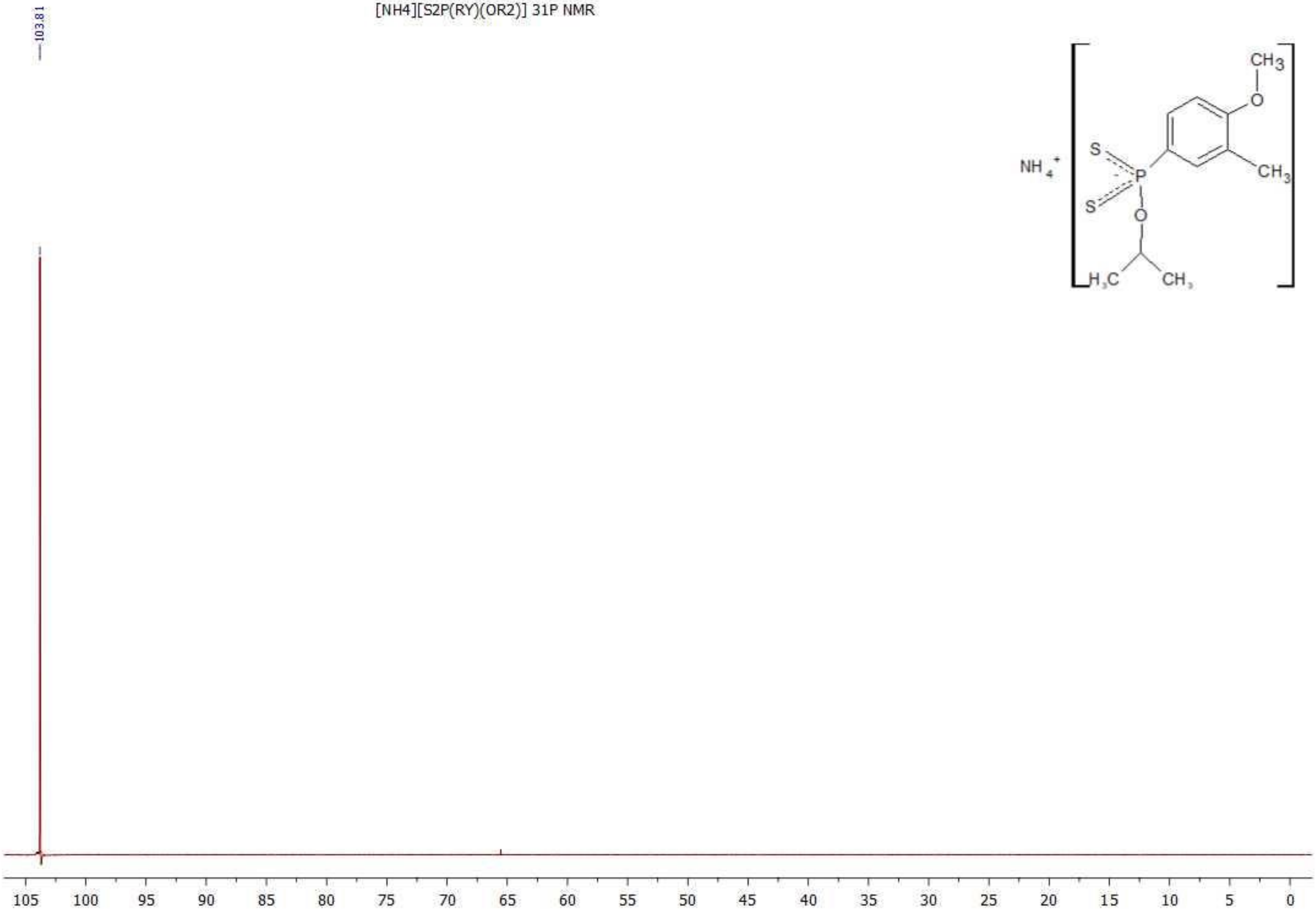


[Ni(S2P(RX)(OR2))2] 31P-NMR

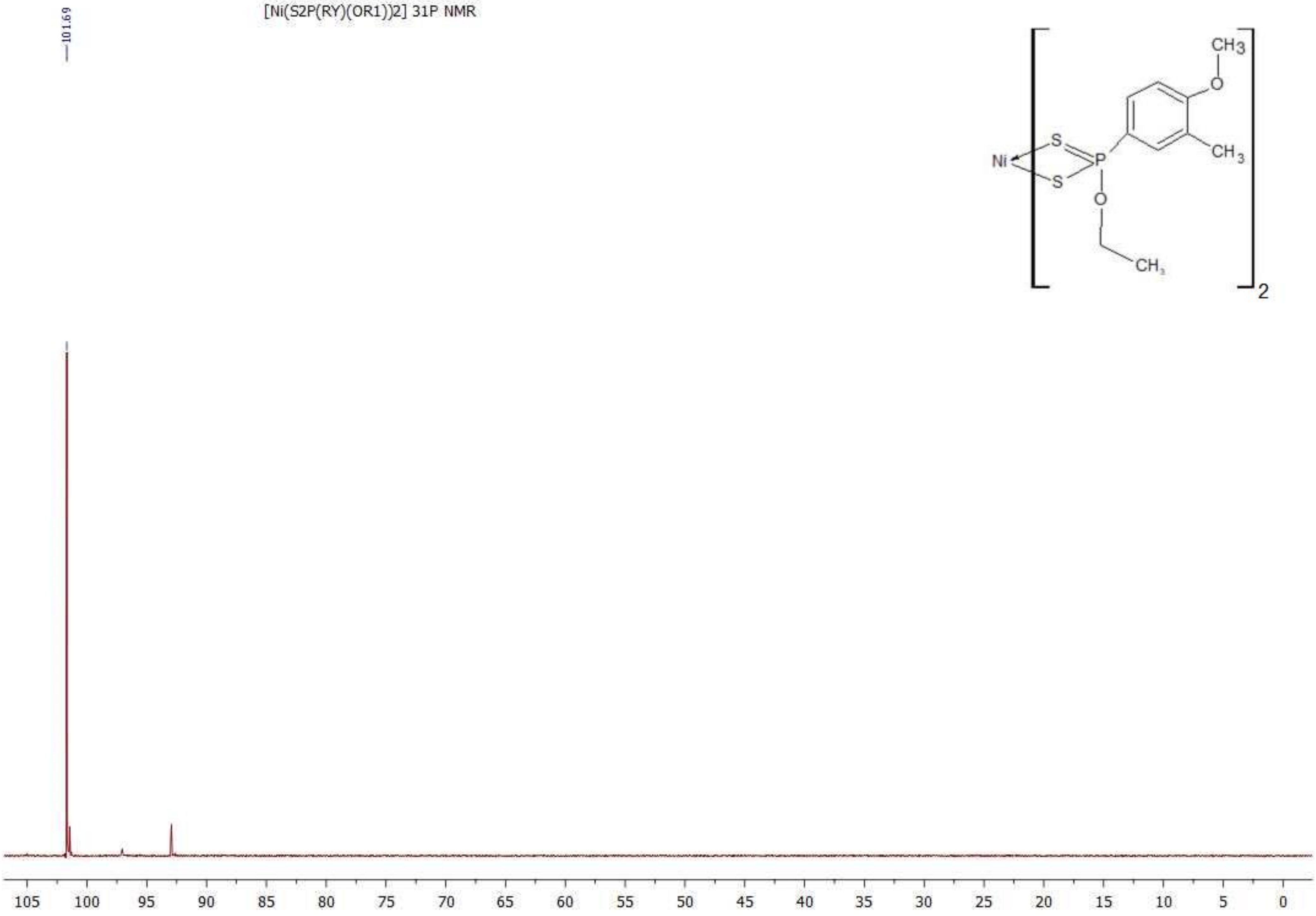


[NH4][S2P(RY)(OR1)] 31P NMR

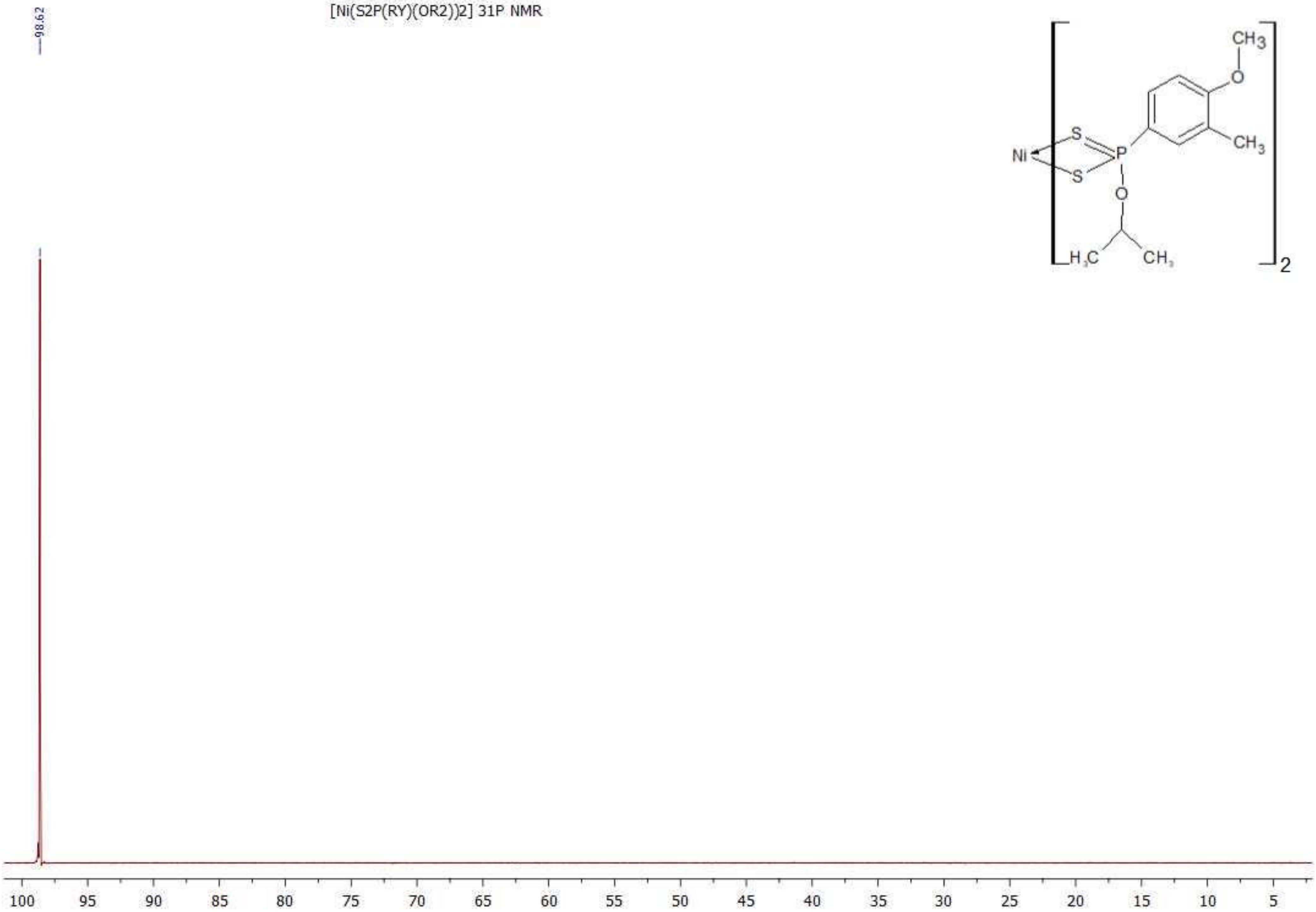



[NH4][S2P(RY)(OR2)] 31P NMR
103.81
NH4+
S
S
P
O
O
CH3
CH3
H3C
CH3
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0

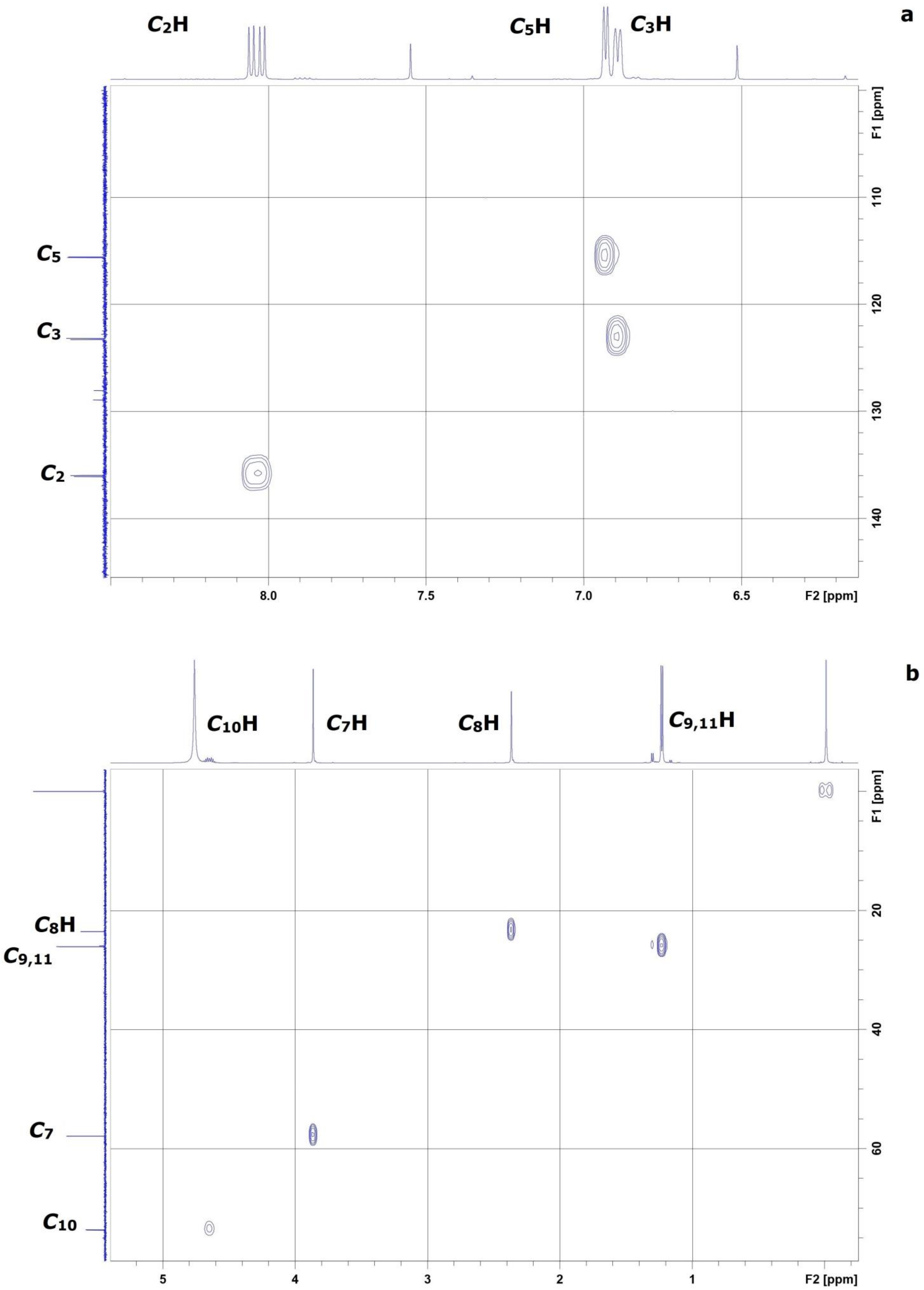
[Ni(S2P(RY)(OR1))2] 31P NMR



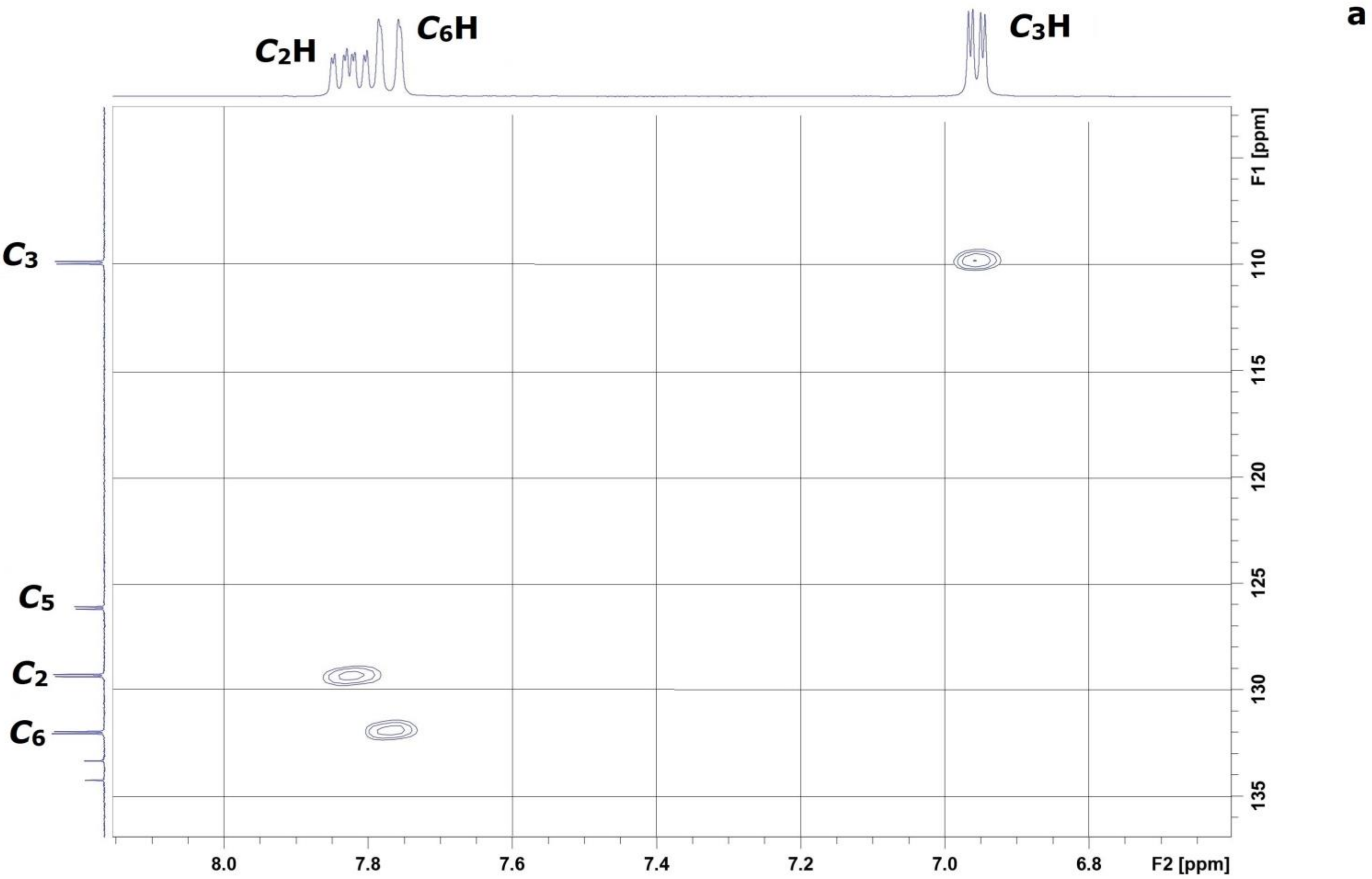
[Ni(S2P(RY)(OR2))2] 31P NMR

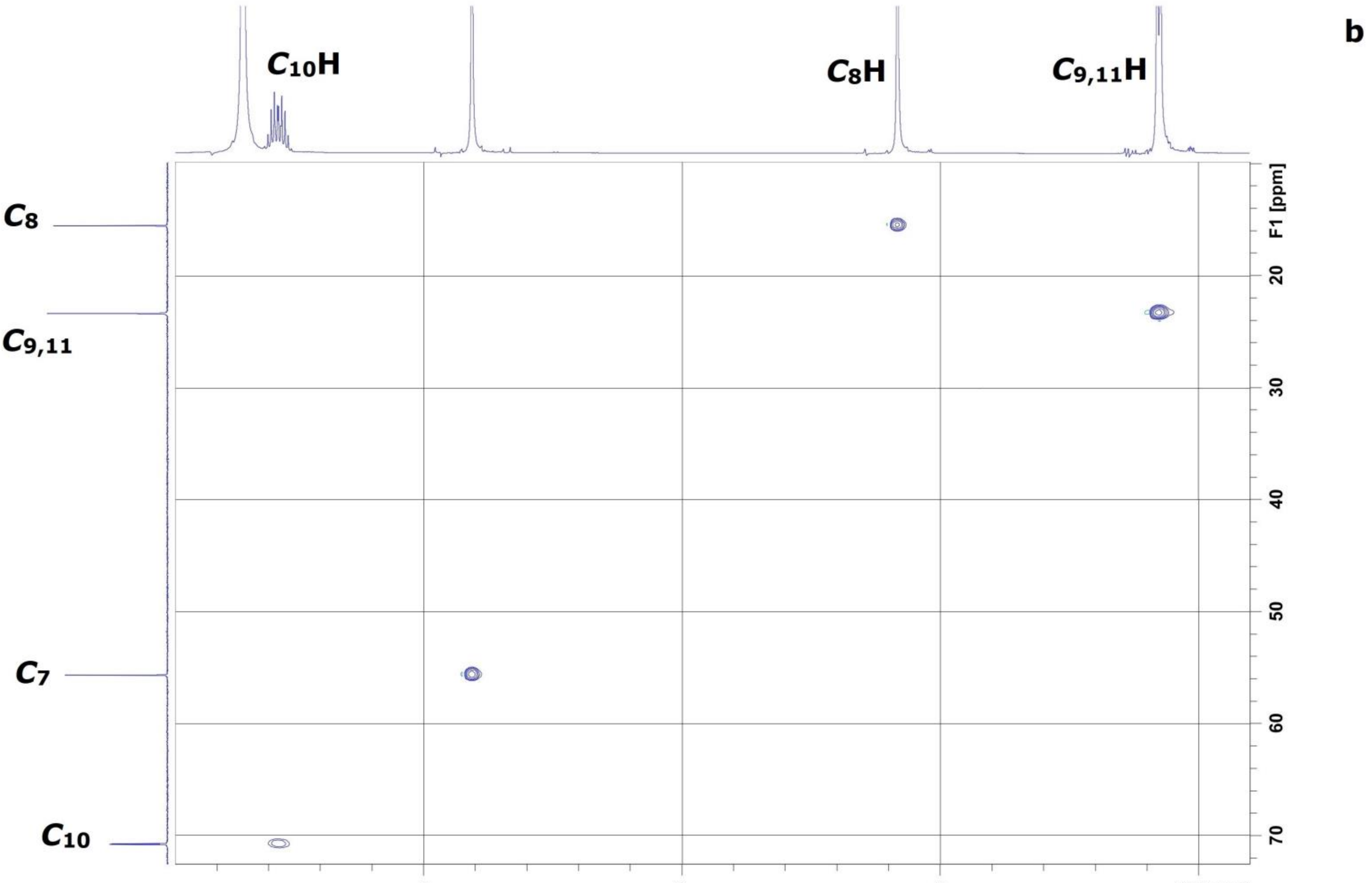


$[NH_4][S_2P(R^x)(OR2)]$

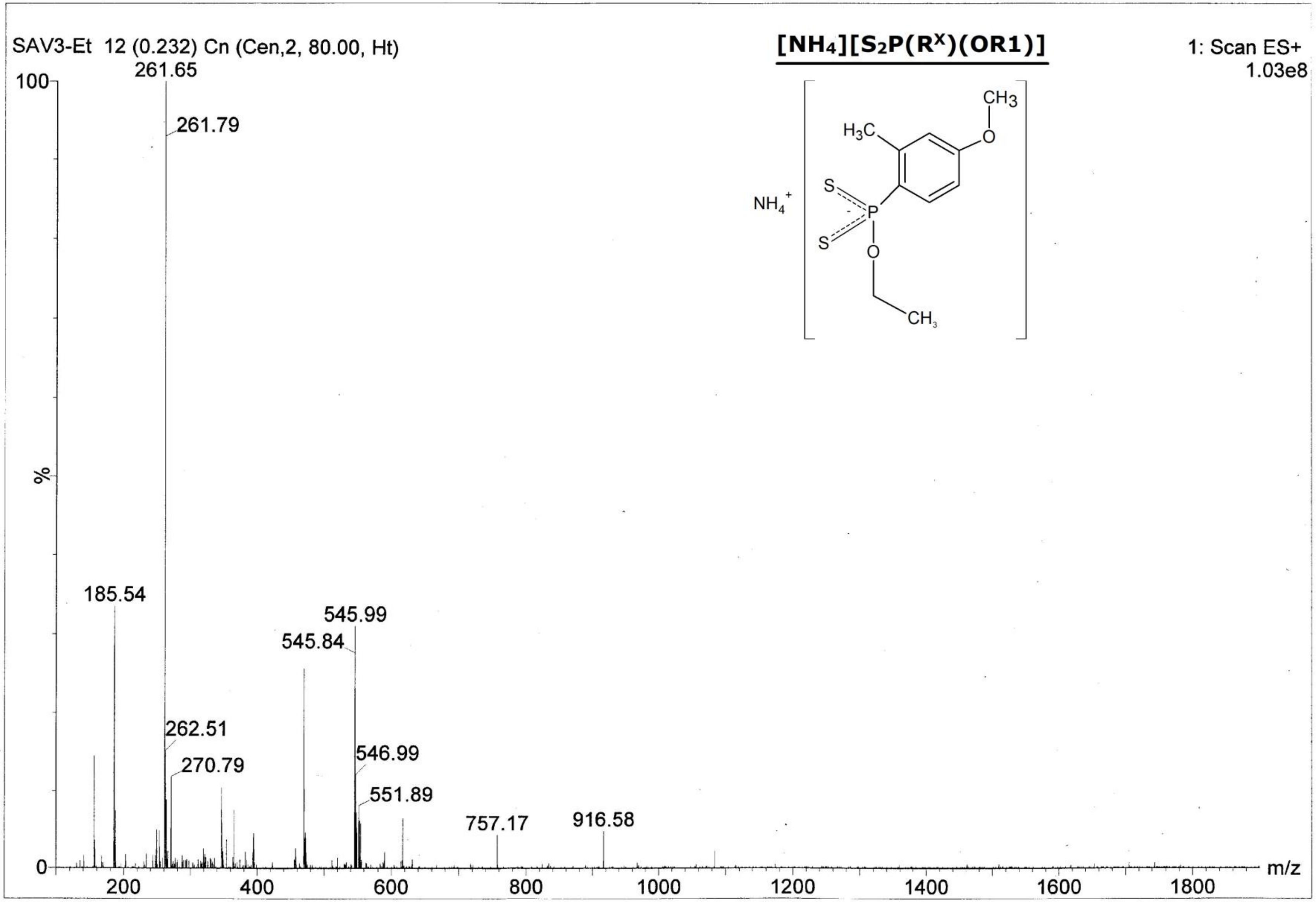


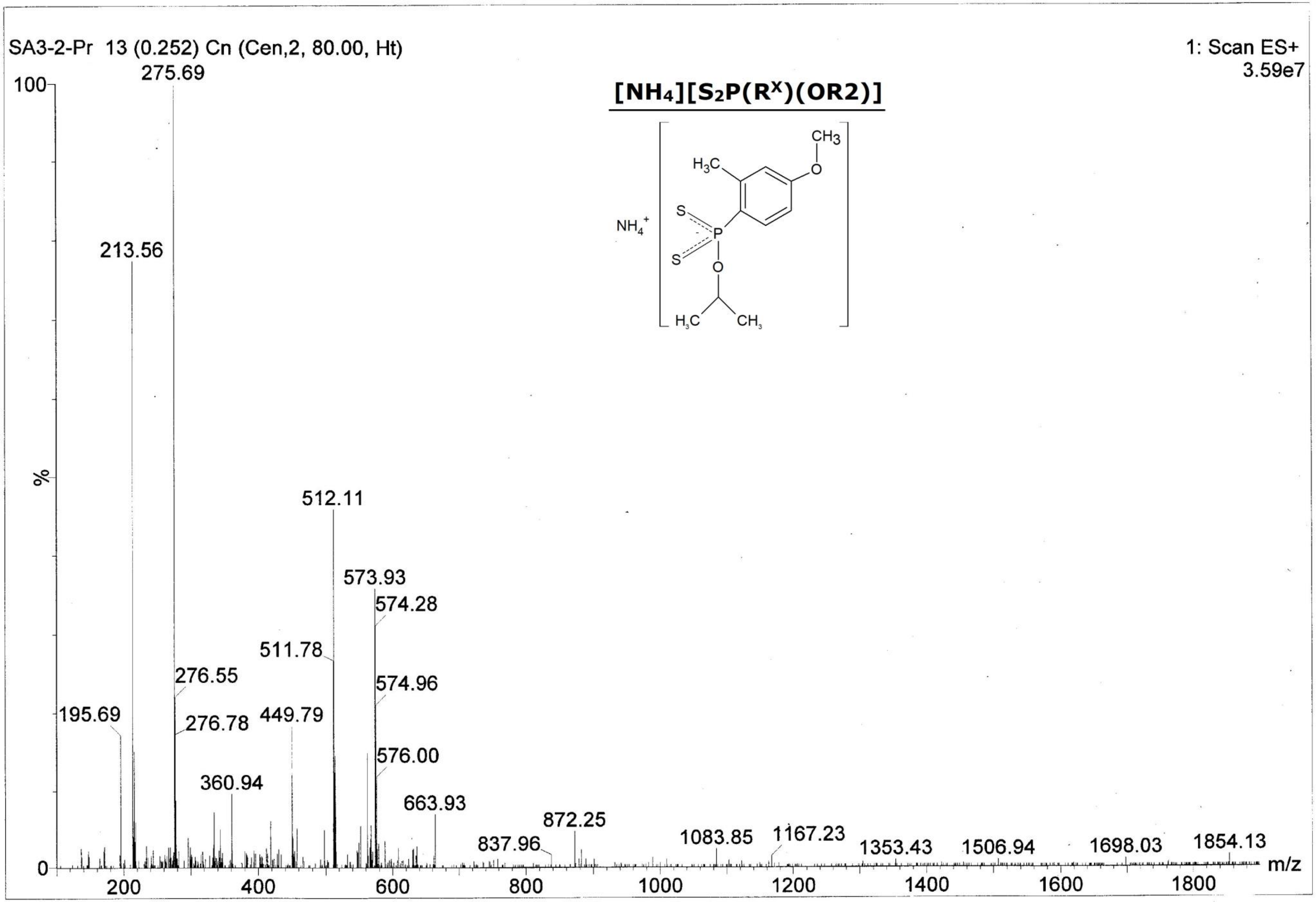
$[NH_4][S_2P(R^y)(OR2)]$

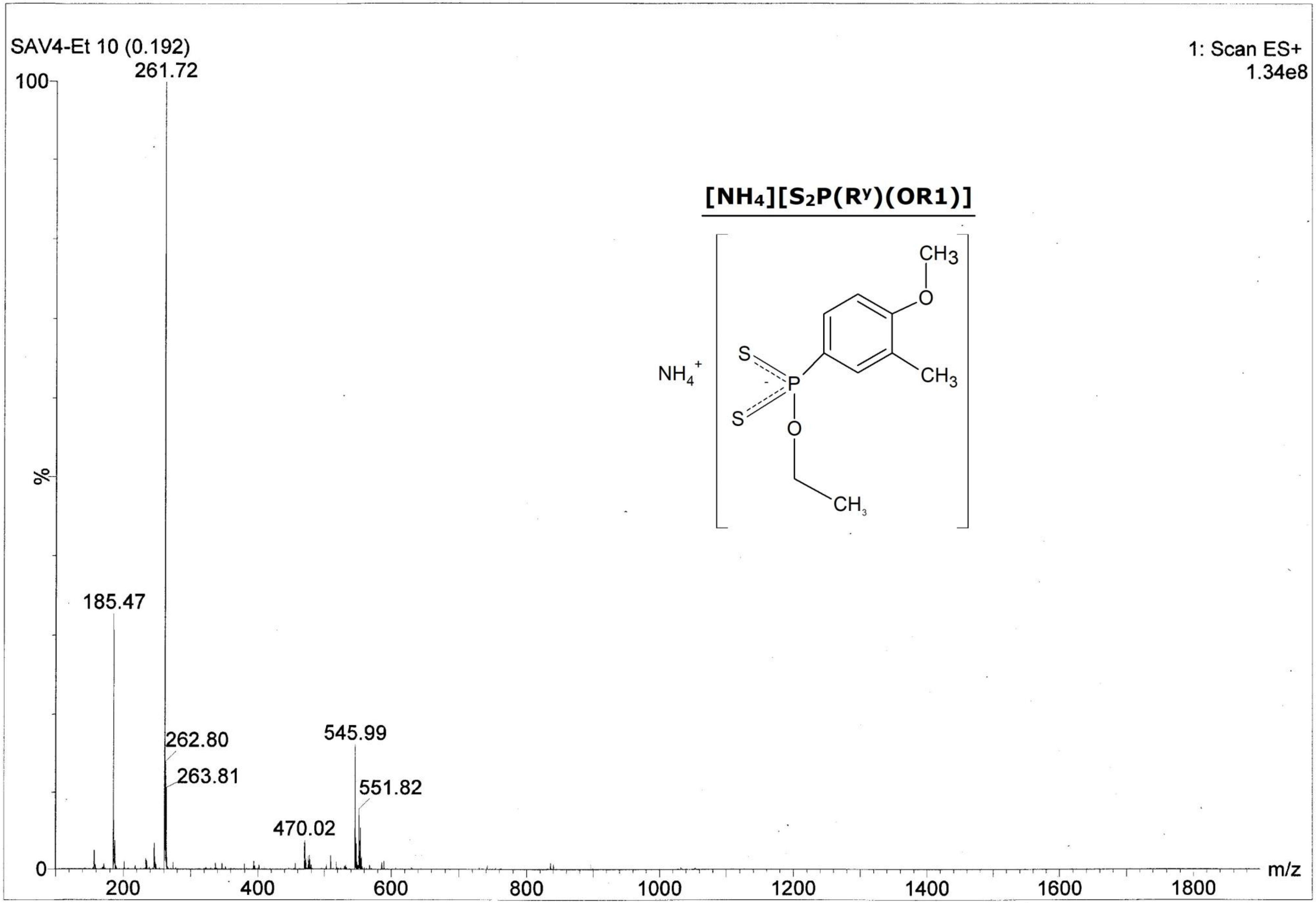


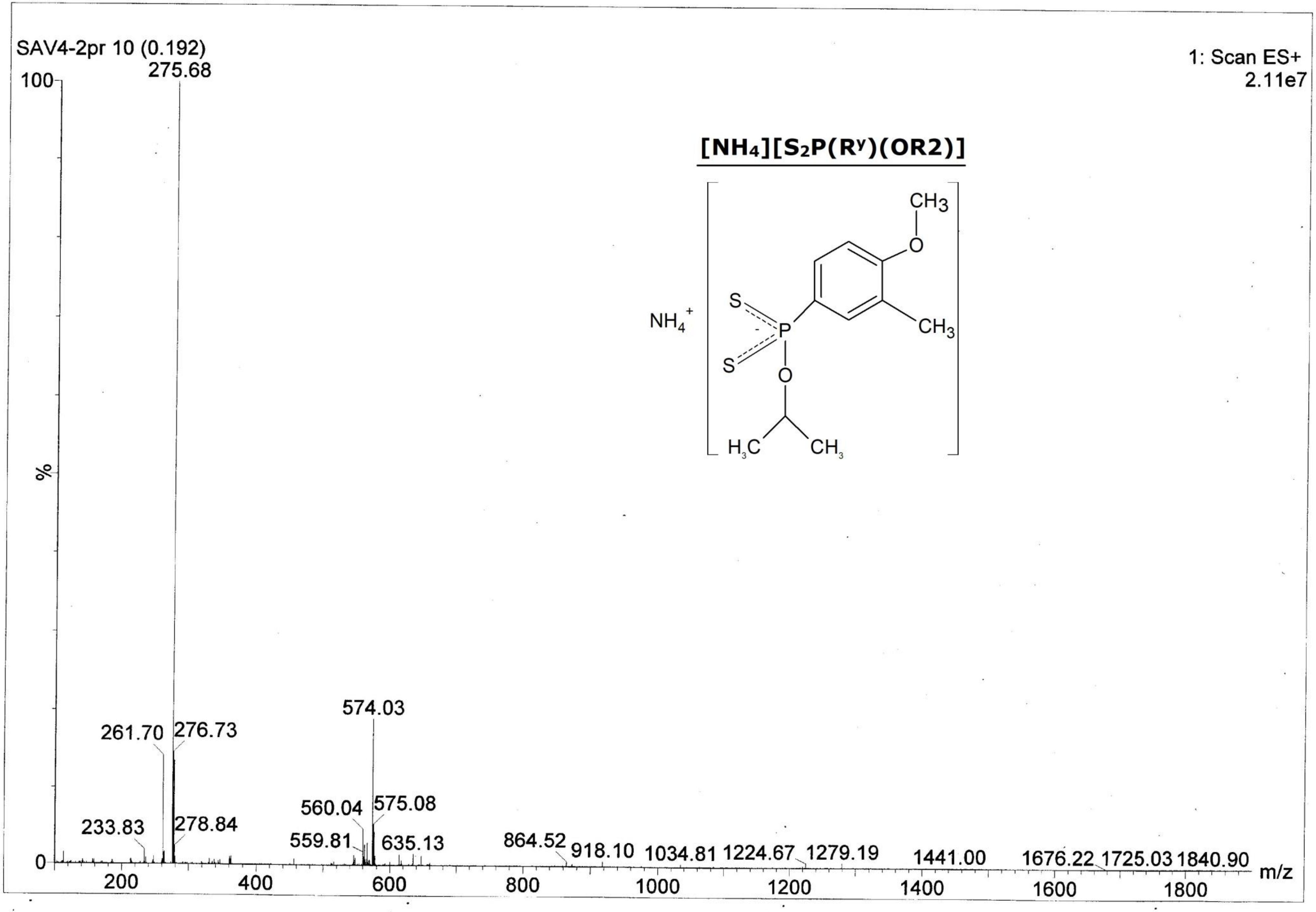


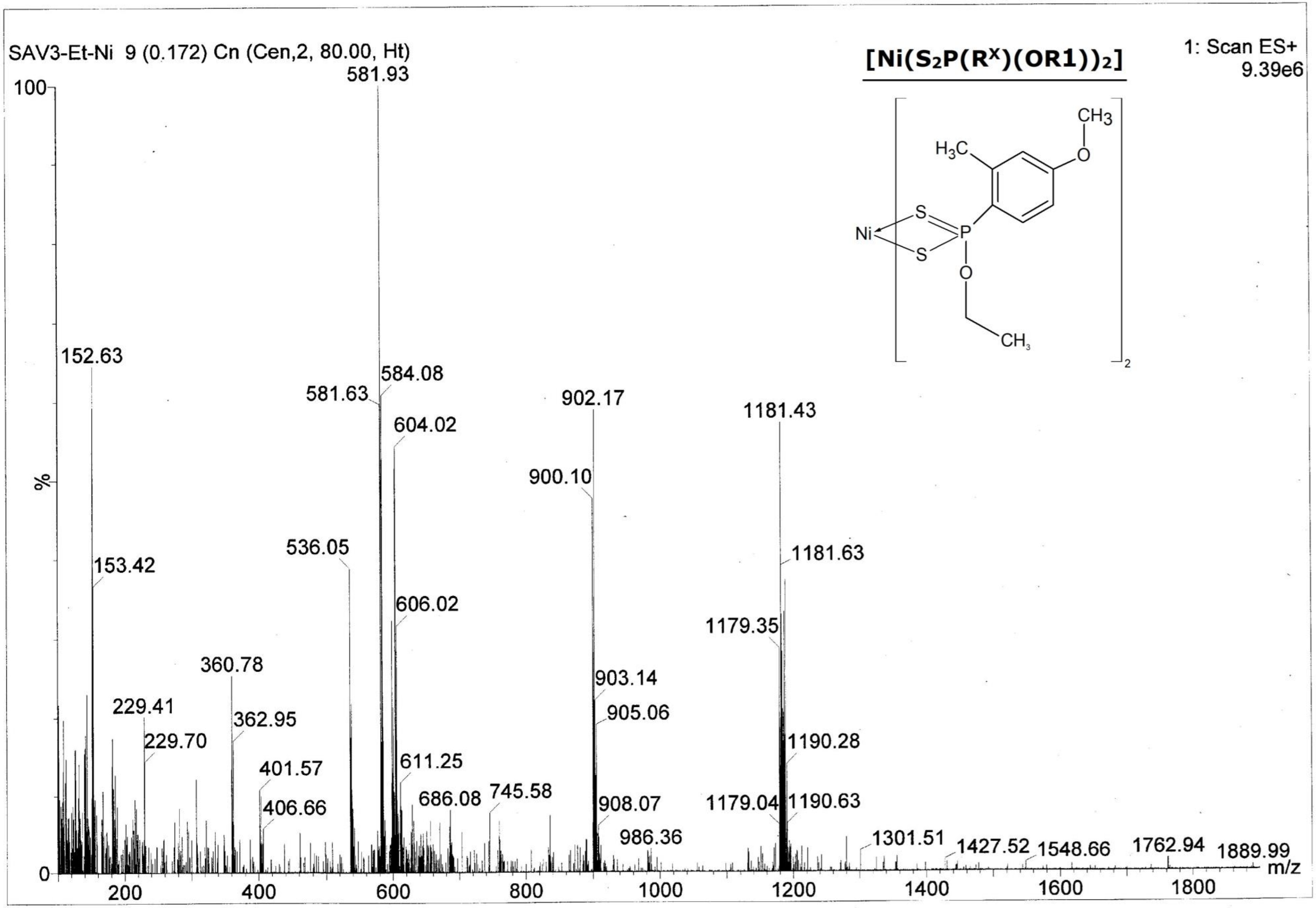
MASS SPECTRA OF THE LIGANDS and Ni(II) COMPLEXES

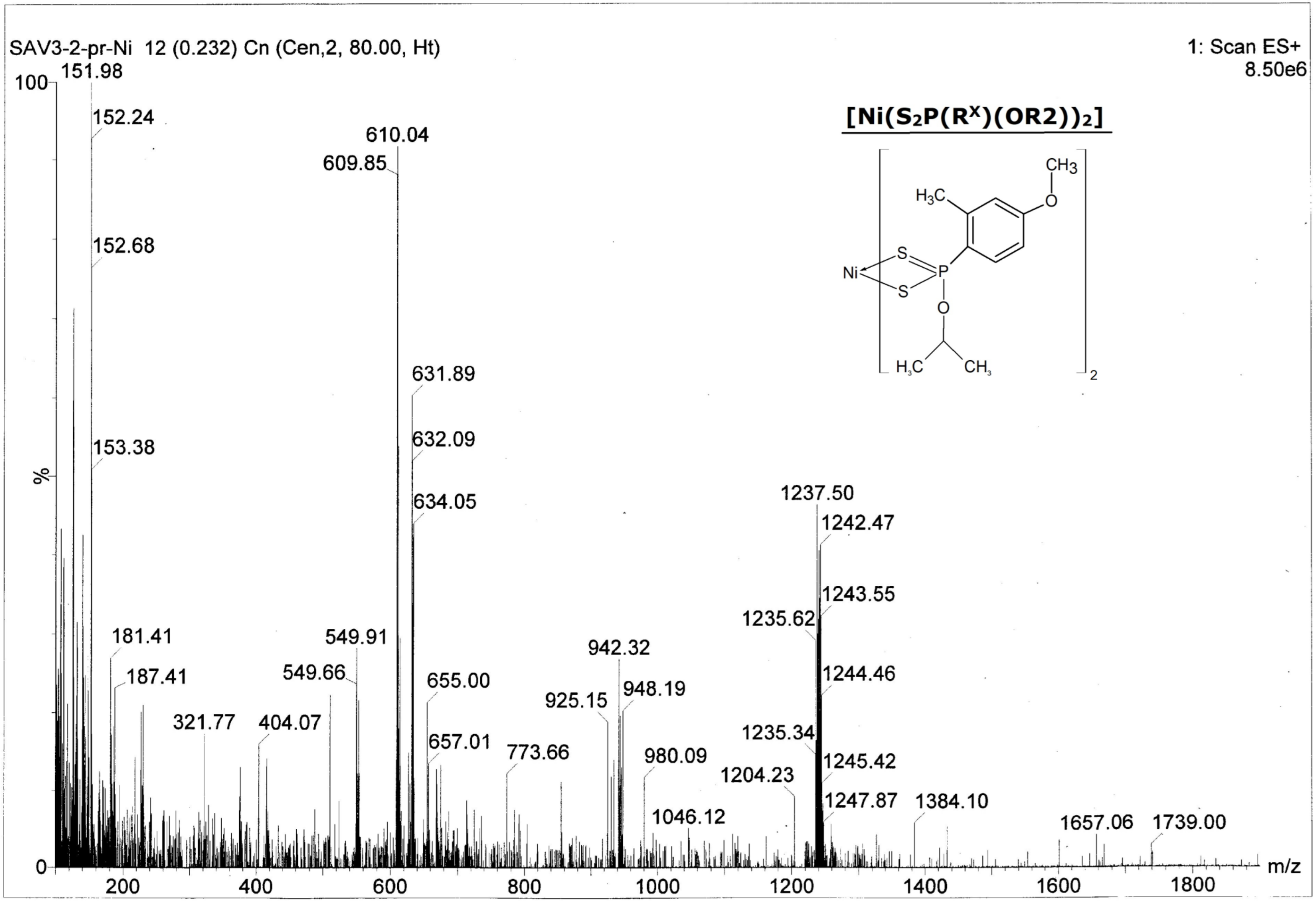


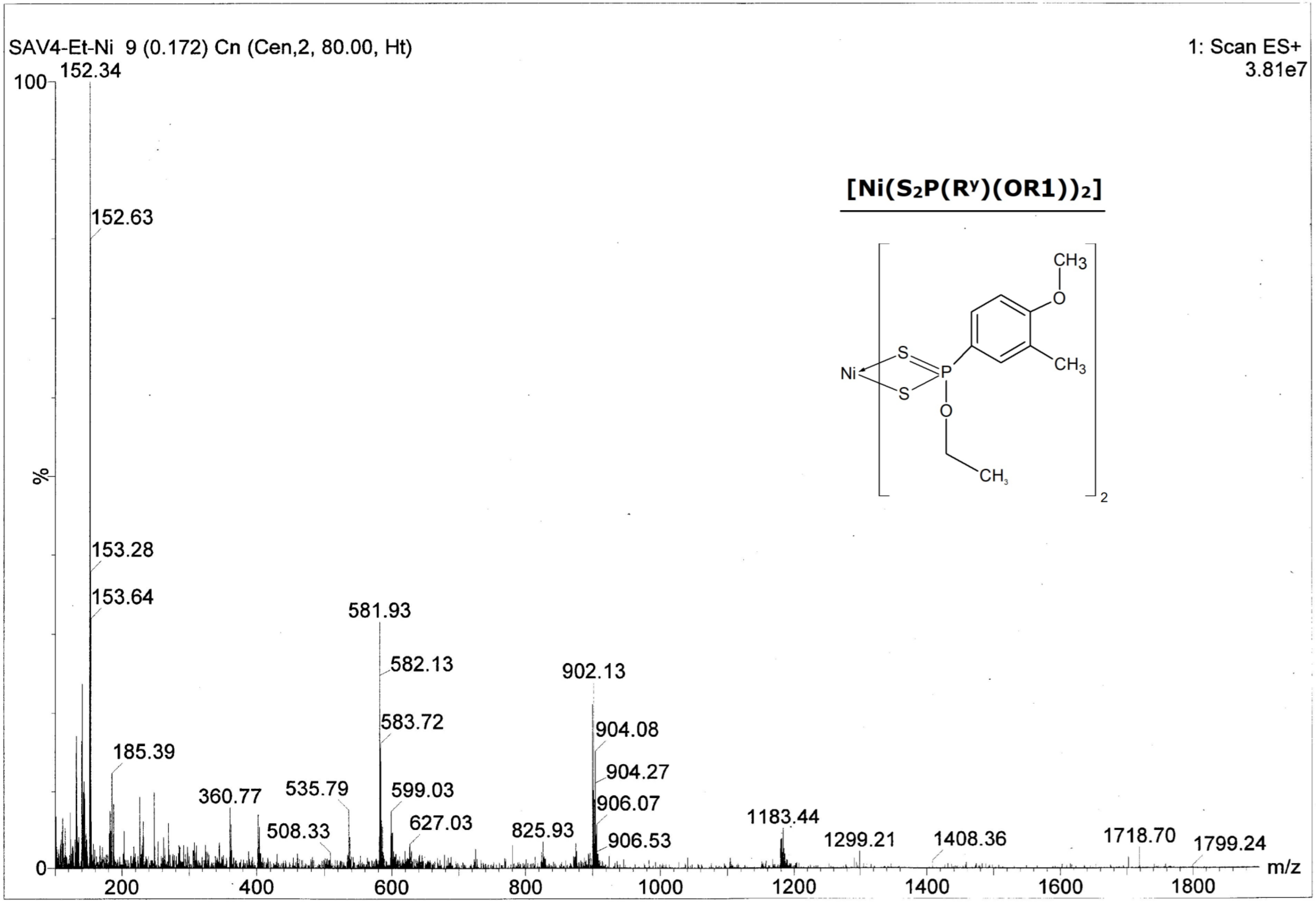

SA3-2-Pr 13 (0.252) Cn (Cen,2, 80.00, Ht)
1: Scan ES+
3.59e7
[NH4][S2P(RX)(OR2)]
NH4+
CH3
H3C
S
P
O
H3C
CH3
100
%
0
275.69
213.56
512.11
573.93
574.28
511.78
276.55
574.96
195.69
276.78
449.79
576.00
360.94
663.93
872.25
837.96
1083.85
1167.23
1353.43
1506.94
1698.03
1854.13
200
400
600
800
1000
1200
1400
1600
1800
m/z

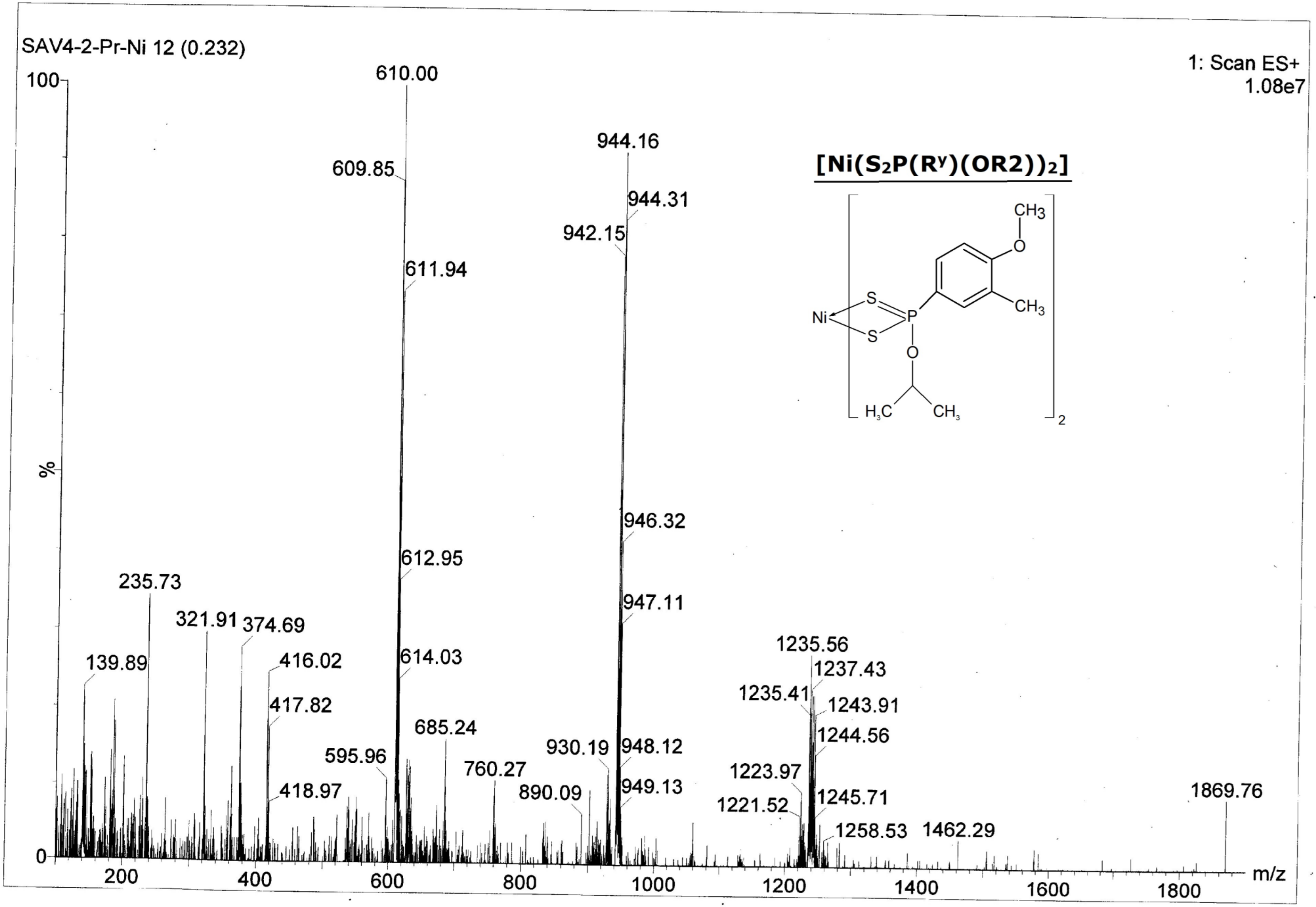

SAV4-Et 10 (0.192)
1: Scan ES+
1.34e8
100
%
0
261.72
185.47
262.80
263.81
545.99
551.82
470.02
200
400
600
800
1000
1200
1400
1600
1800
m/z
[NH4][S2P(Ry)(OR1)]
NH4+
S
S
P
O
O
CH3
CH3
CH3


SAV4-2pr 10 (0.192)
1: Scan ES+
2.11e7
100
%
0
275.68
261.70
276.73
233.83
278.84
574.03
560.04
575.08
559.81
635.13
864.52
918.10
1034.81
1224.67
1279.19
1441.00
1676.22
1725.03
1840.90
200
400
600
800
1000
1200
1400
1600
1800
m/z
$[NH_4][S_2P(R^y)(OR2)]$
NH_4^+
S
S
P
O
O
CH_3
CH_3
H_3C
CH_3


SAV3-Et-Ni 9 (0.172) Cn (Cen,2, 80.00, Ht)
1: Scan ES+
9.39e6
[Ni(S2P(Rx)(OR1))2]
CH3
H3C
O
S
Ni
P
S
O
CH3
2
100
%
0
581.93
152.63
584.08
581.63
902.17
1181.43
604.02
900.10
536.05
1181.63
153.42
606.02
1179.35
360.78
903.14
229.41
905.06
362.95
229.70
1190.28
401.57
611.25
406.66
686.08
745.58
908.07
1179.04
1190.63
986.36
1301.51
1427.52
1548.66
1762.94
1889.99
200
400
600
800
1000
1200
1400
1600
1800
m/z


SAV3-2-pr-Ni 12 (0.232) Cn (Cen,2, 80.00, Ht)
1: Scan ES+
8.50e6
[Ni(S₂P(R^X)(OR2))₂]
CH3
H3C
O
S
Ni
P
S
O
H3C
CH3
2
100
%
0
151.98
152.24
152.68
153.38
181.41
187.41
321.77
404.07
549.66
549.91
609.85
610.04
631.89
632.09
634.05
655.00
657.01
773.66
925.15
942.32
948.19
980.09
1046.12
1204.23
1235.34
1235.62
1237.50
1242.47
1243.55
1244.46
1245.42
1247.87
1384.10
1657.06
1739.00
200
400
600
800
1000
1200
1400
1600
1800
m/z


SAV4-Et-Ni 9 (0.172) Cn (Cen,2, 80.00, Ht)
1: Scan ES+
3.81e7
100
%
0
152.34
152.63
153.28
153.64
185.39
360.77
508.33
535.79
581.93
582.13
583.72
599.03
627.03
825.93
902.13
904.08
904.27
906.07
906.53
1183.44
1299.21
1408.36
1718.70
1799.24
200
400
600
800
1000
1200
1400
1600
1800
m/z
[Ni(S₂P(Rʸ)(OR1))₂]
Ni
S
S
P
O
CH3
CH3
O
CH3
2


SAV4-2-Pr-Ni 12 (0.232)
1: Scan ES+
1.08e7
100
%
0
610.00
609.85
611.94
612.95
614.03
944.16
944.31
942.15
946.32
947.11
948.12
949.13
930.19
890.09
235.73
139.89
321.91
374.69
416.02
417.82
418.97
595.96
685.24
760.27
1235.56
1237.43
1235.41
1243.91
1244.56
1223.97
1245.71
1221.52
1258.53
1462.29
1869.76
200
400
600
800
1000
1200
1400
1600
1800
m/z
[Ni(S₂P(Rʸ)(OR2))₂]
CH3
O
CH3
Ni
S
S
P
O
H3C
CH3
2