Synthesis of Unsymmetrical Phosphorus Disulfides

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Supporting Information

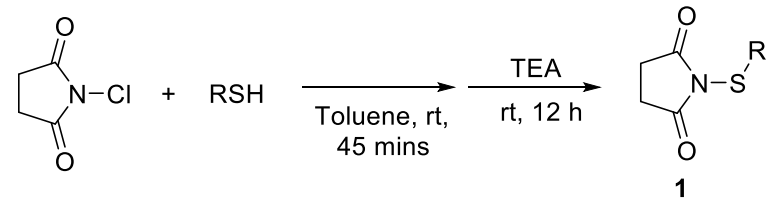
1. General information

All reactions were carried out under air atmosphere in oven-dried glassware with magnetic stirring bar. Dry solvents (THF, toluene, ACN, diethyl ether, and DCM) were obtained by solvent purification system under argon. All commercially available reagents were used as received without further purification. The tubes used for the reaction were showed in **Figure S1**. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on 0.25 mm aluminum-backed silica gel 60-F plates. Visualization was accompanied with UV light and $KMnO_4$ solution. Concentration under reduced pressure refers to the removal of volatiles using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr). Infrared (IR) spectra were recorded on an IR spectrometer with KBr wafers or a film on KBr plate. High-resolution mass spectra (HRMS) were recorded on LCMS-IT-TOF mass spectrometer using ESI (electrospray ionization) or APCI (Atmospheric Pressure Chemical Ionization). ^1H NMR spectra were recorded in $CDCl_3$ on 400 MHz NMR spectrometer. The ^1H chemical shifts are referenced to residual solvent signals at δ 7.26 ($CHCl_3$) or δ 0.00 (TMS). ^1H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets). ^{13}C NMR spectra were proton decoupled and recorded in $CDCl_3$ on 100.5 MHz NMR spectrometer. The ^{13}C chemical shifts are referenced to solvent signals at δ 77.16 ($CDCl_3$). ^{31}P NMR spectra were proton decoupled and recorded in $CDCl_3$ on 162 MHz NMR spectrometer. ^{31}P chemical shifts are reported relative to 85% H_3PO_4 (0.00 ppm) as an external standard.

Figure S1. Pictorial description of reaction tubes for the reaction.

2. General experimental procedure

2.1. General procedure for the synthesis of thiosuccinimide 1



1

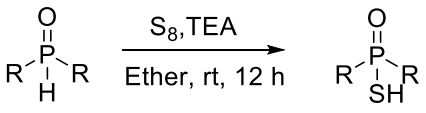
To a solution of thiol (1.0 mmol) in toluene (3.0 mL) was added N-chlorosuccinimide (1.0 mmol) portionwise and was stirred for 45 minutes at room temperature. After 45 min stirring, triethyl amine (1.0 mmol) was added dropwise, and the reaction mixture was stirred for 12 hours. The residue was concentrated under reduced pressure and subjected to column chromatography on silica gel to give the corresponding thiosuccinimides **1**.

2.2. General procedure for the synthesis of acyl thiosuccinimide 1p

1p

To a solution of potassium thiolate (5.0 mmol) in acetone (25.0 mL) was added N-chlorosuccinimide (5.0 mmol) at room temperature. The reaction mixture was stirred for 12 hours. After stirring for 12 hours at room temperature, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography on silica gel to give the corresponding acyl thio succinimide **1p**.

2.3. General procedure for the synthesis of thiophosphoric acid 2

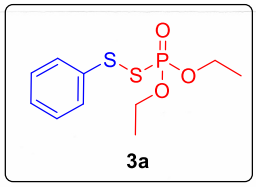


2

To a solution of H-phosphonate (1.0 mmol) in ether (5.0 mL) was added triethylamine (1.1 mmol), followed by elemental sulfur (1.05 mmol). The reaction was stirred for 12 hours and then washed with 1M HCl (3 X 5.0 mL), followed by washing with brine. The organic extract was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give compound **2**.

3. ^{1}H, ^{13}C, and ^{31}P NMR spectra

^{1}H NMR (400 MHz) in $CDCl_3$



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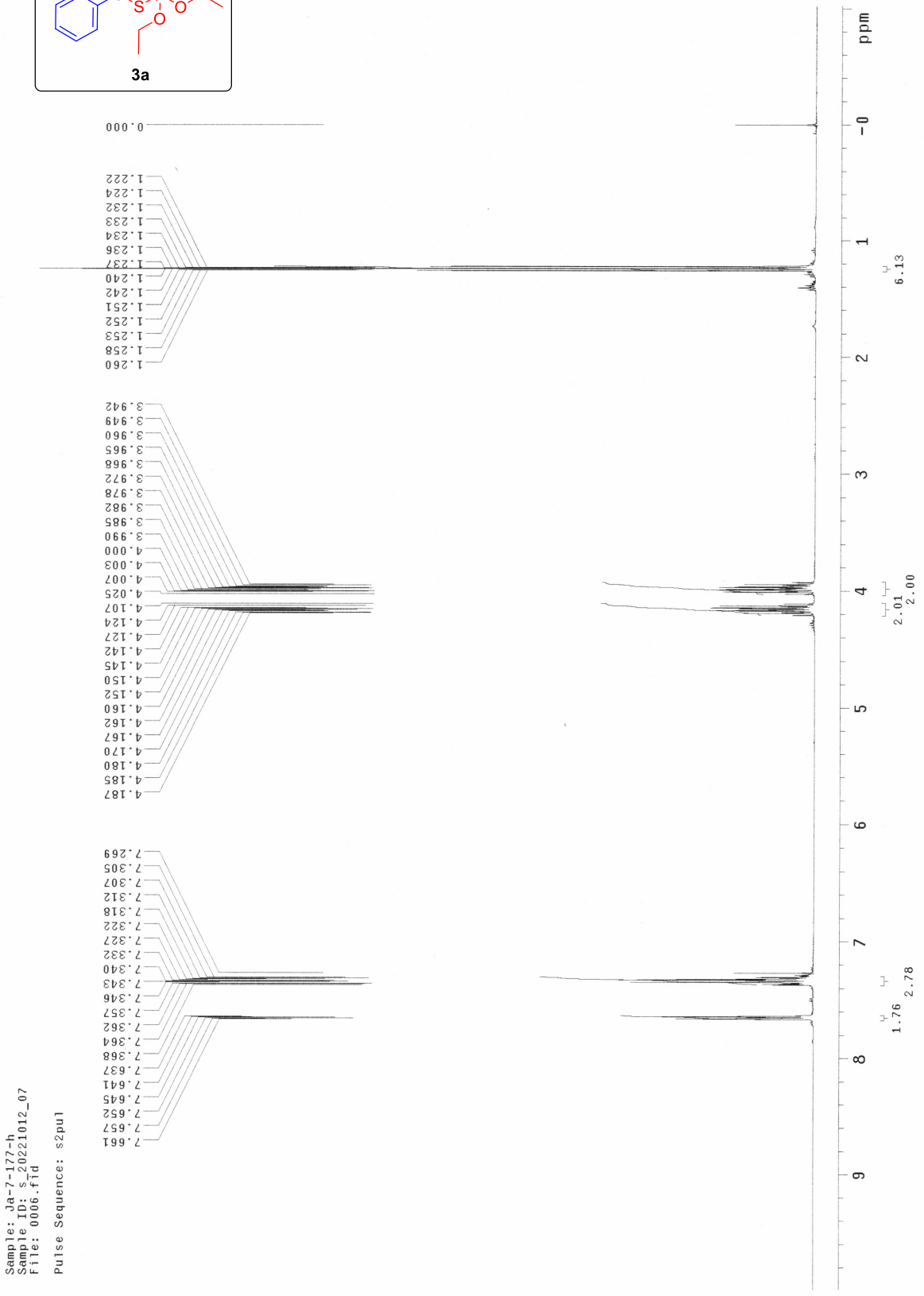

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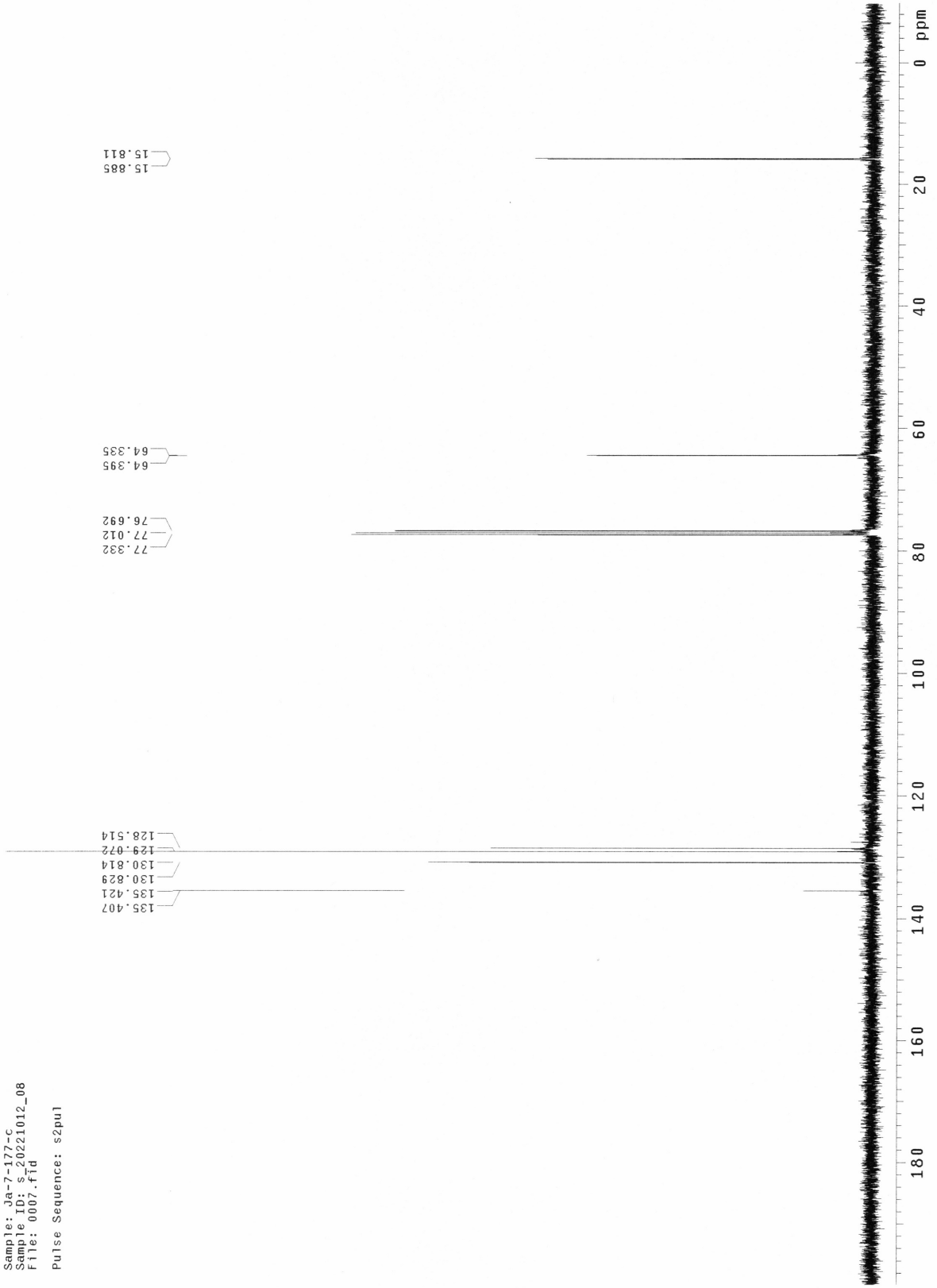
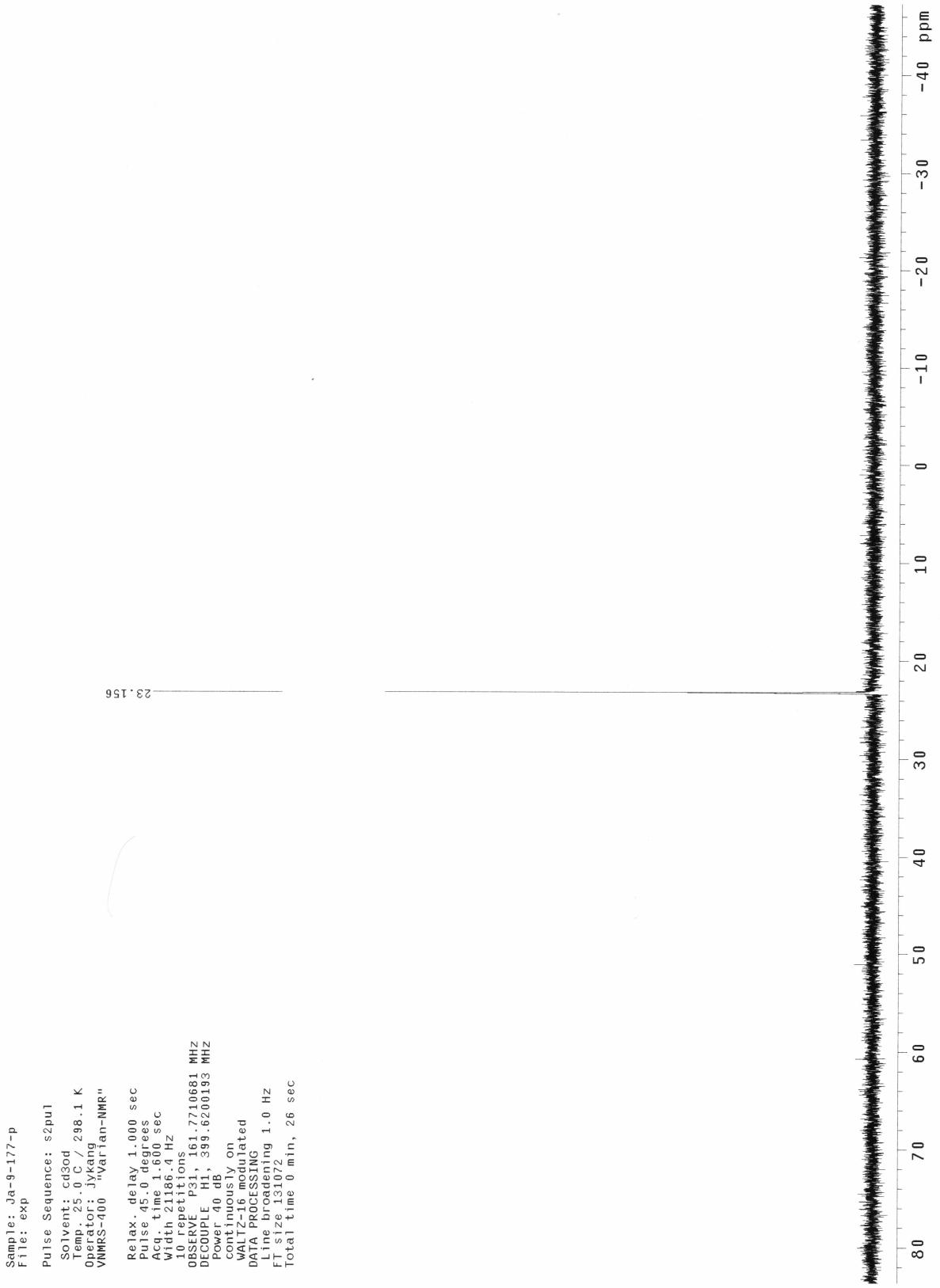
Pulse Sequence: s2pul

^{13}C NMR (100.5 MHz) in $CDCl_3$



^{31}P NMR (162 MHz) in $CDCl_3$



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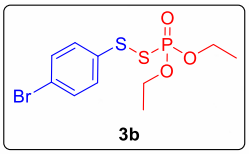

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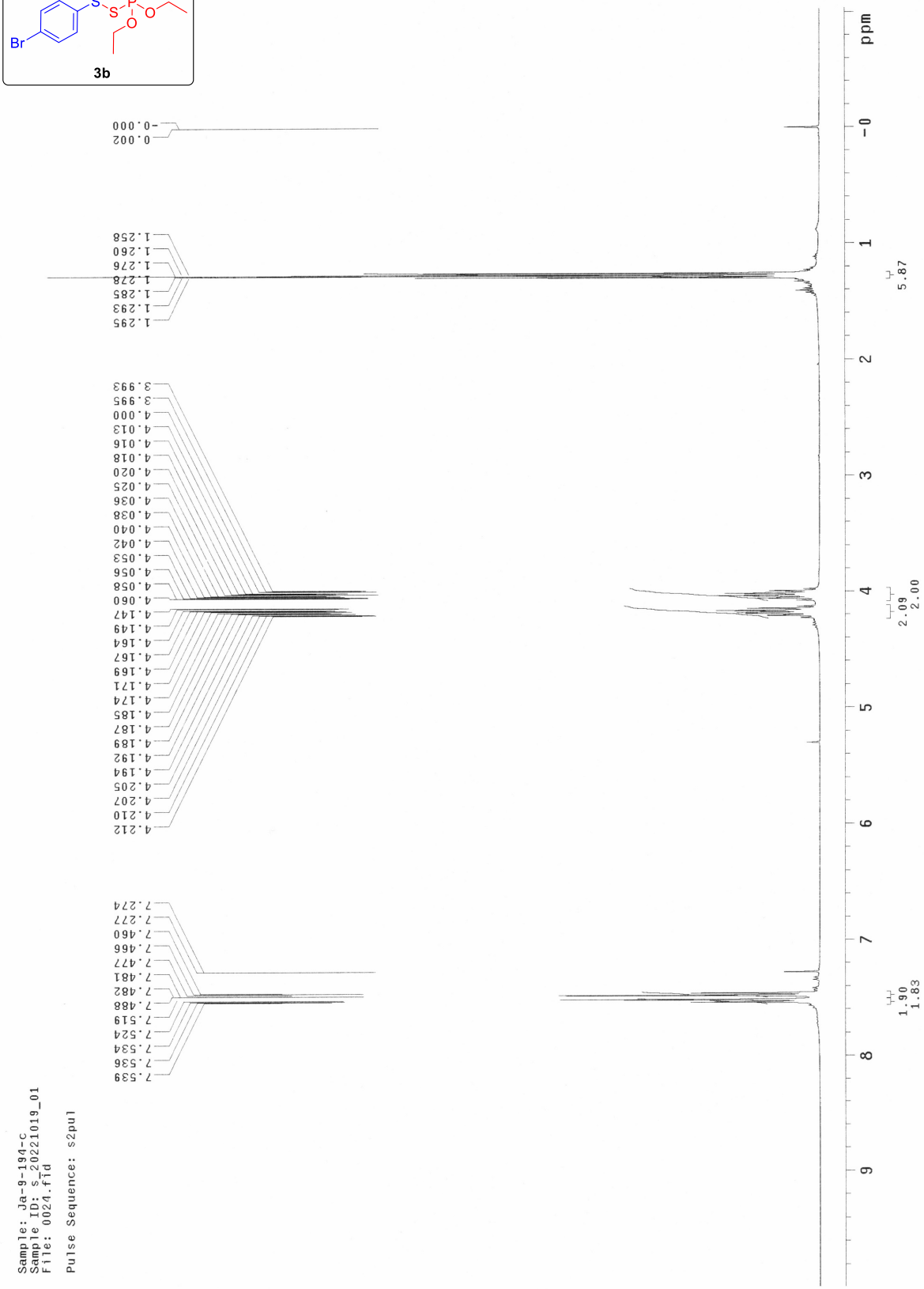
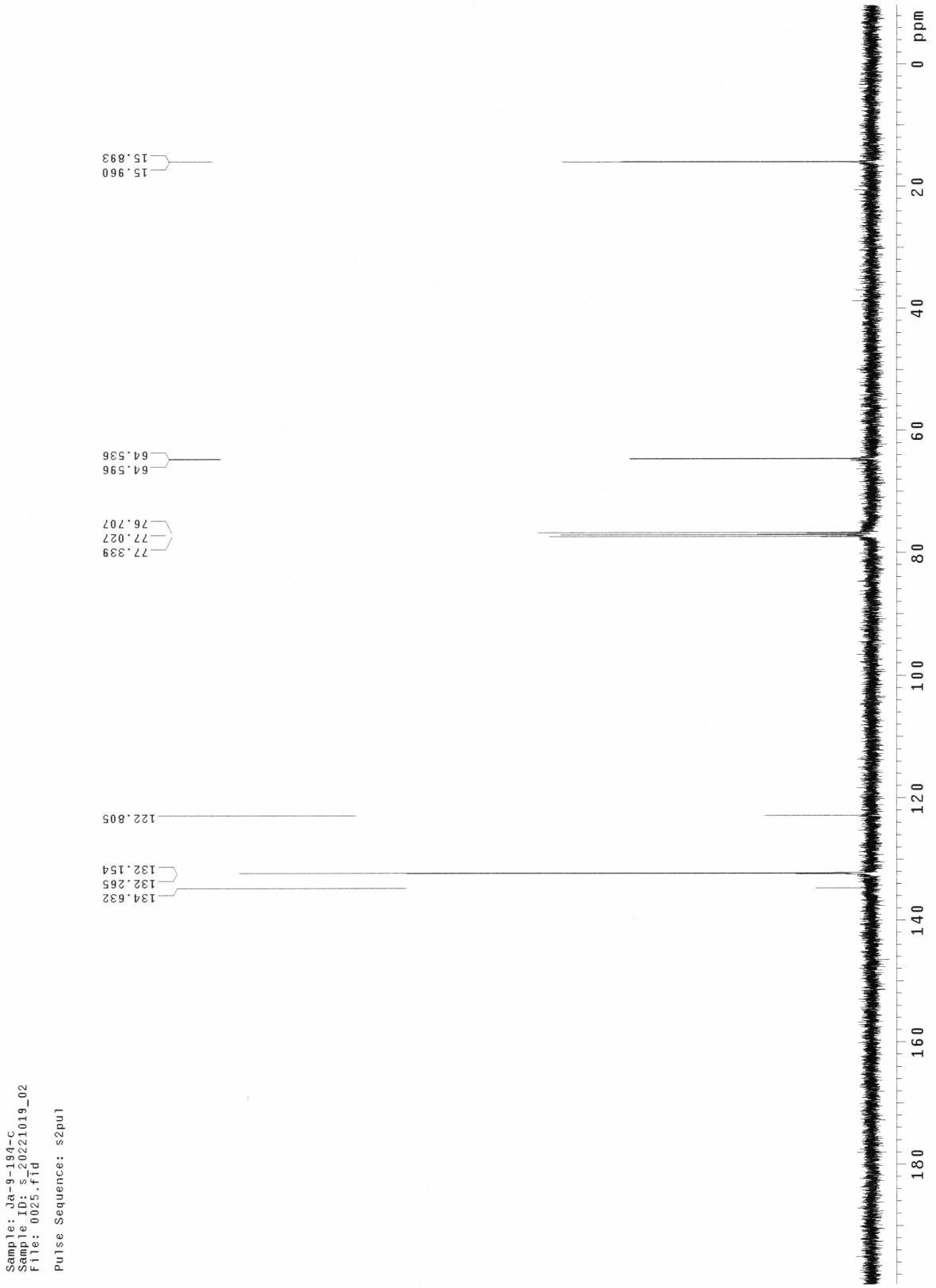
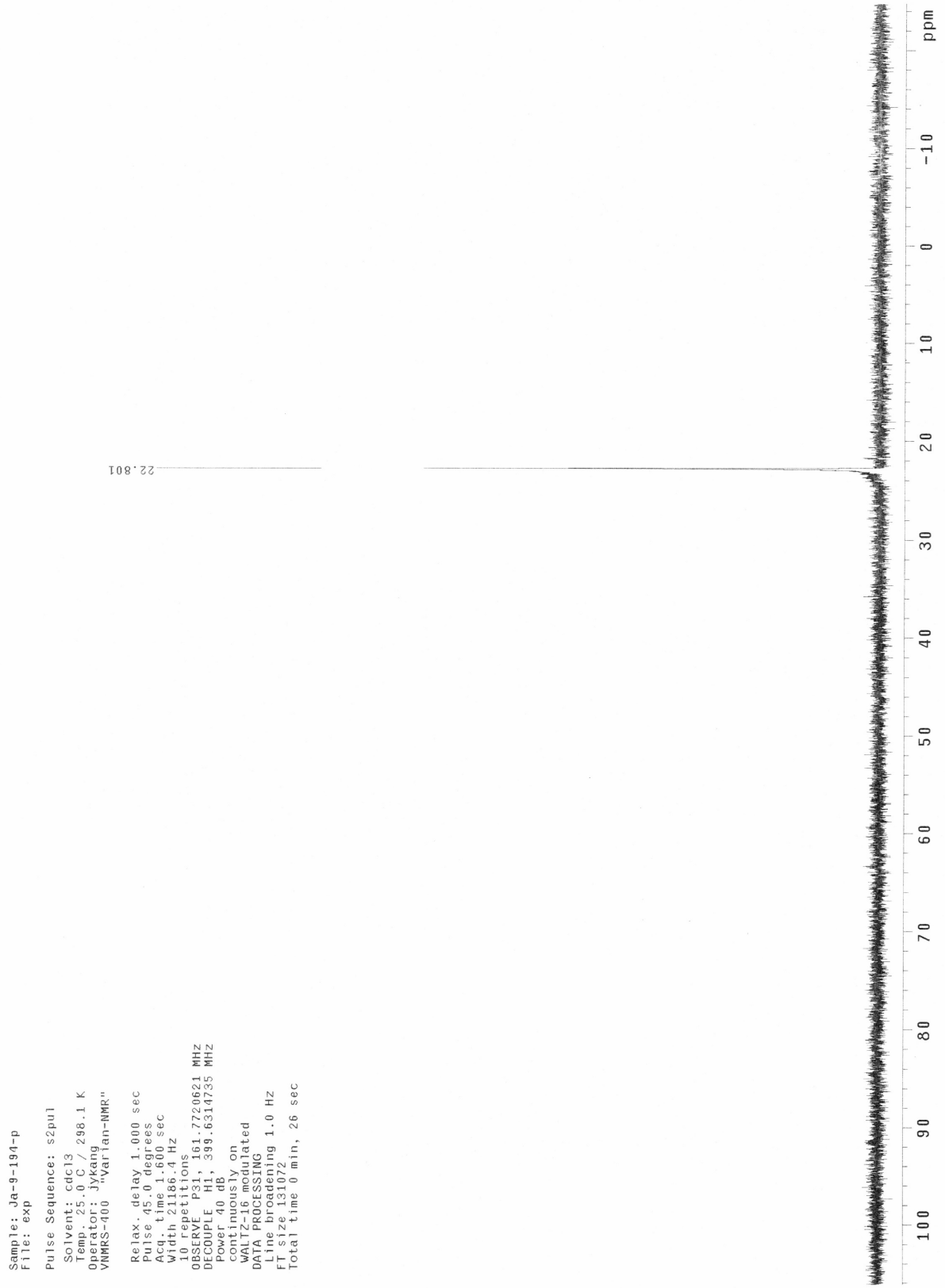


^{13}C NMR (100.5 MHz) in $CDCl_3$



^{31}P NMR (162 MHz) in $CDCl_3$



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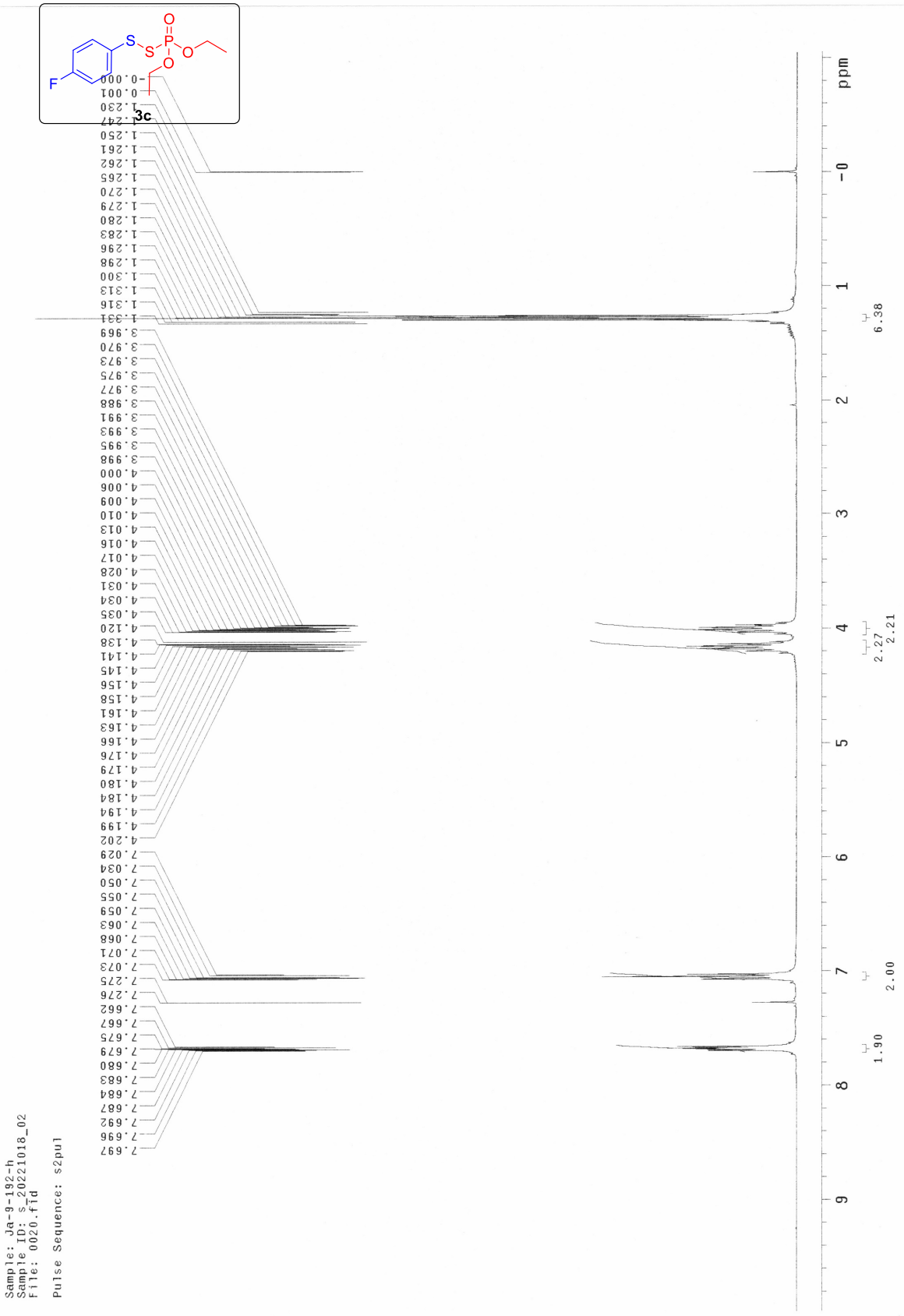

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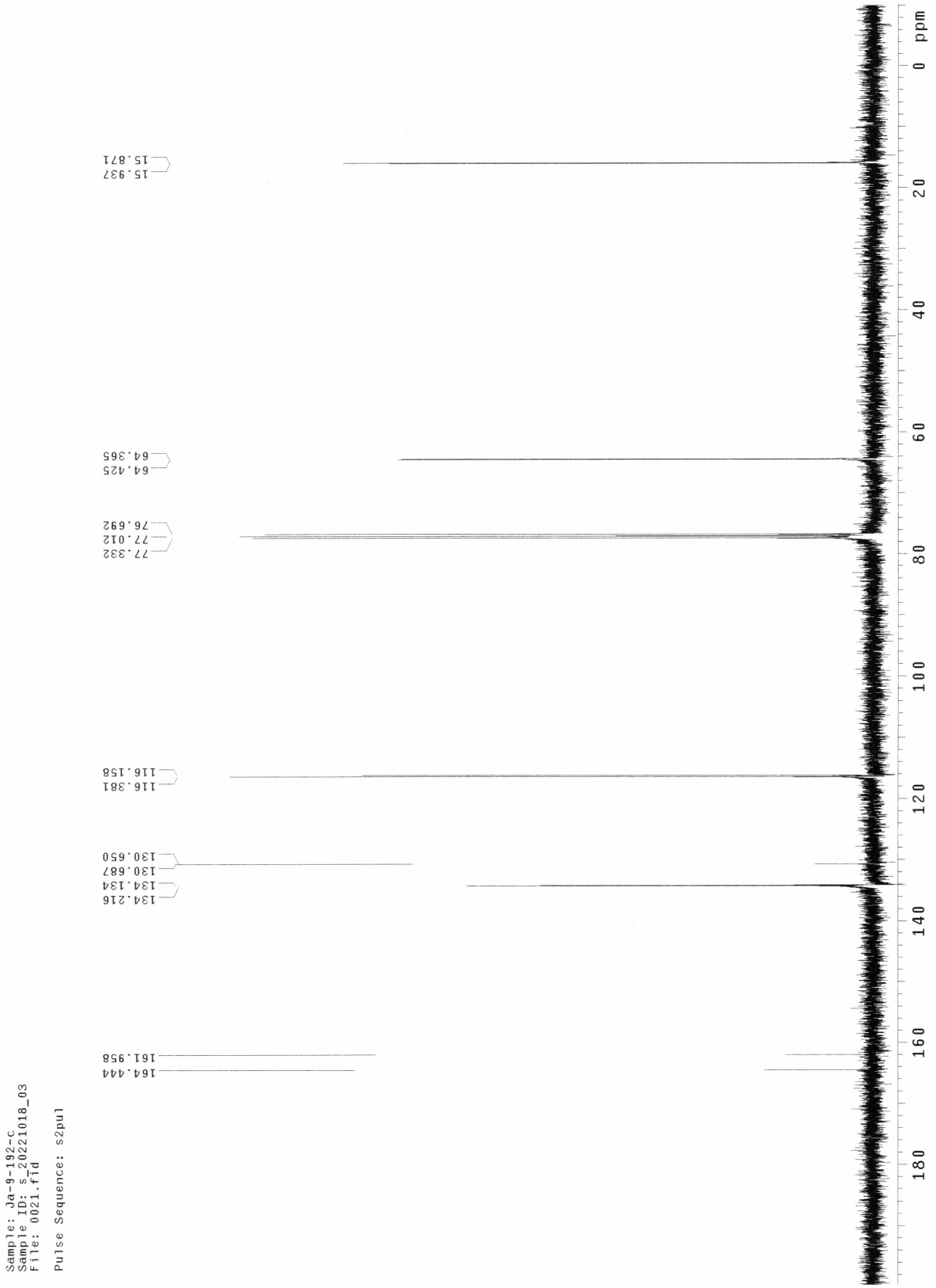

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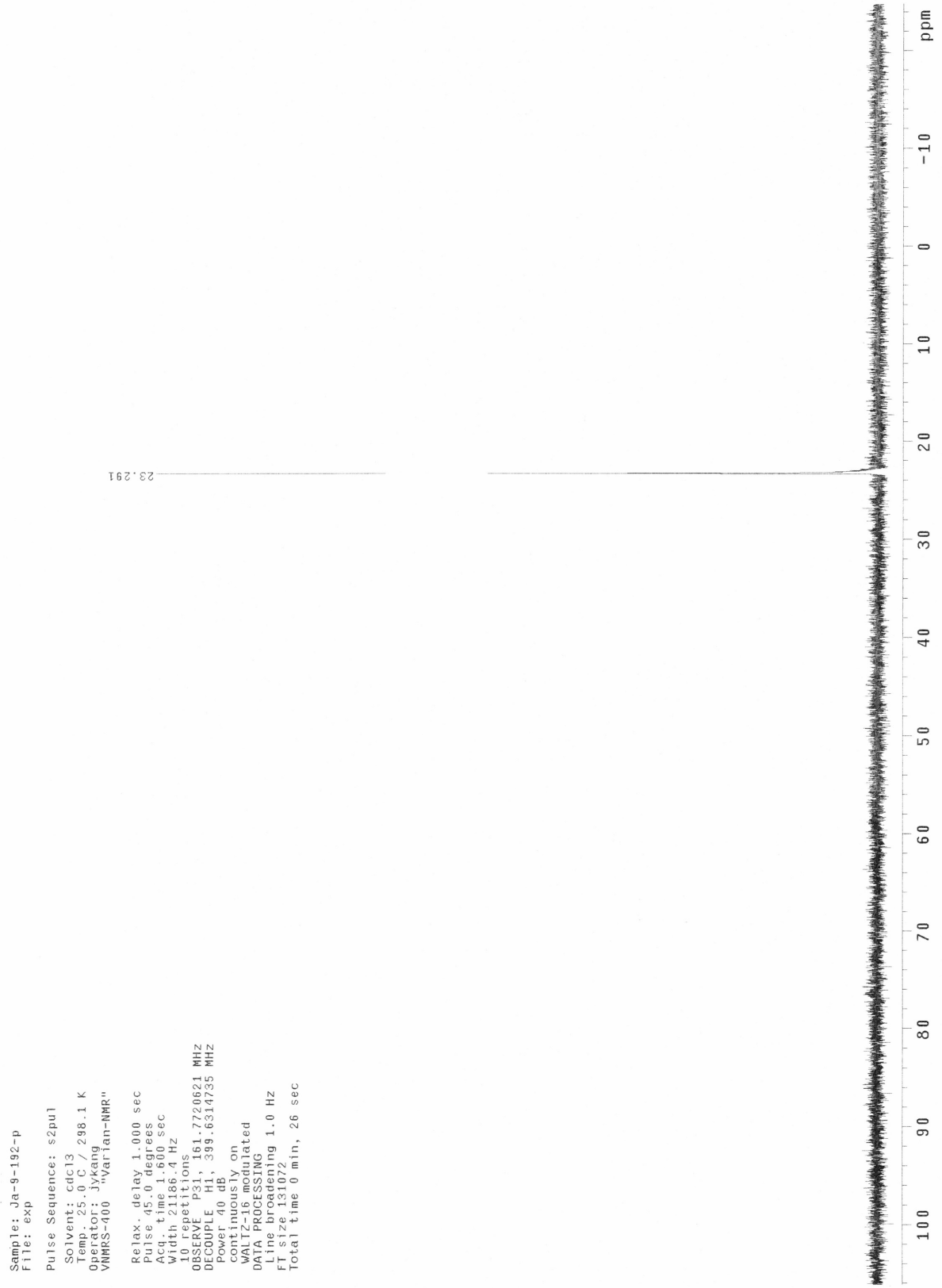

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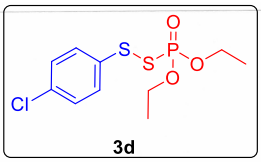

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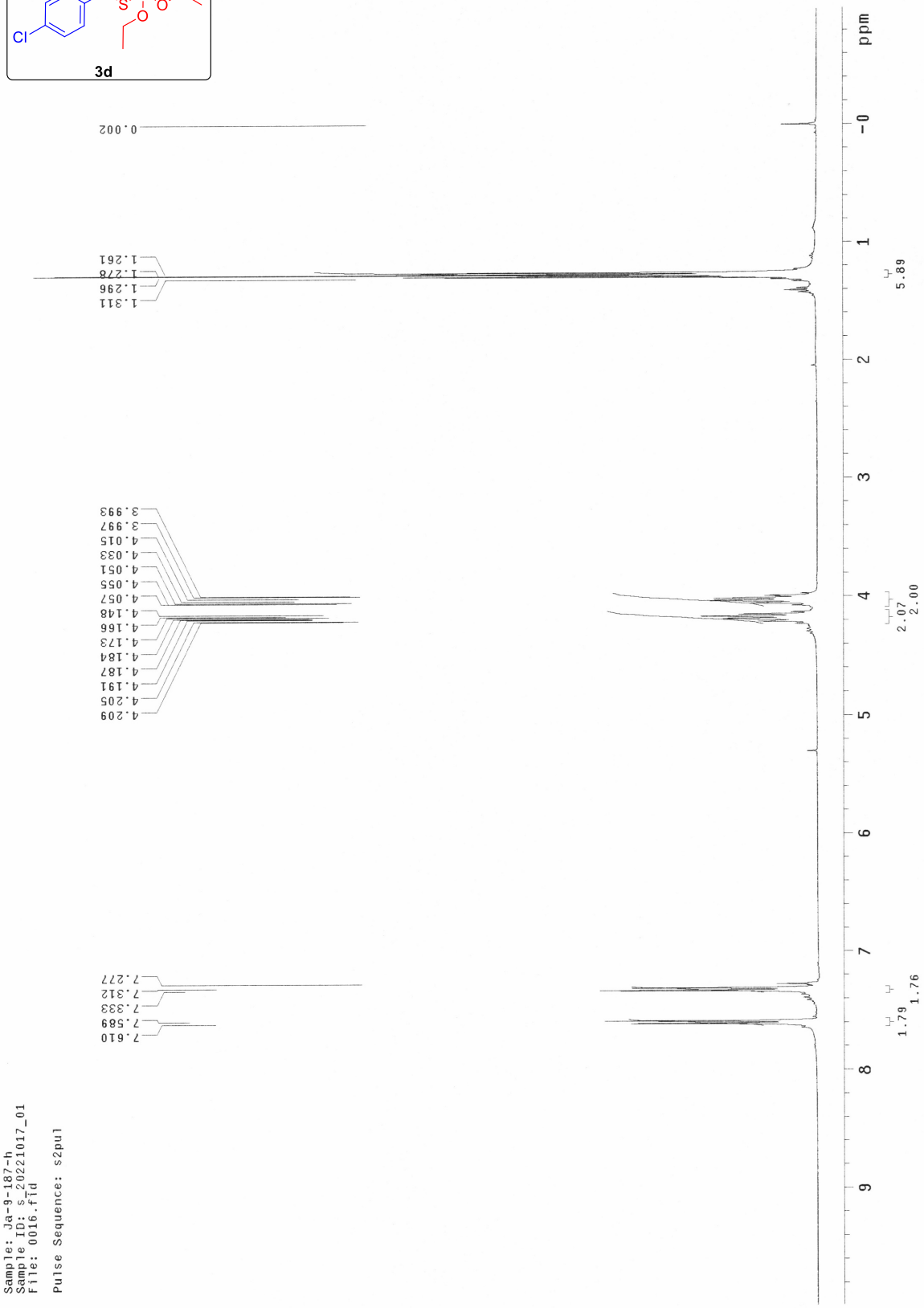
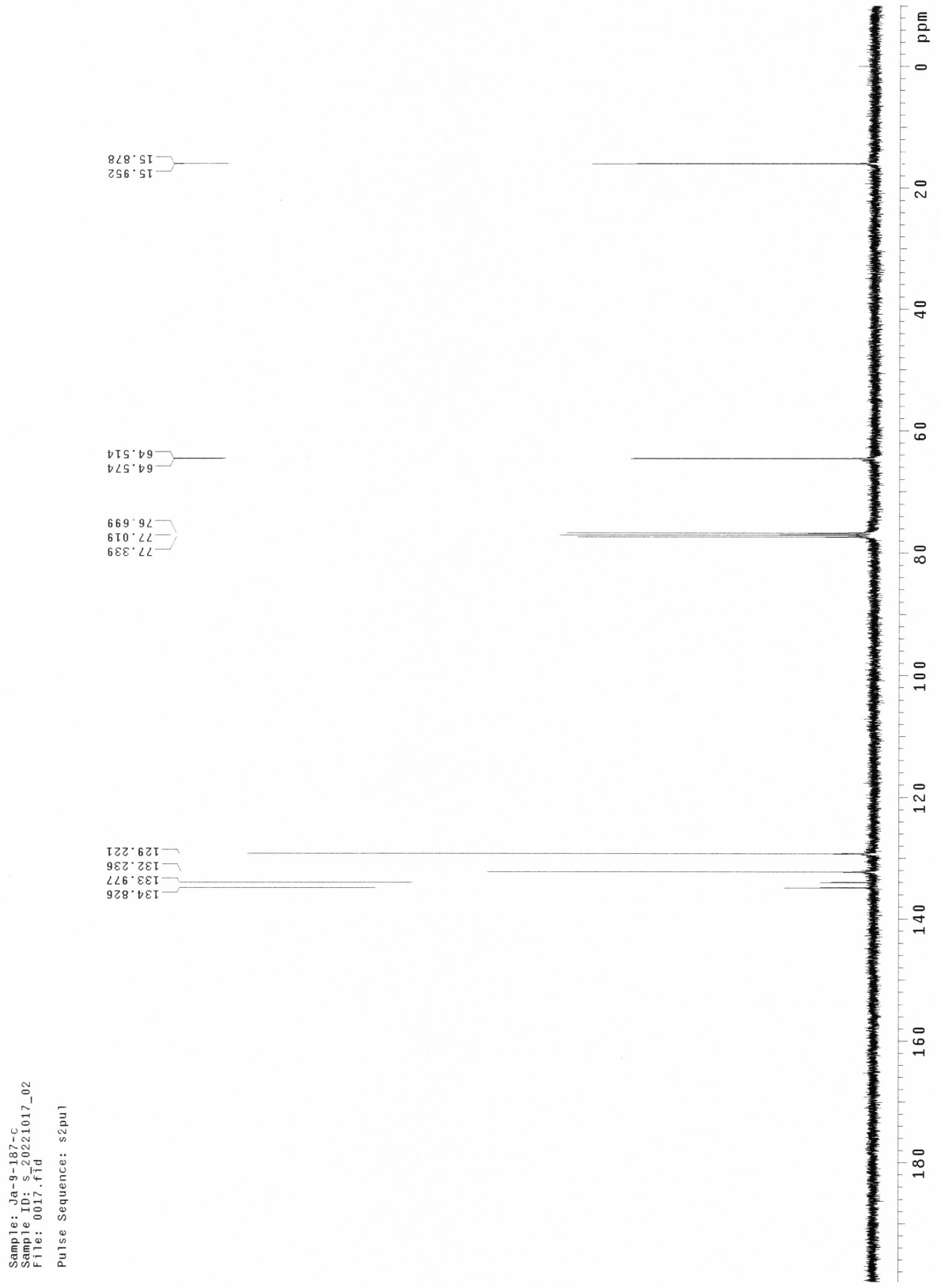


^{13}C NMR (100.5 MHz) in $CDCl_3$



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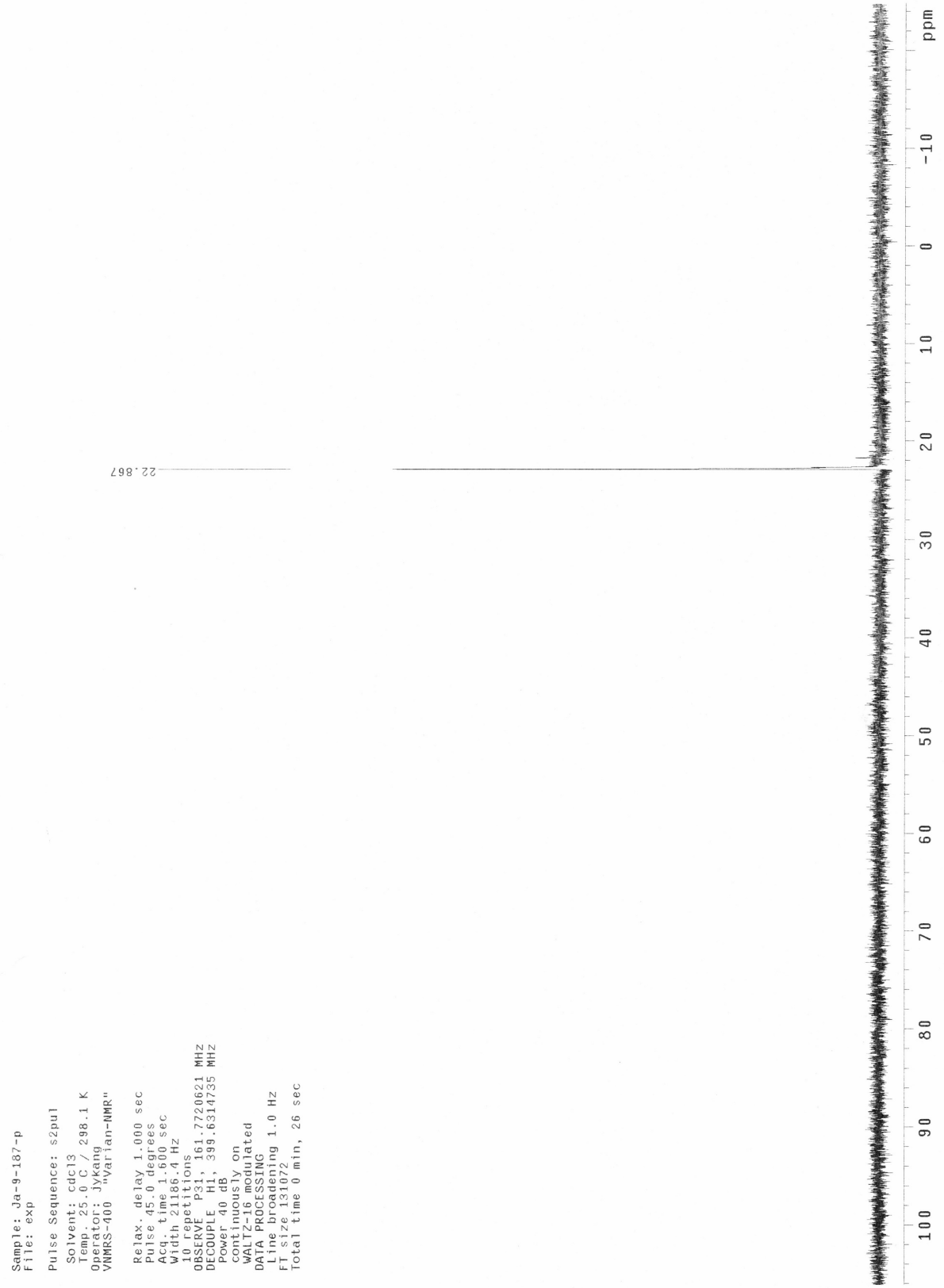

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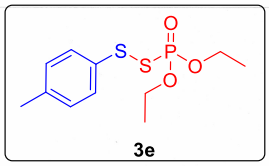

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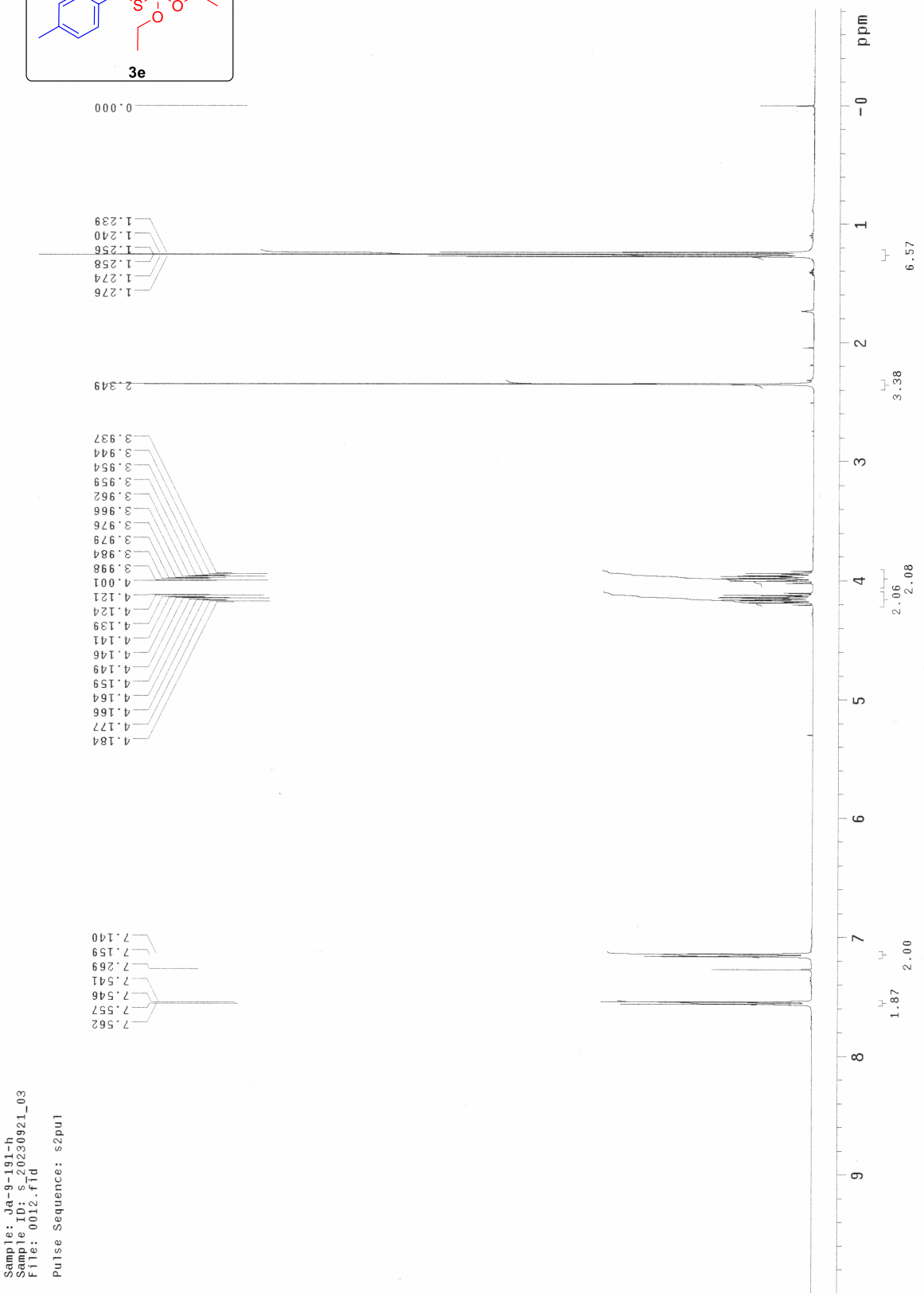

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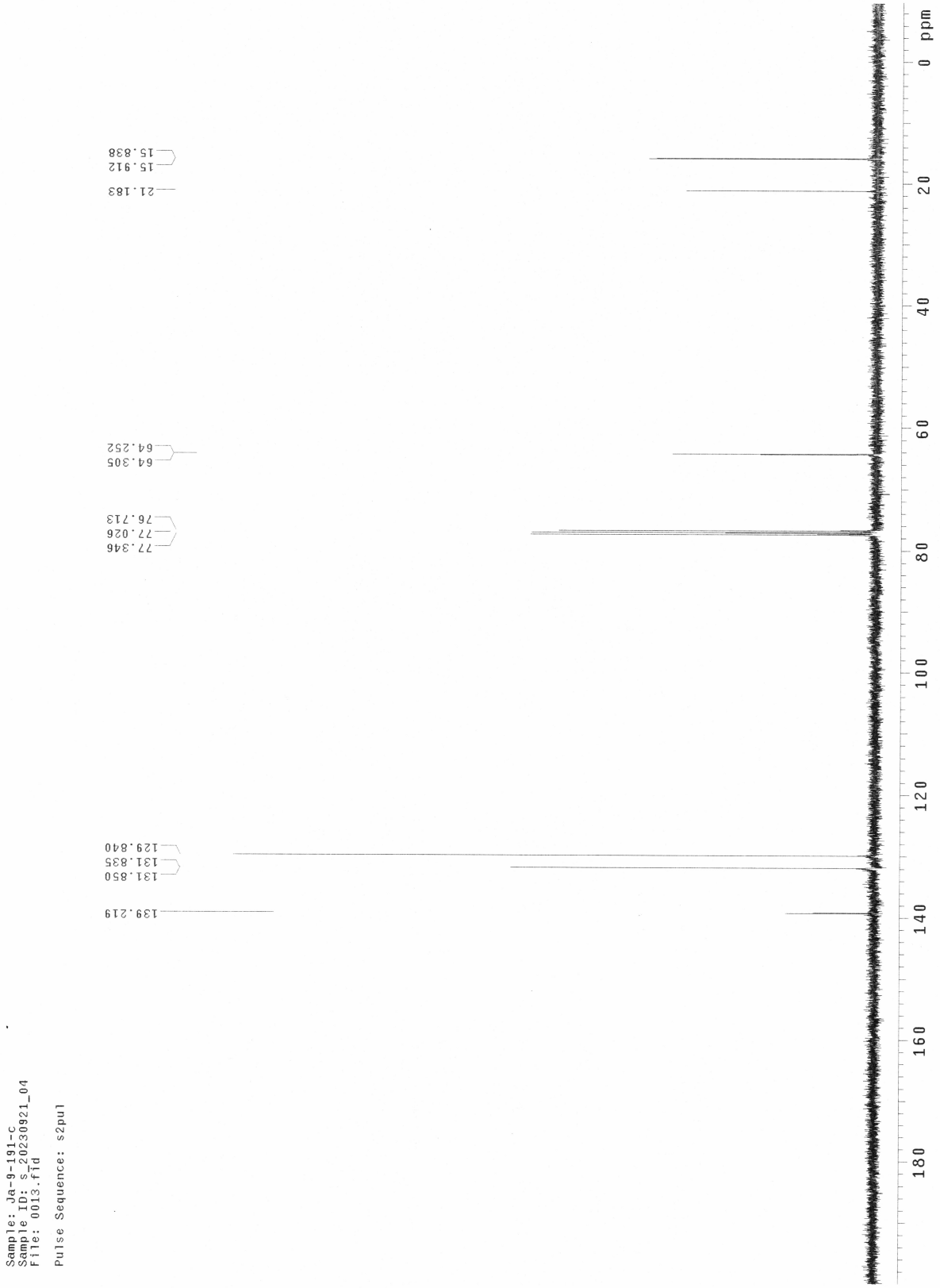

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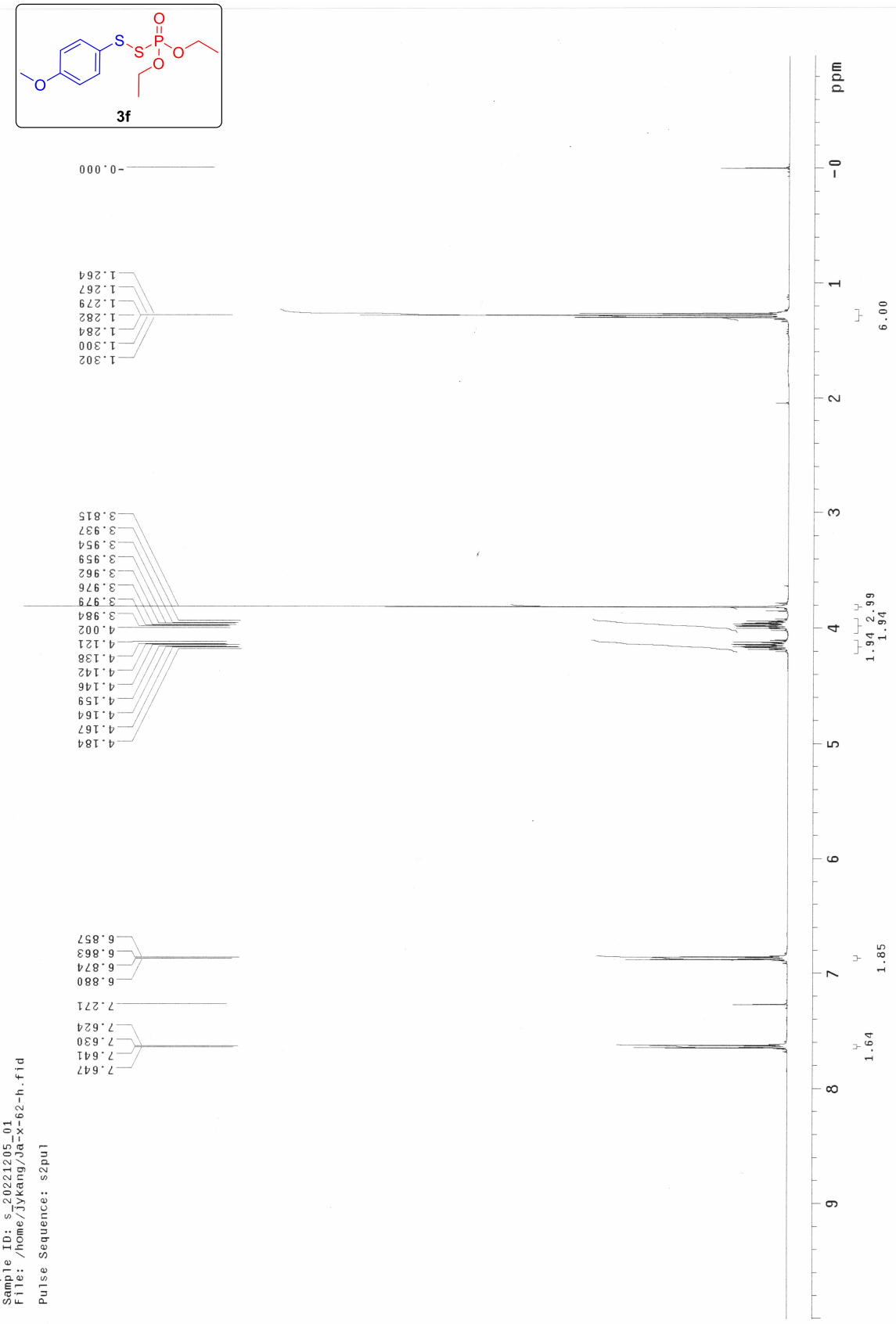

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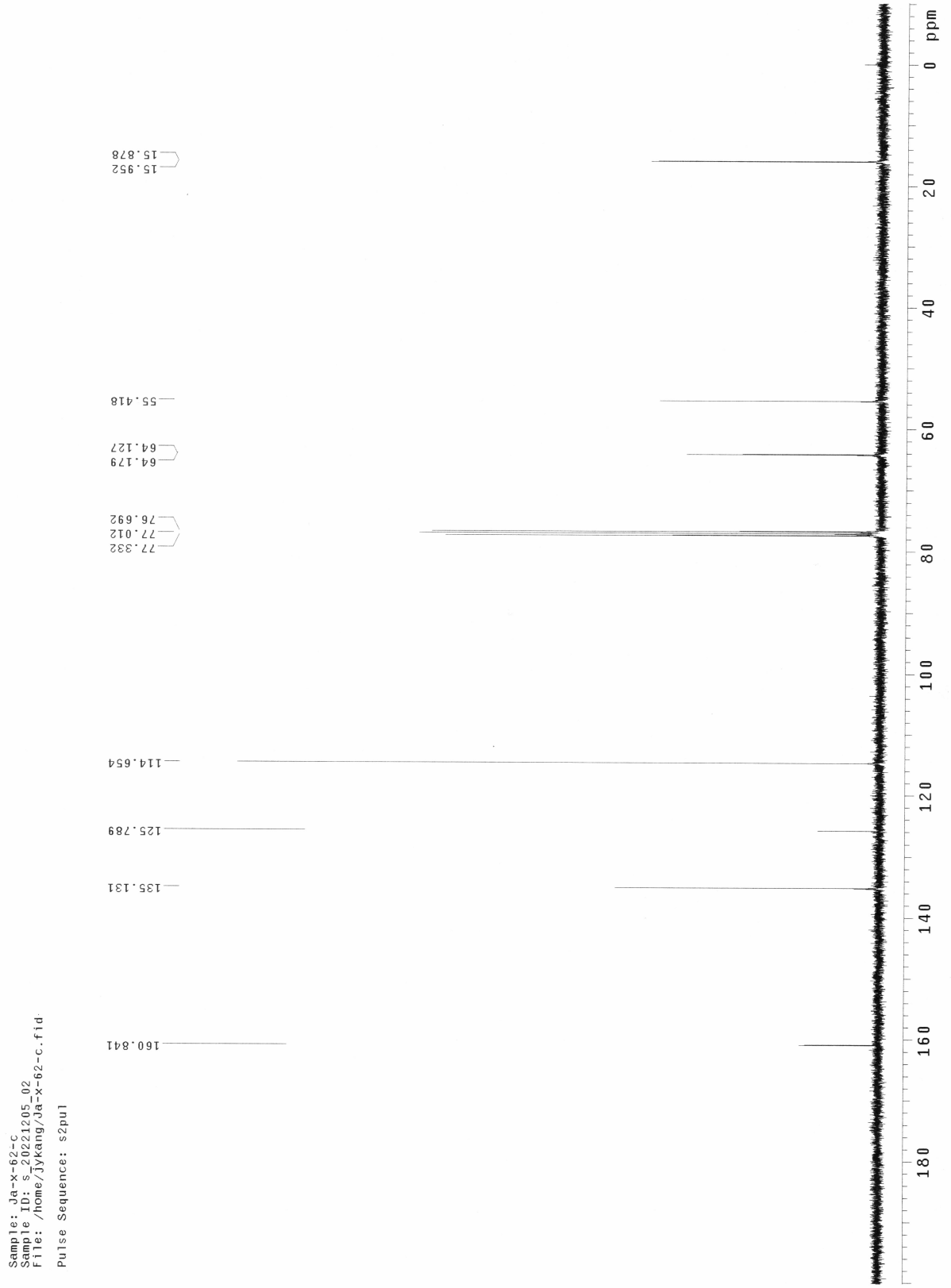

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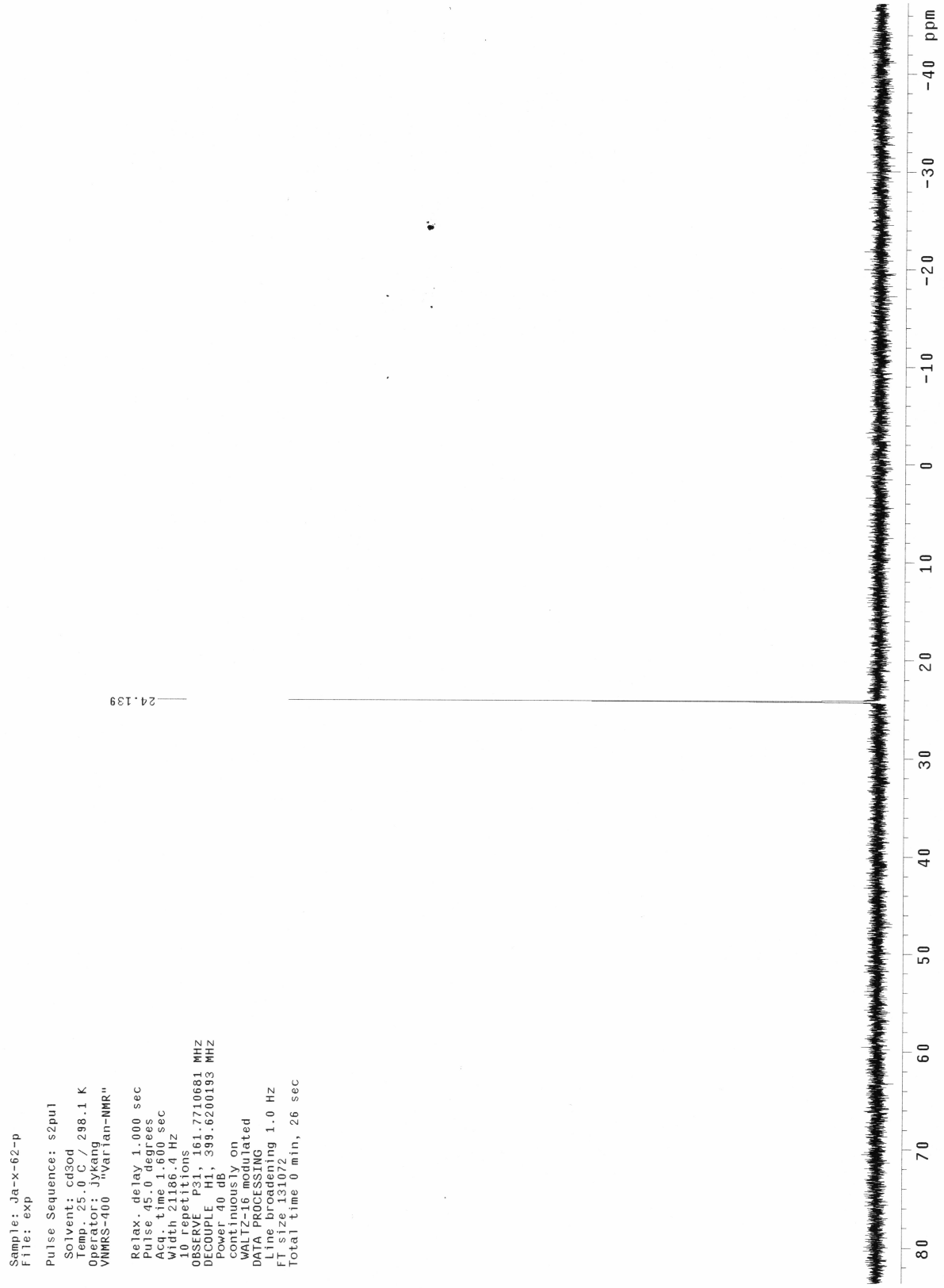

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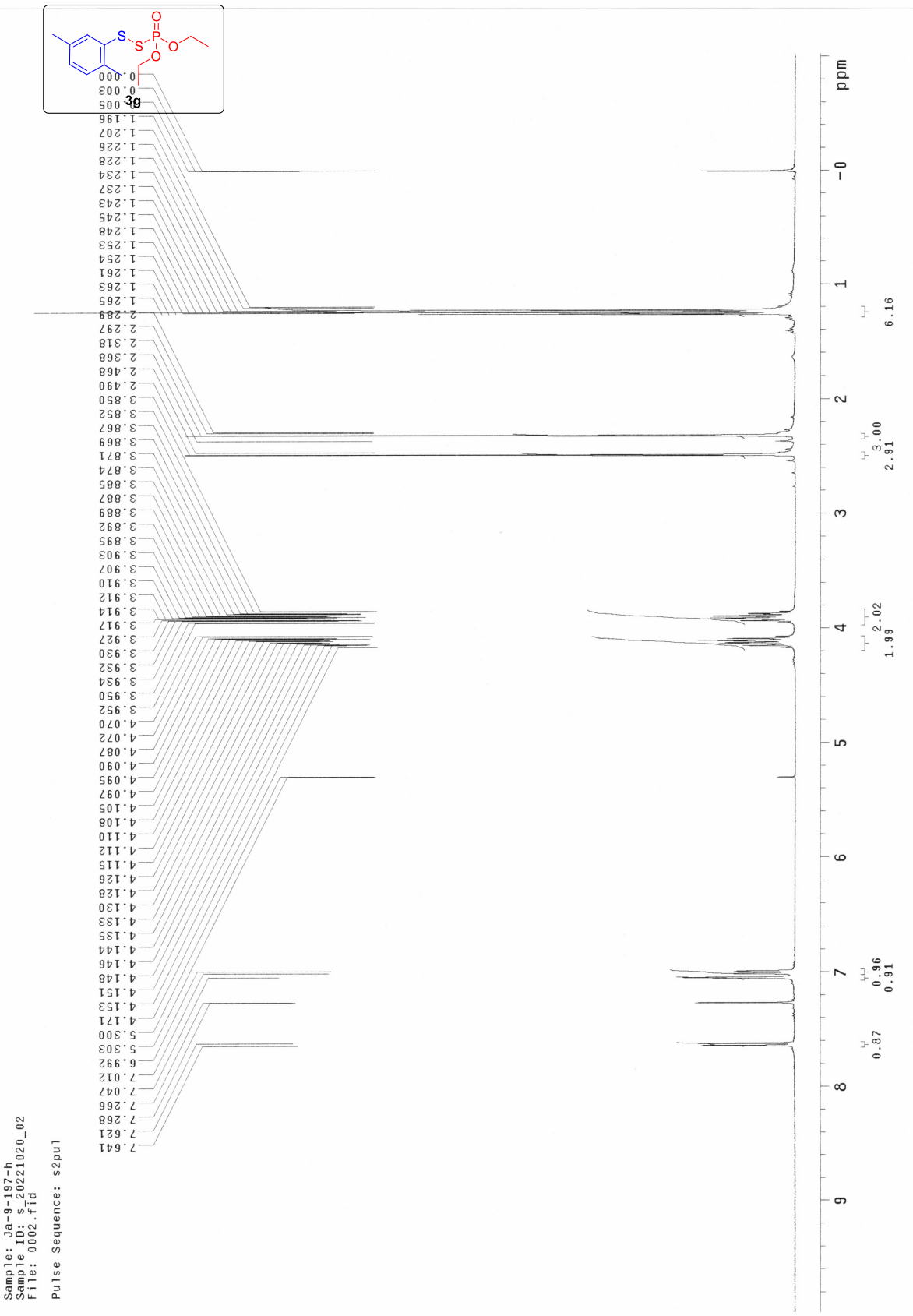

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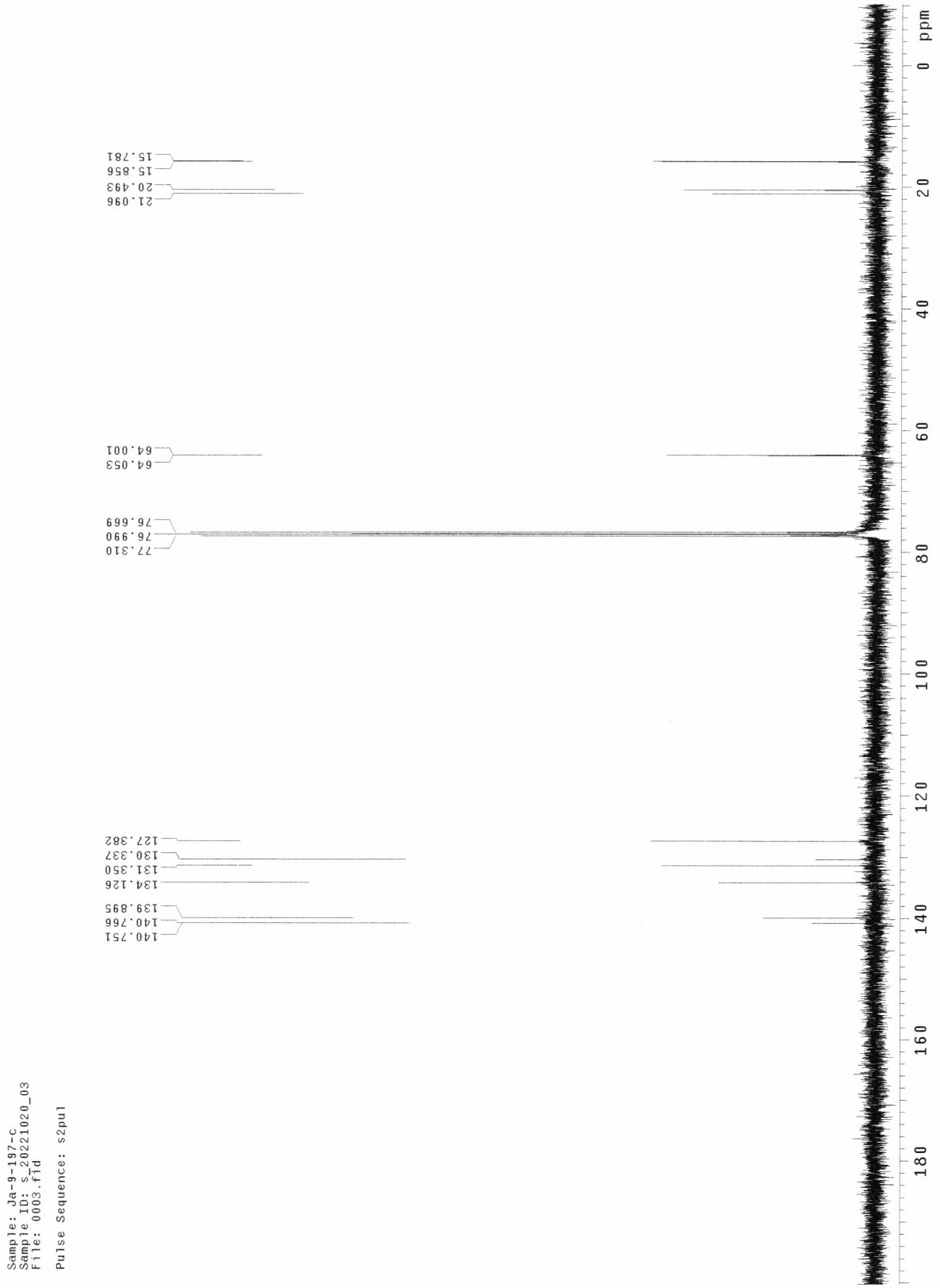

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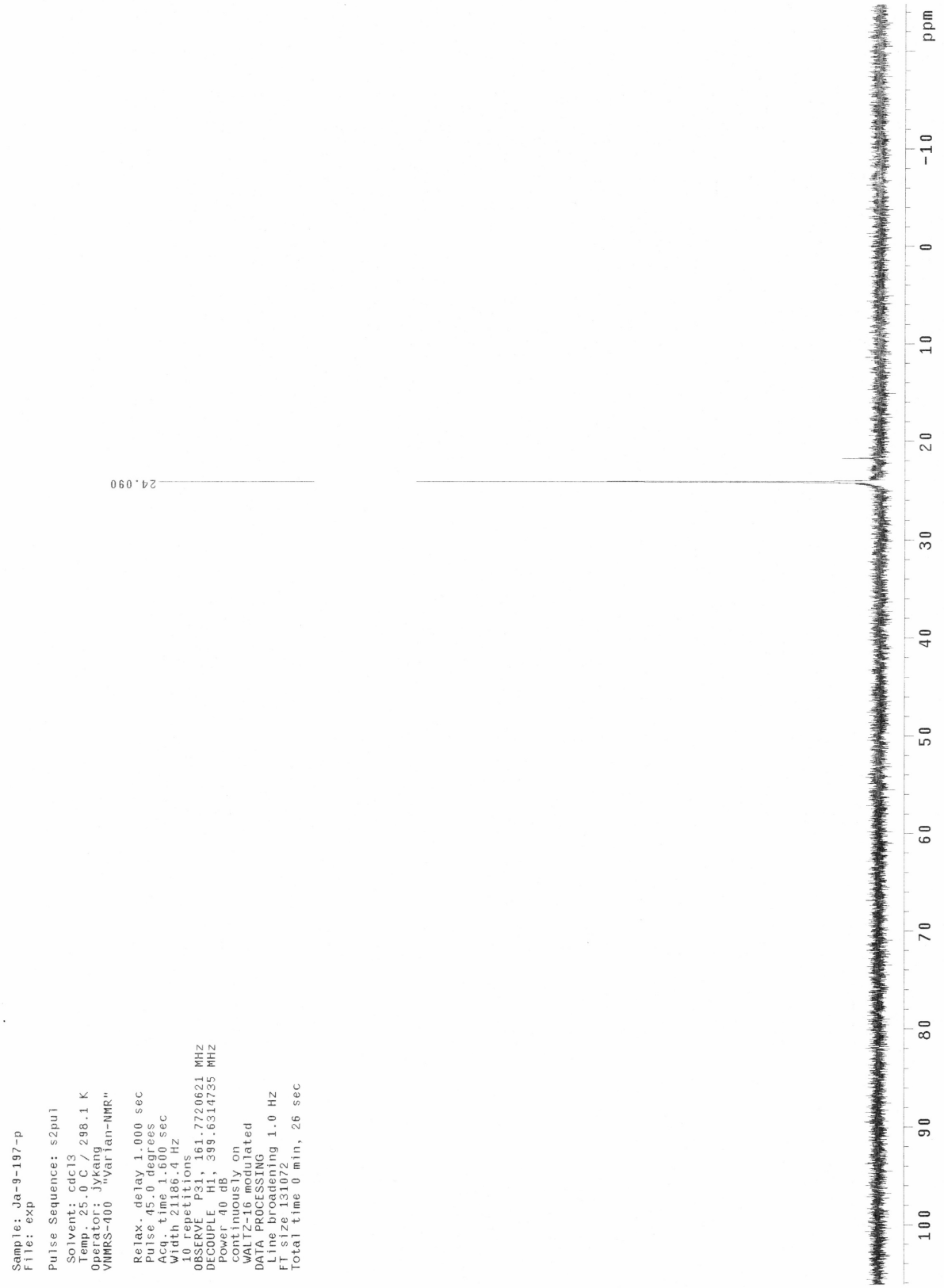

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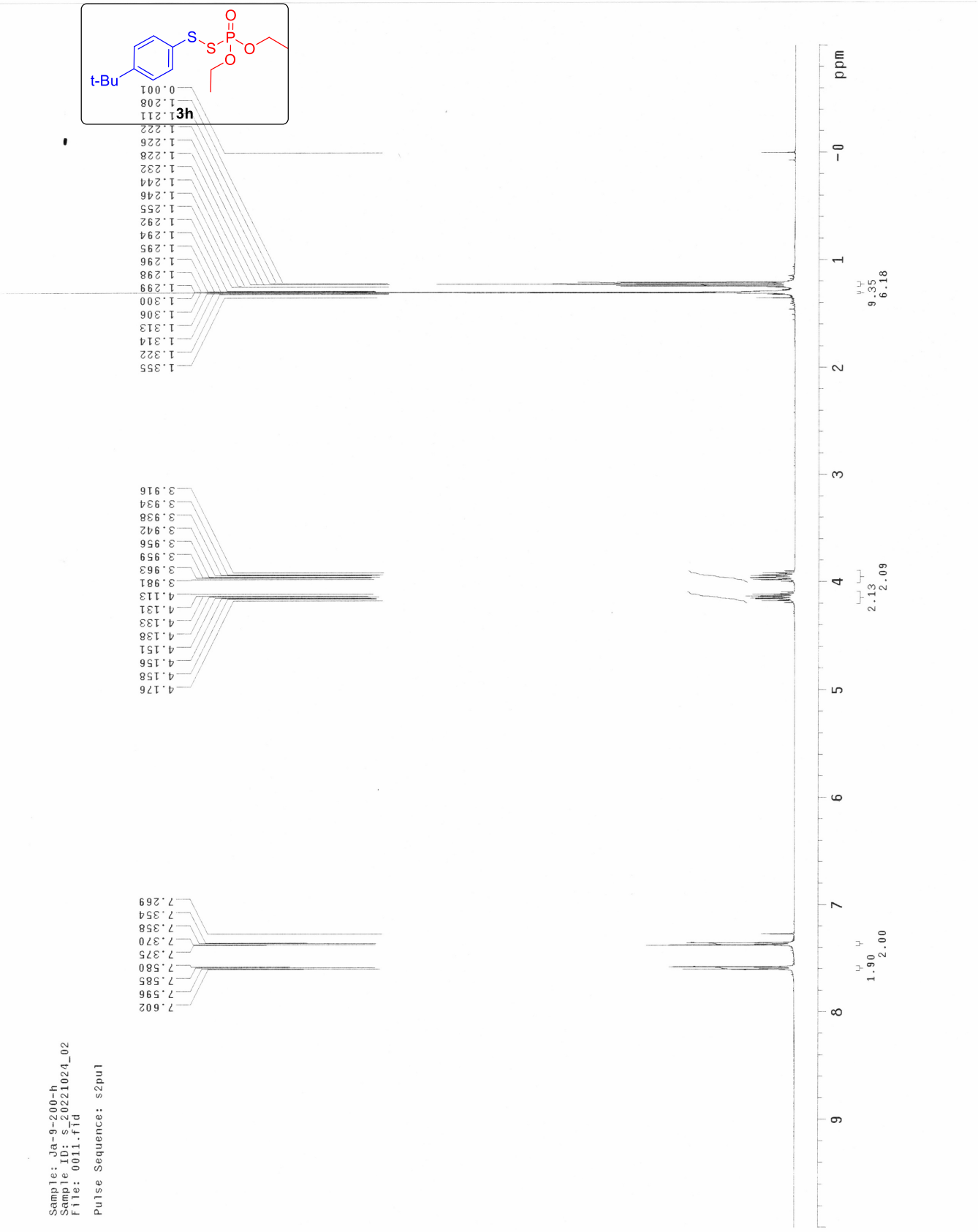

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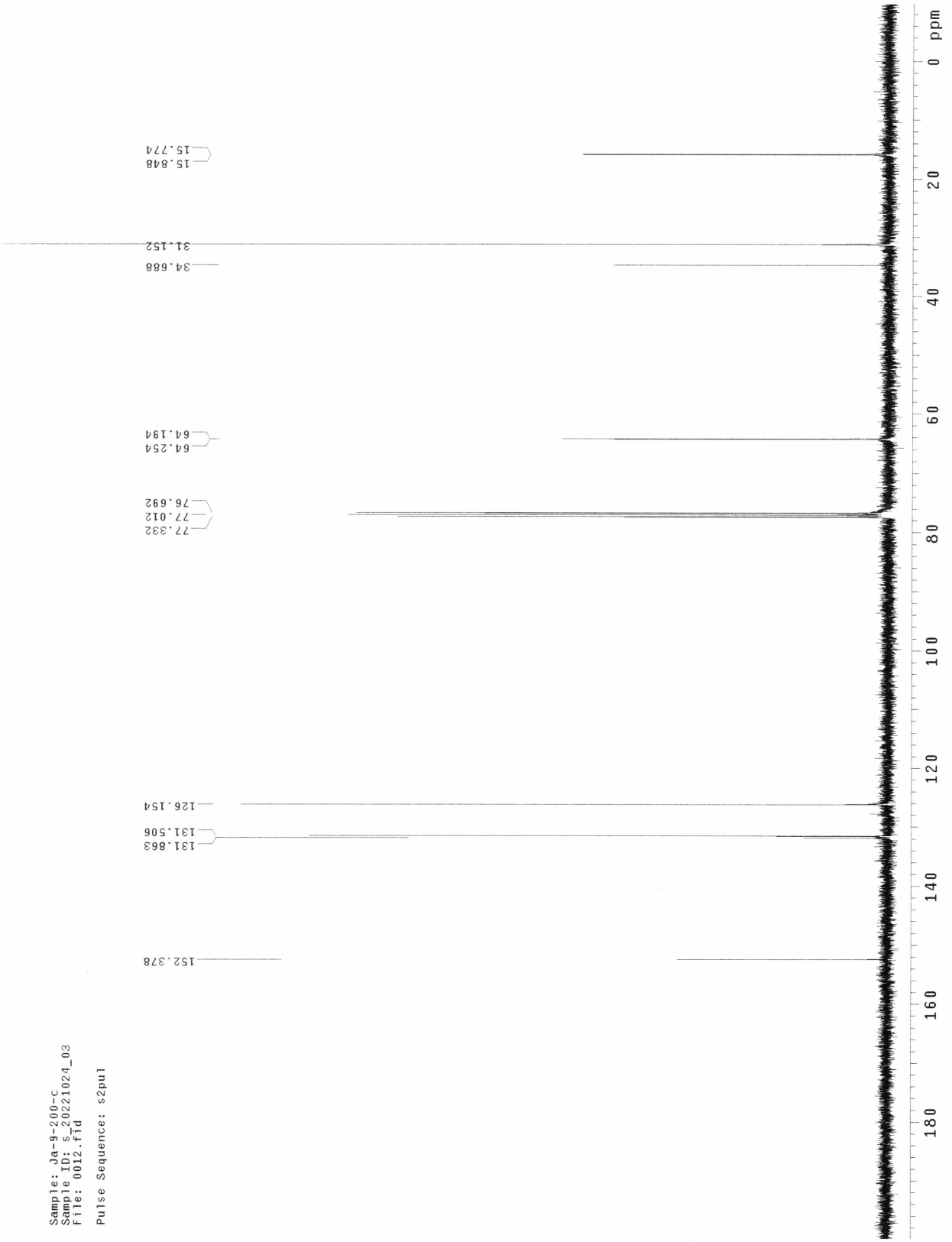

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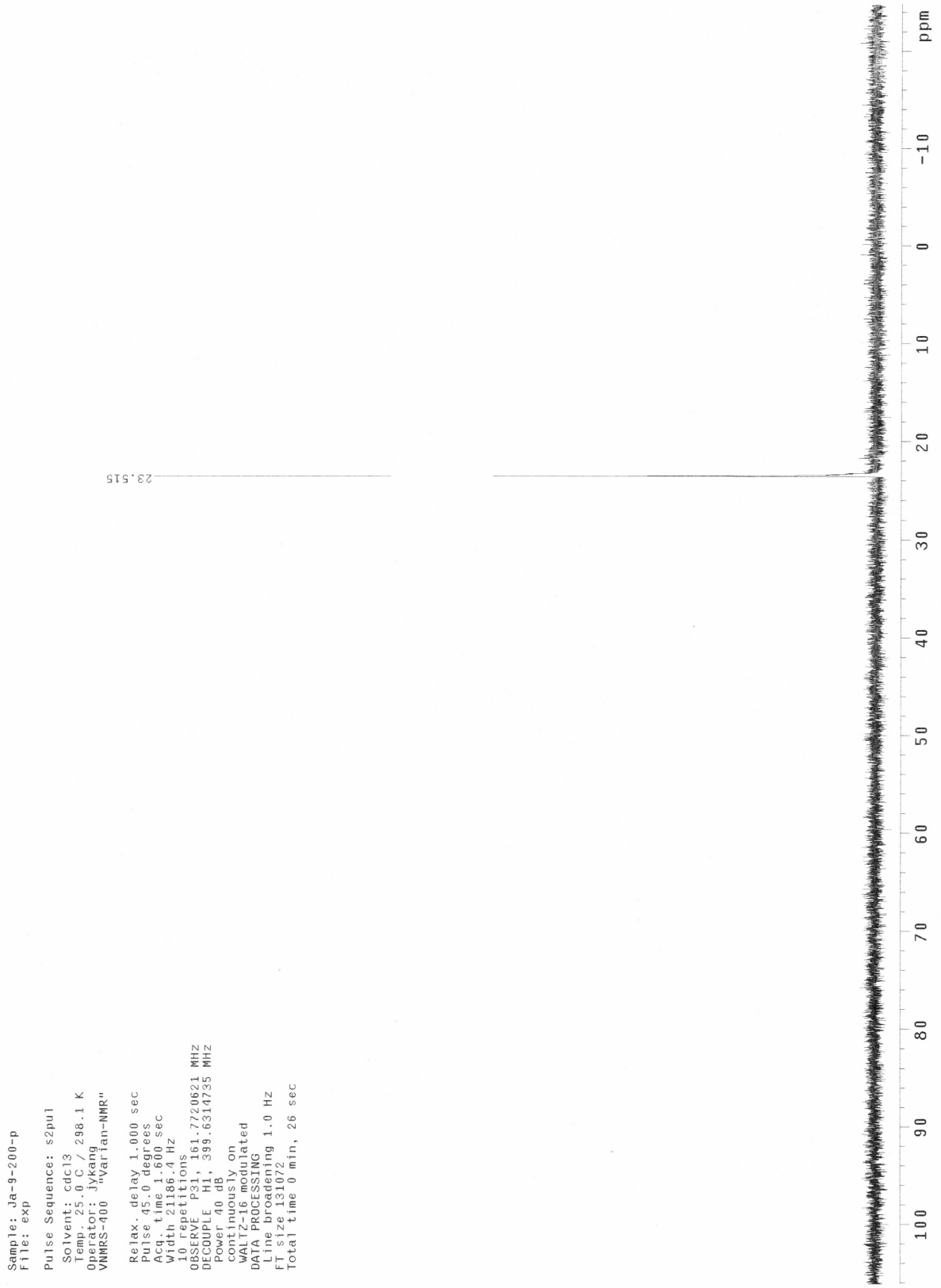

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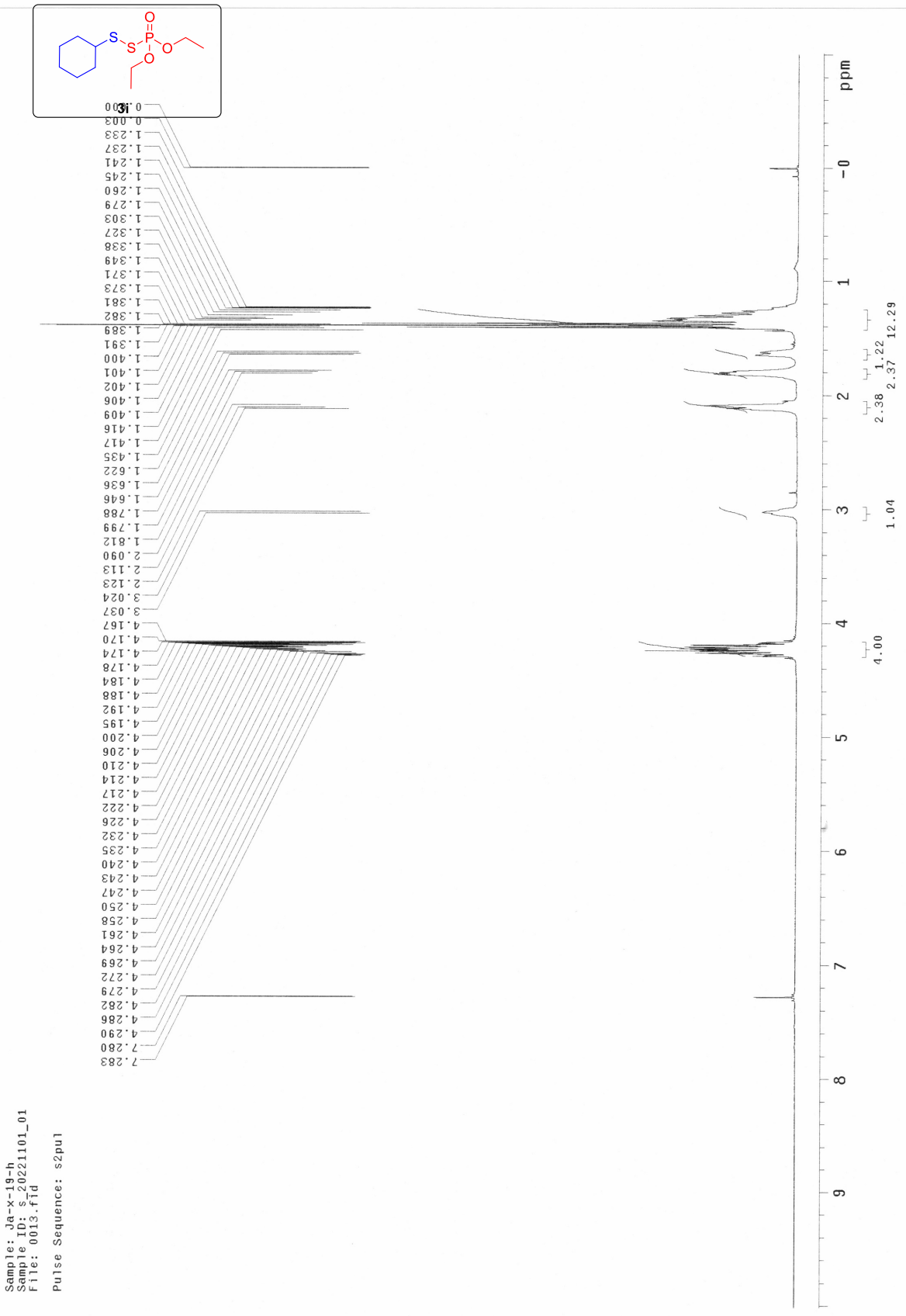

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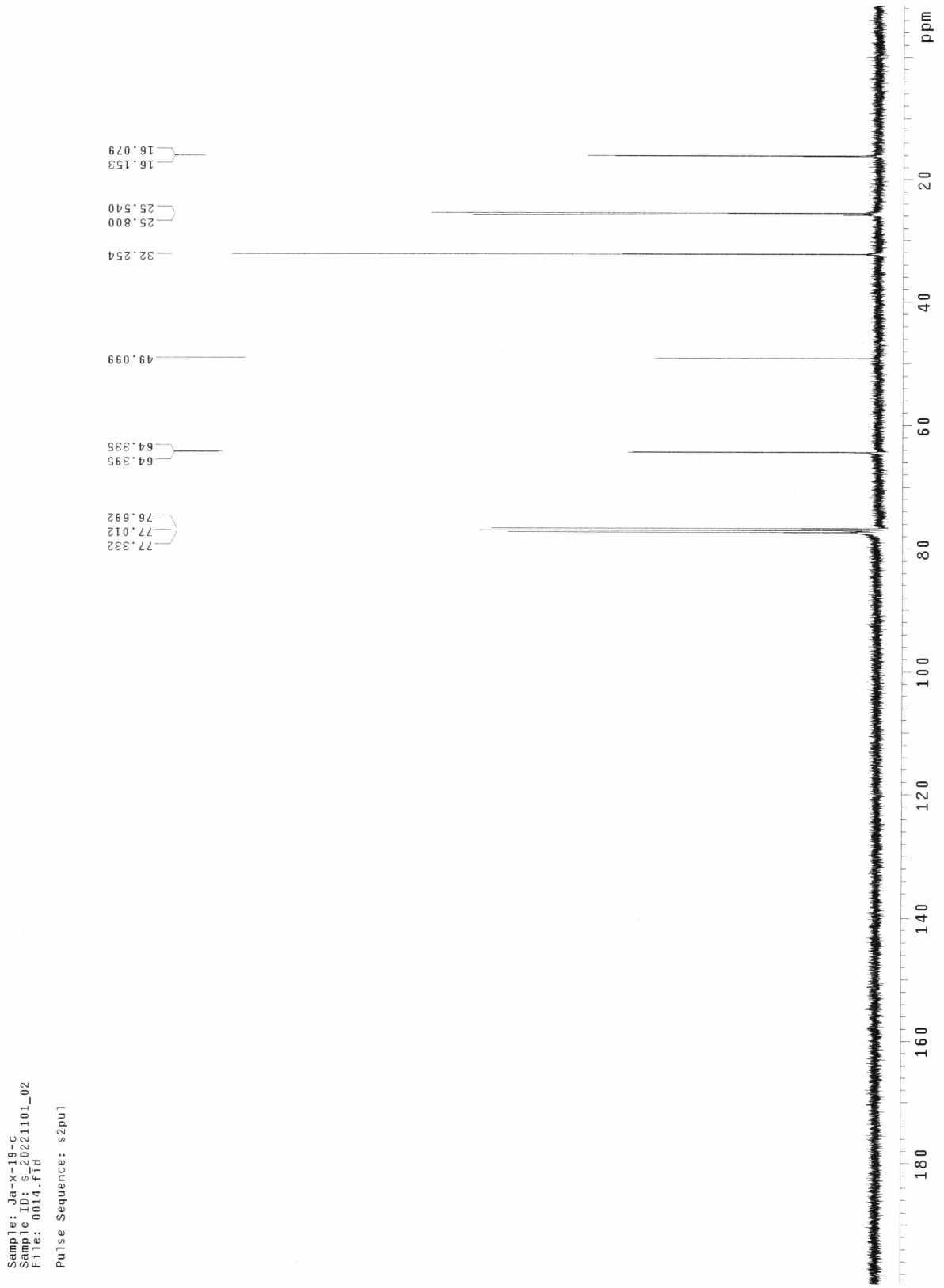

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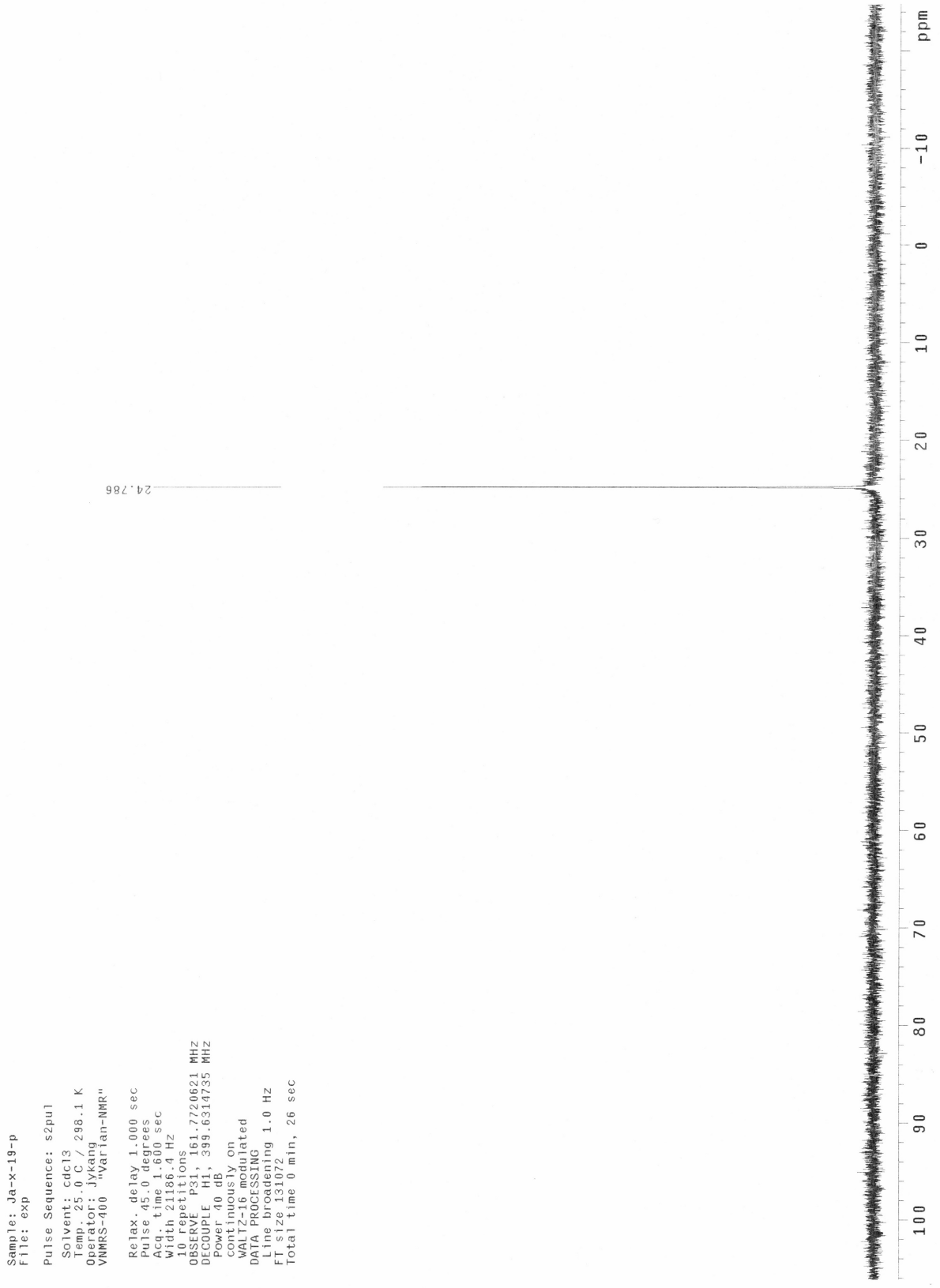

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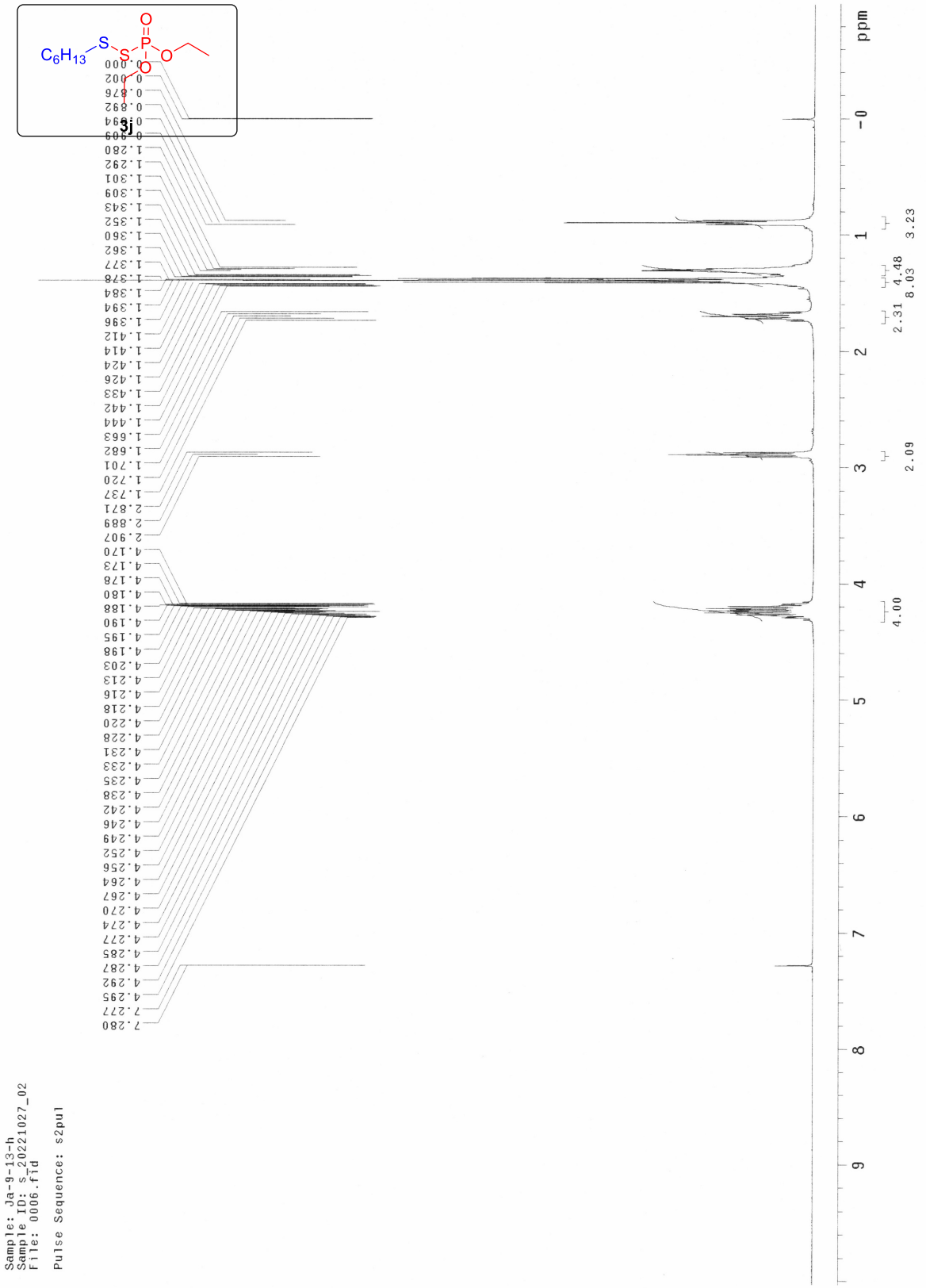

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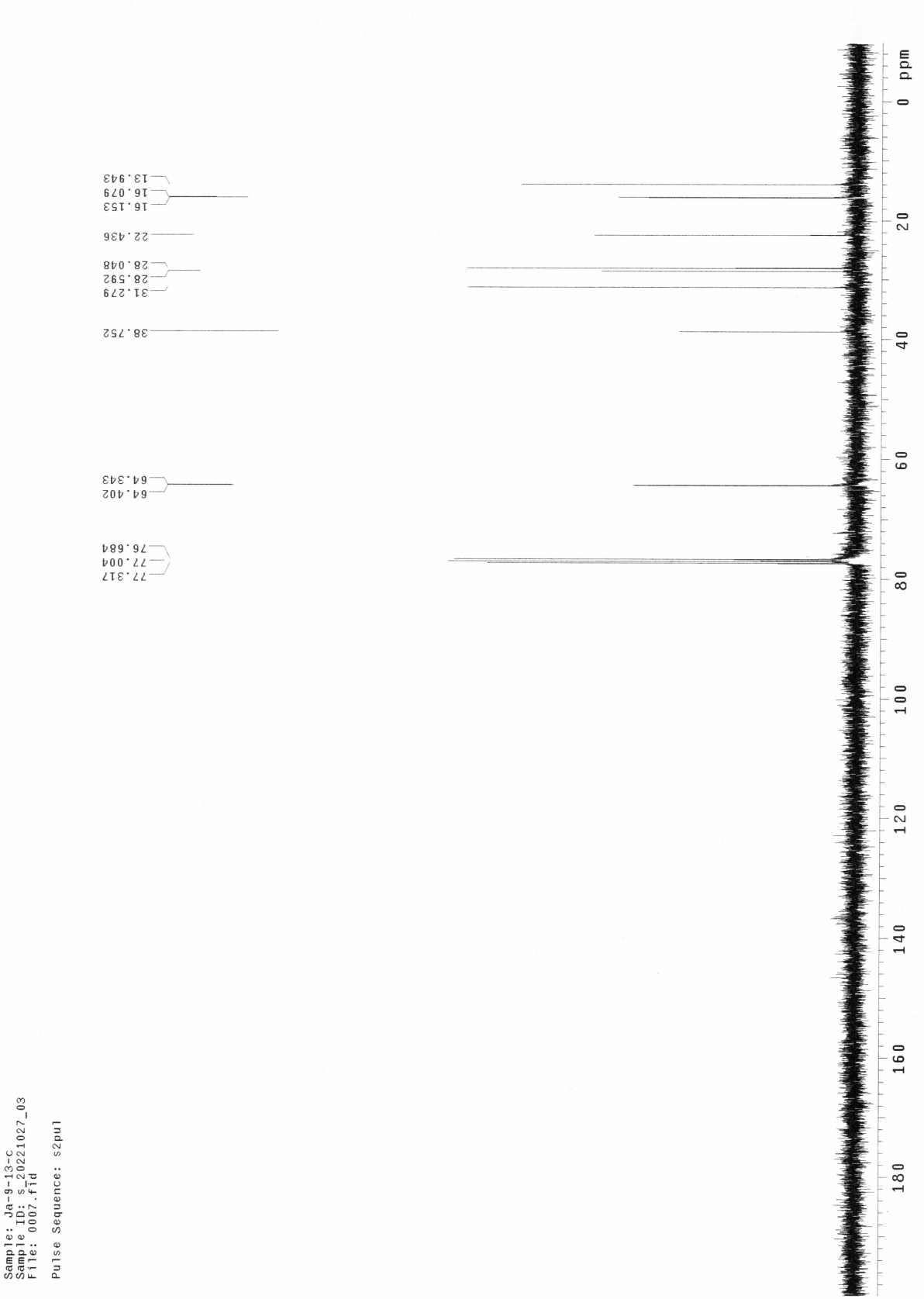

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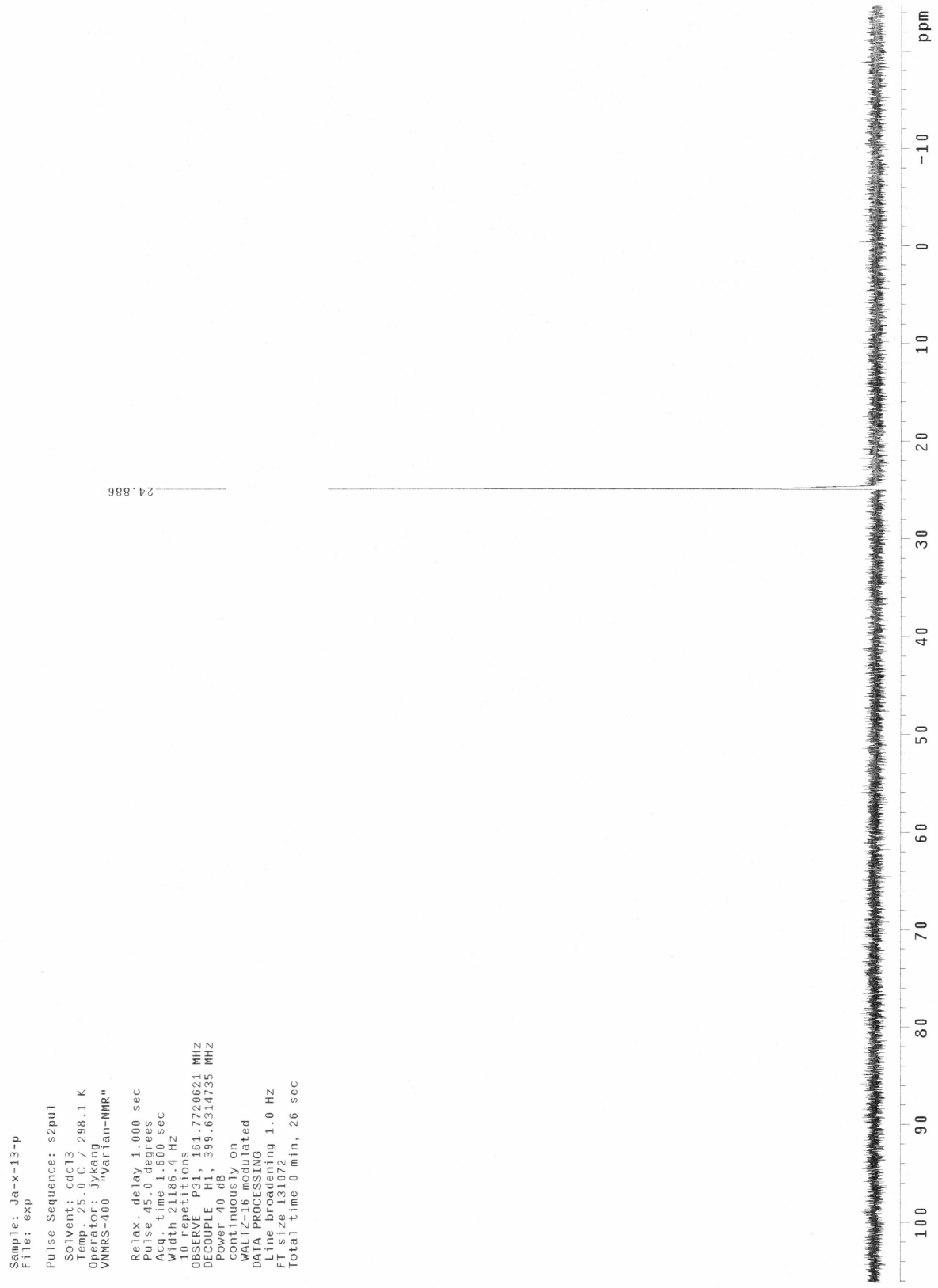

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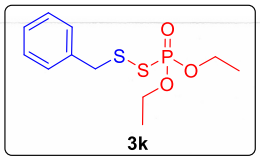

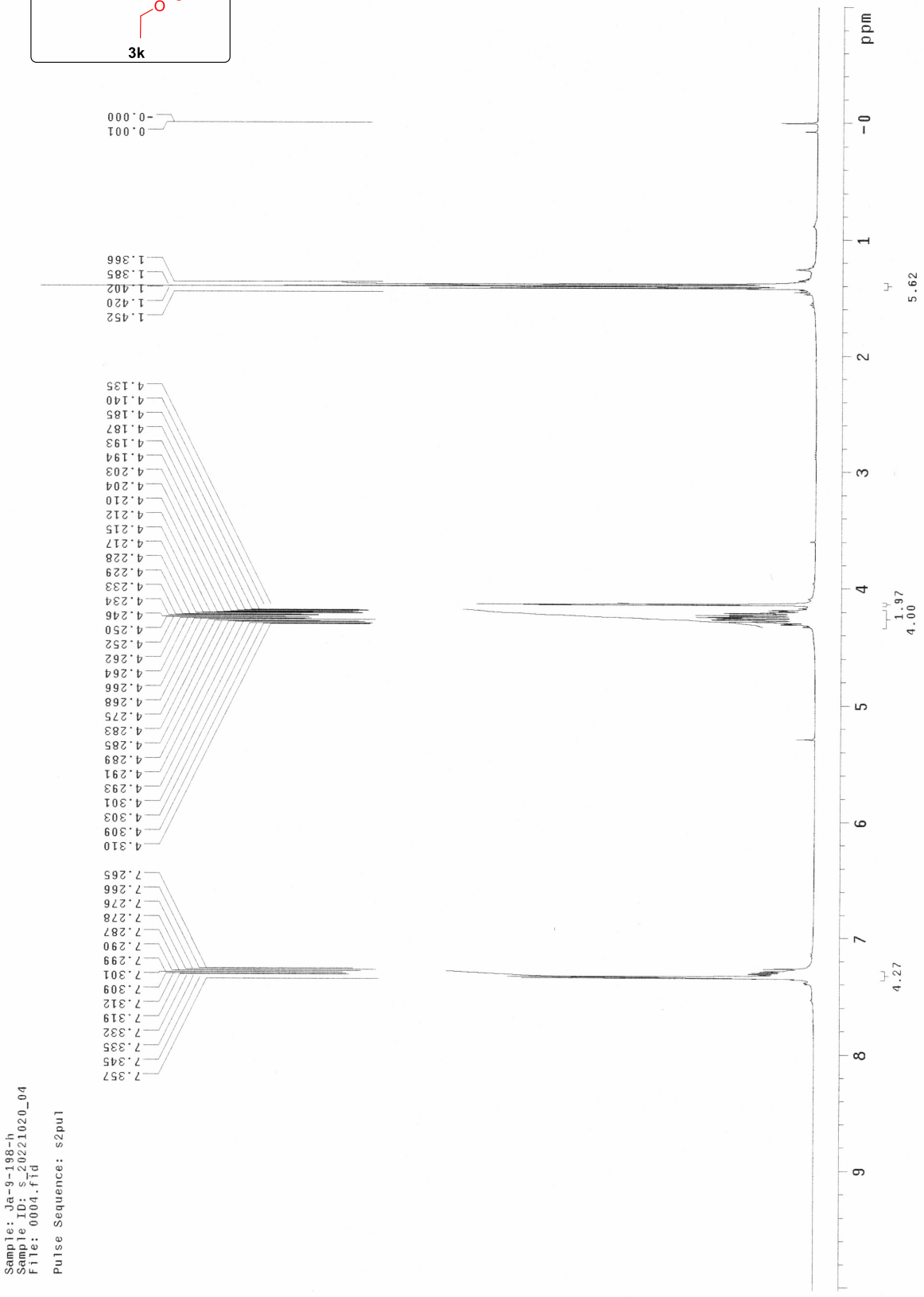

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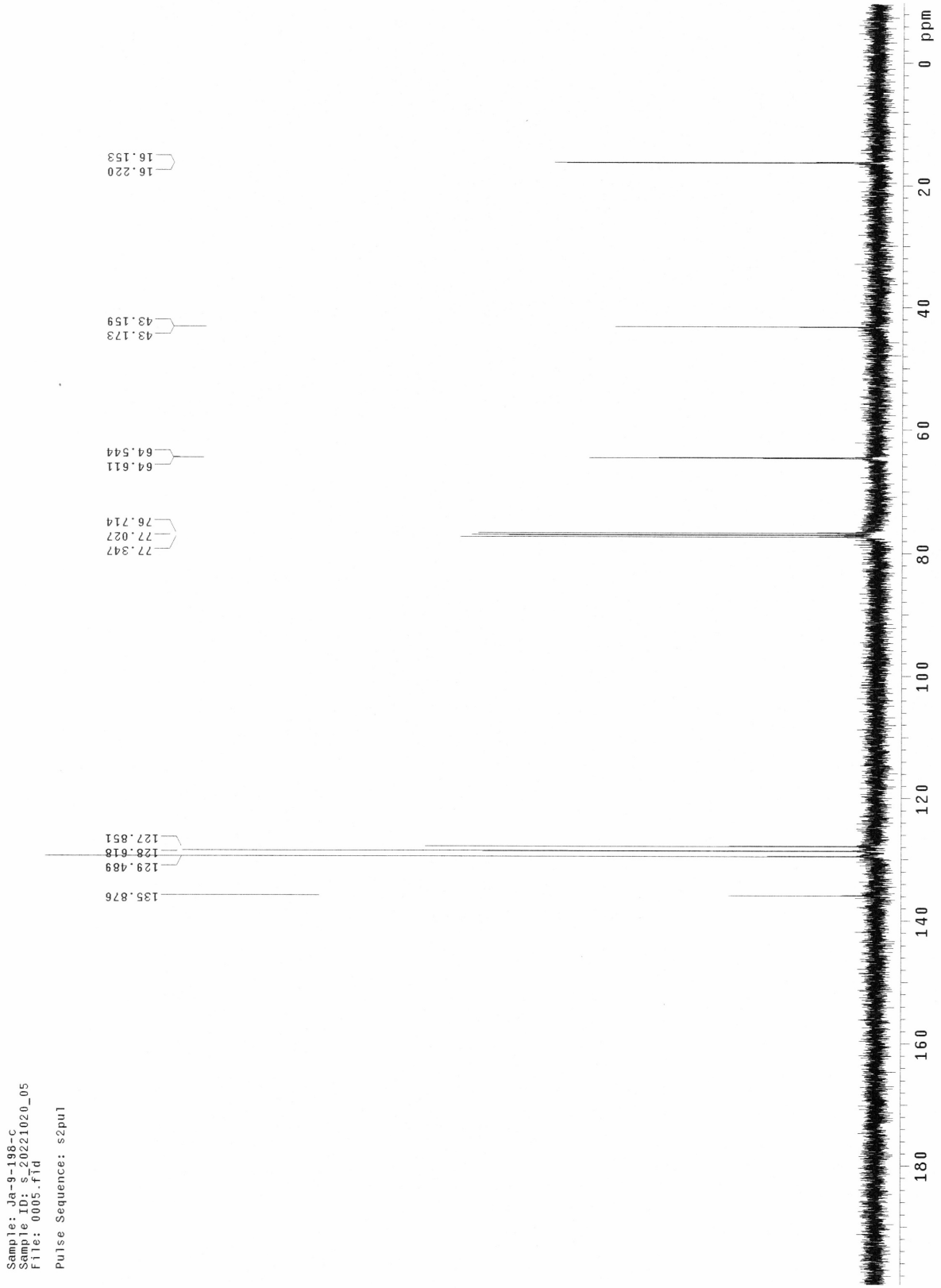

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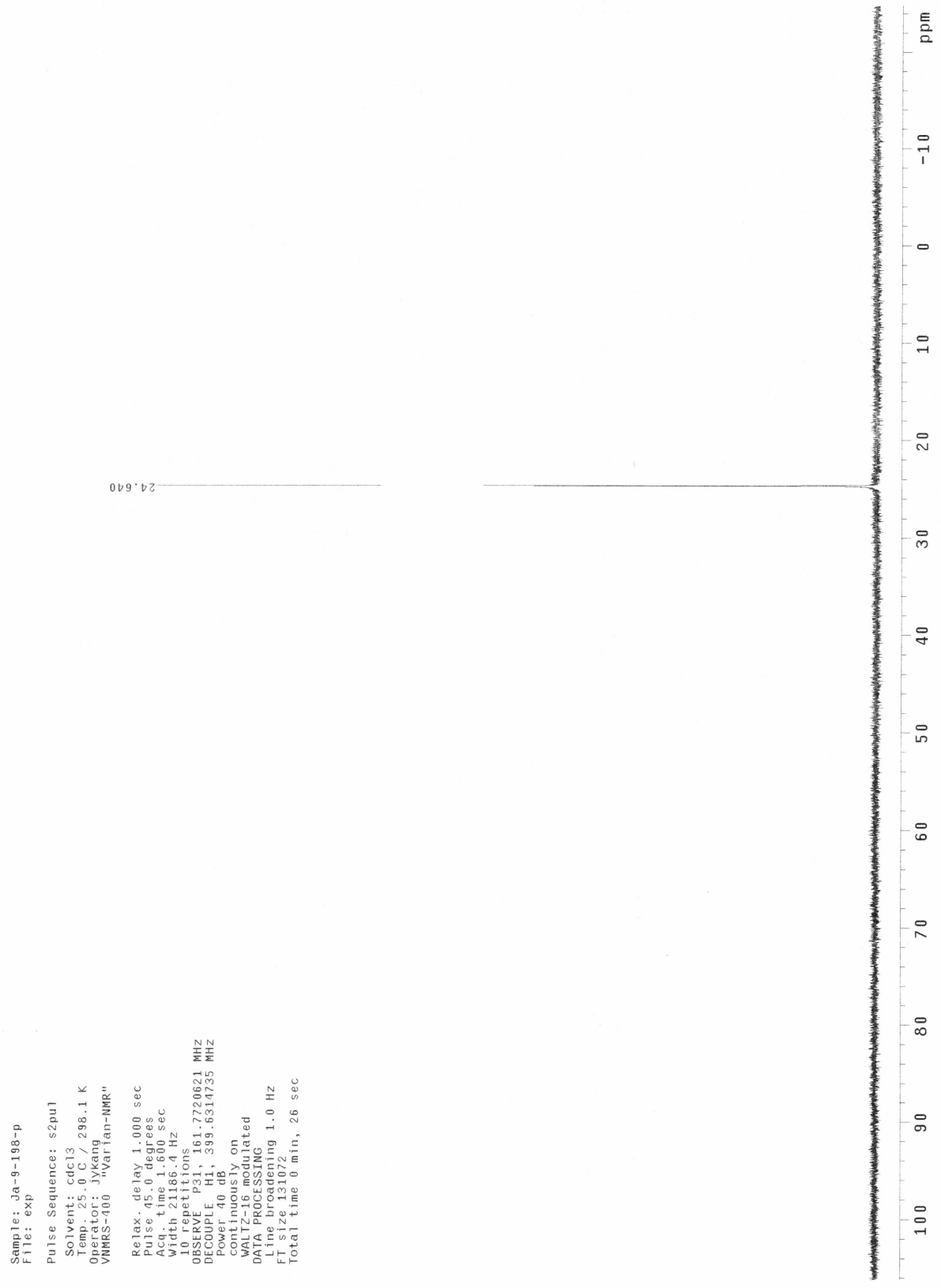

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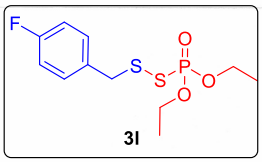

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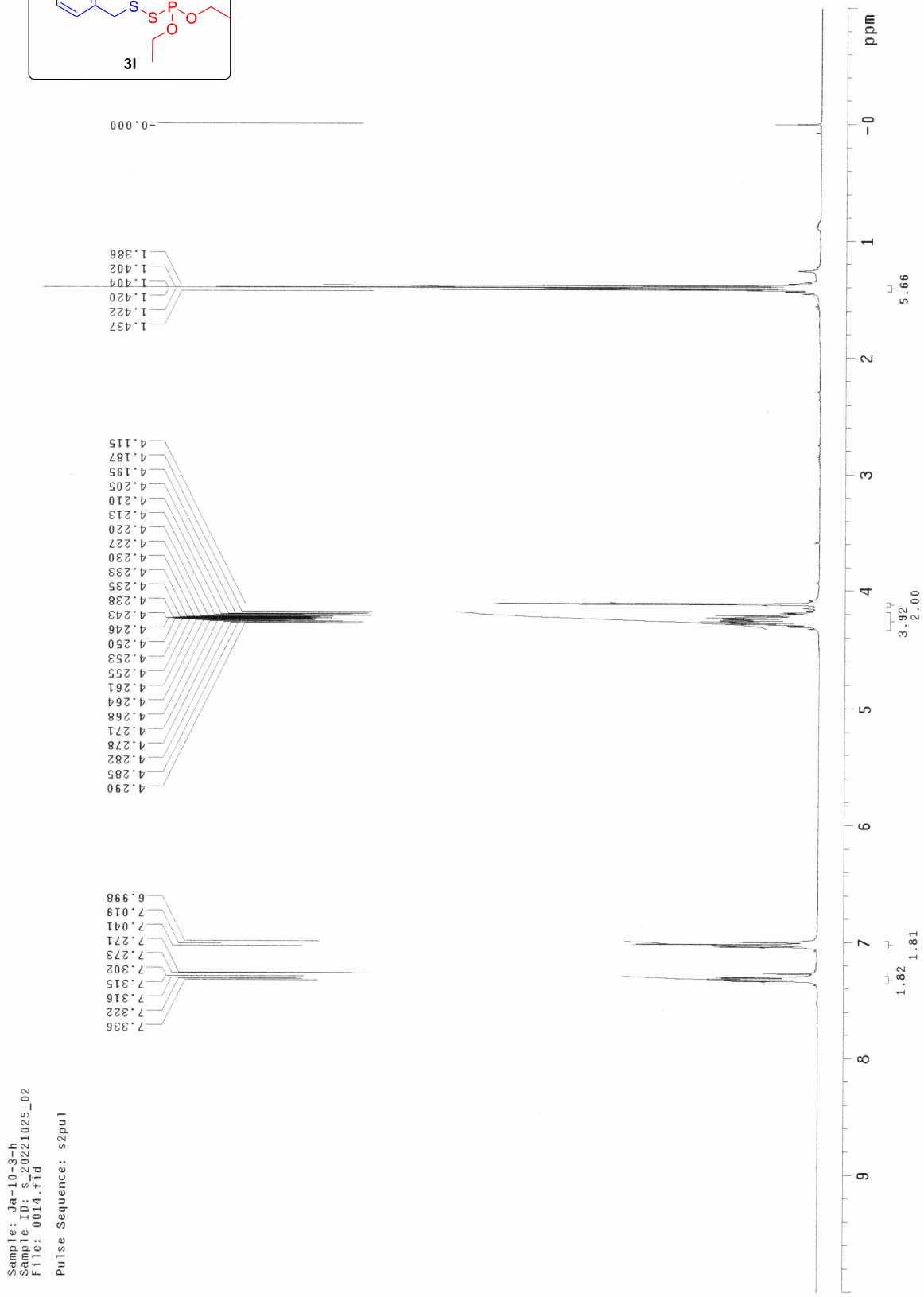

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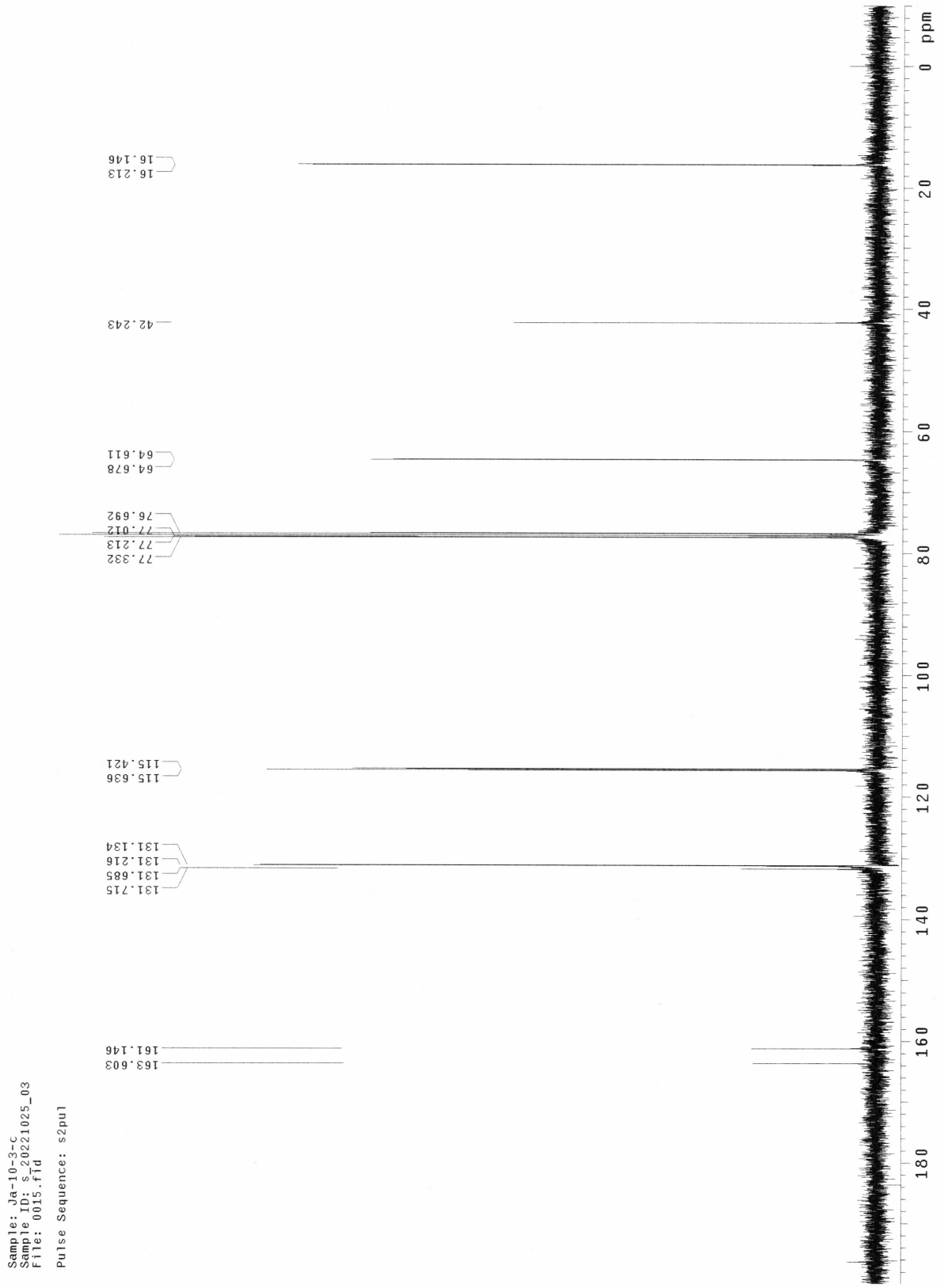

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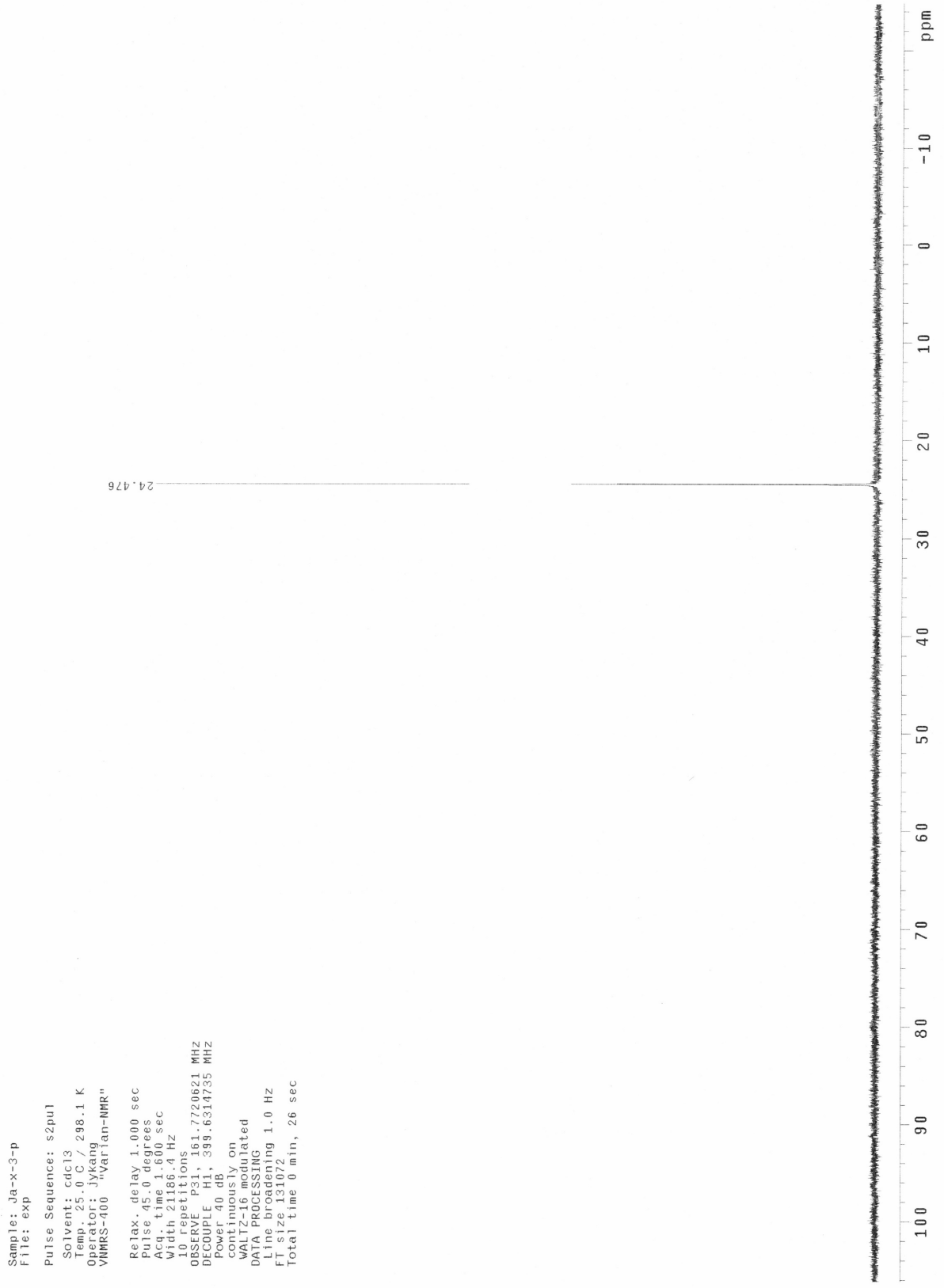

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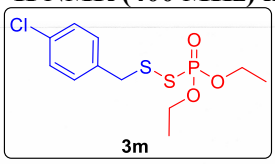

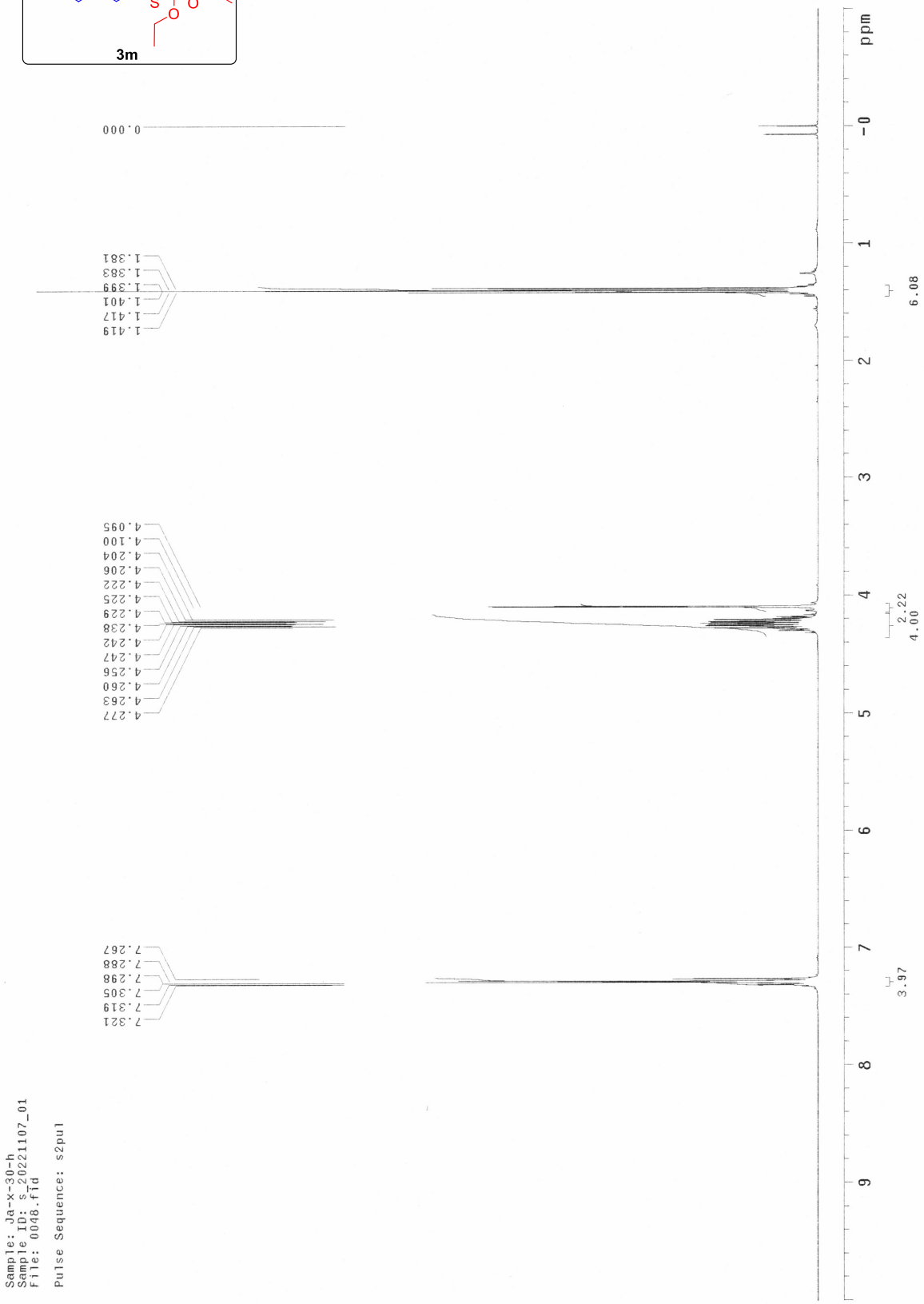

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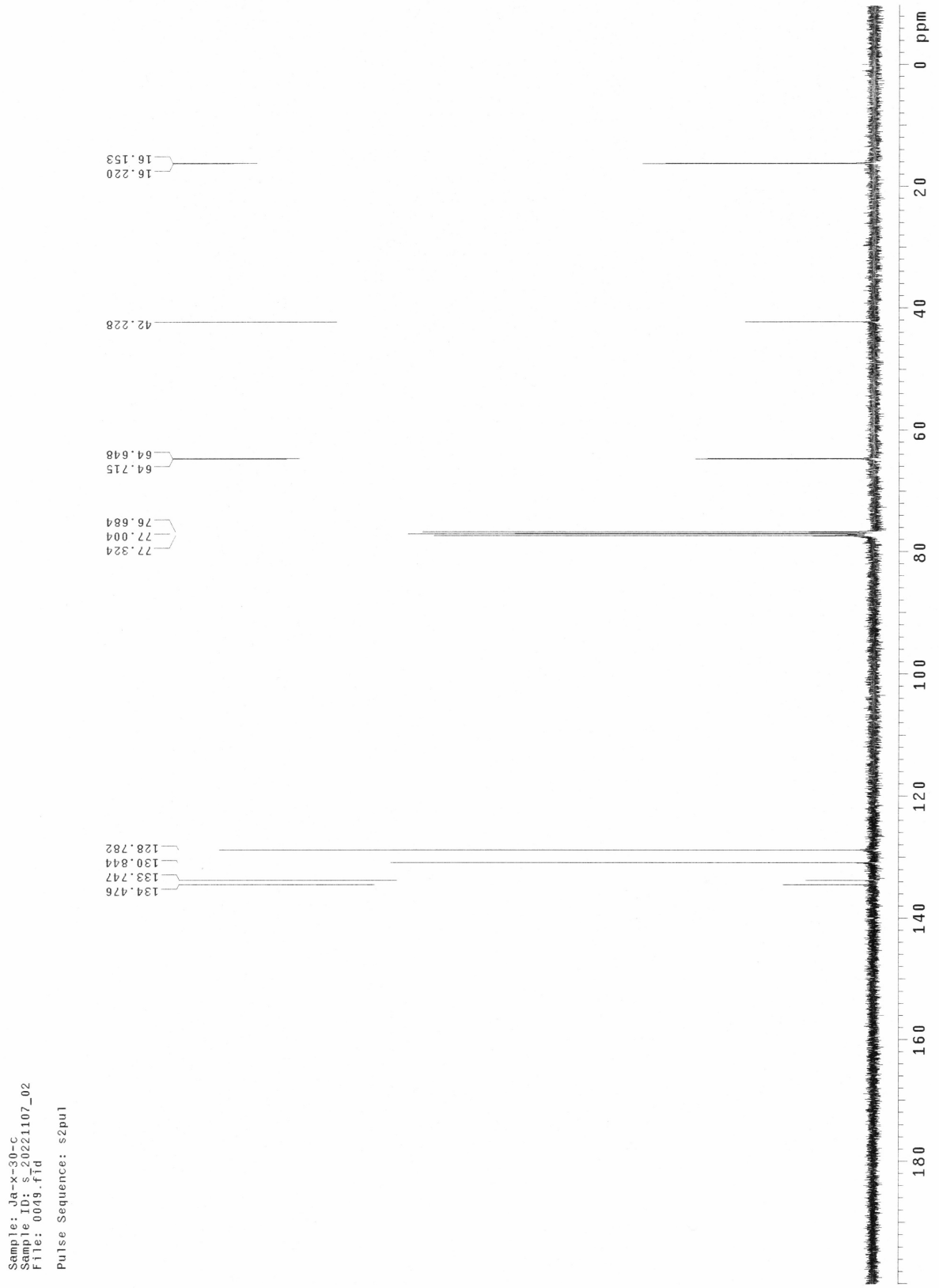

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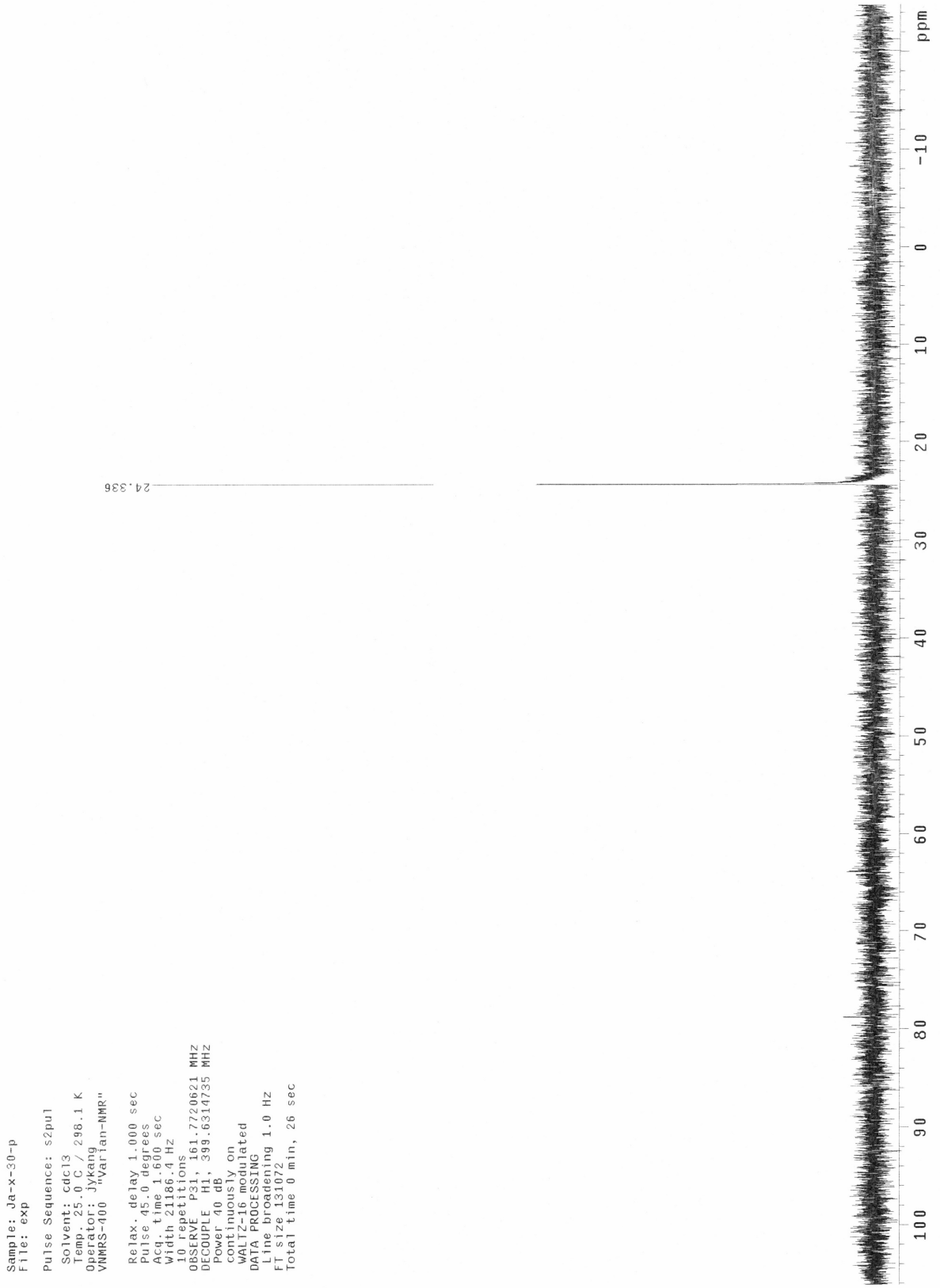

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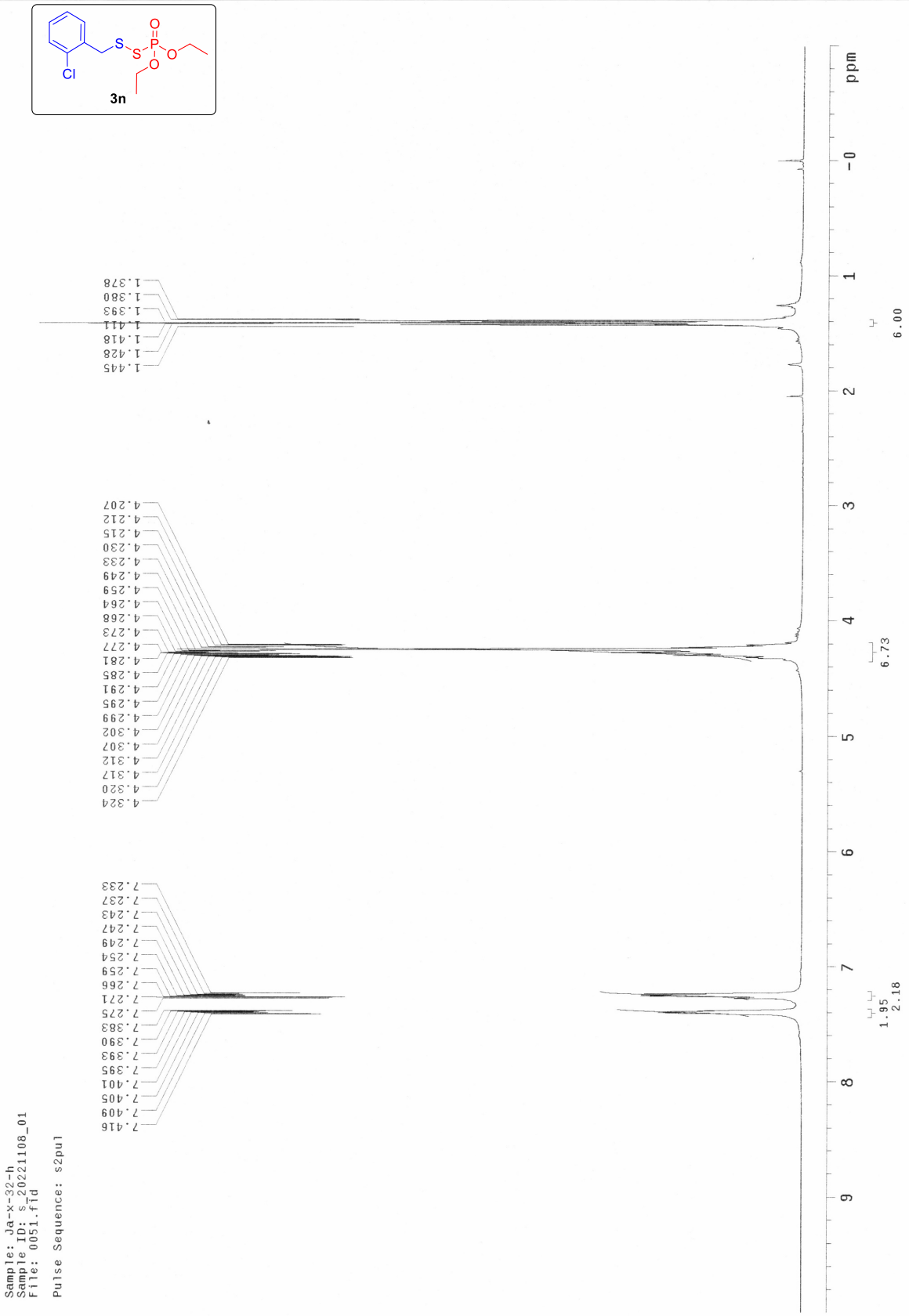

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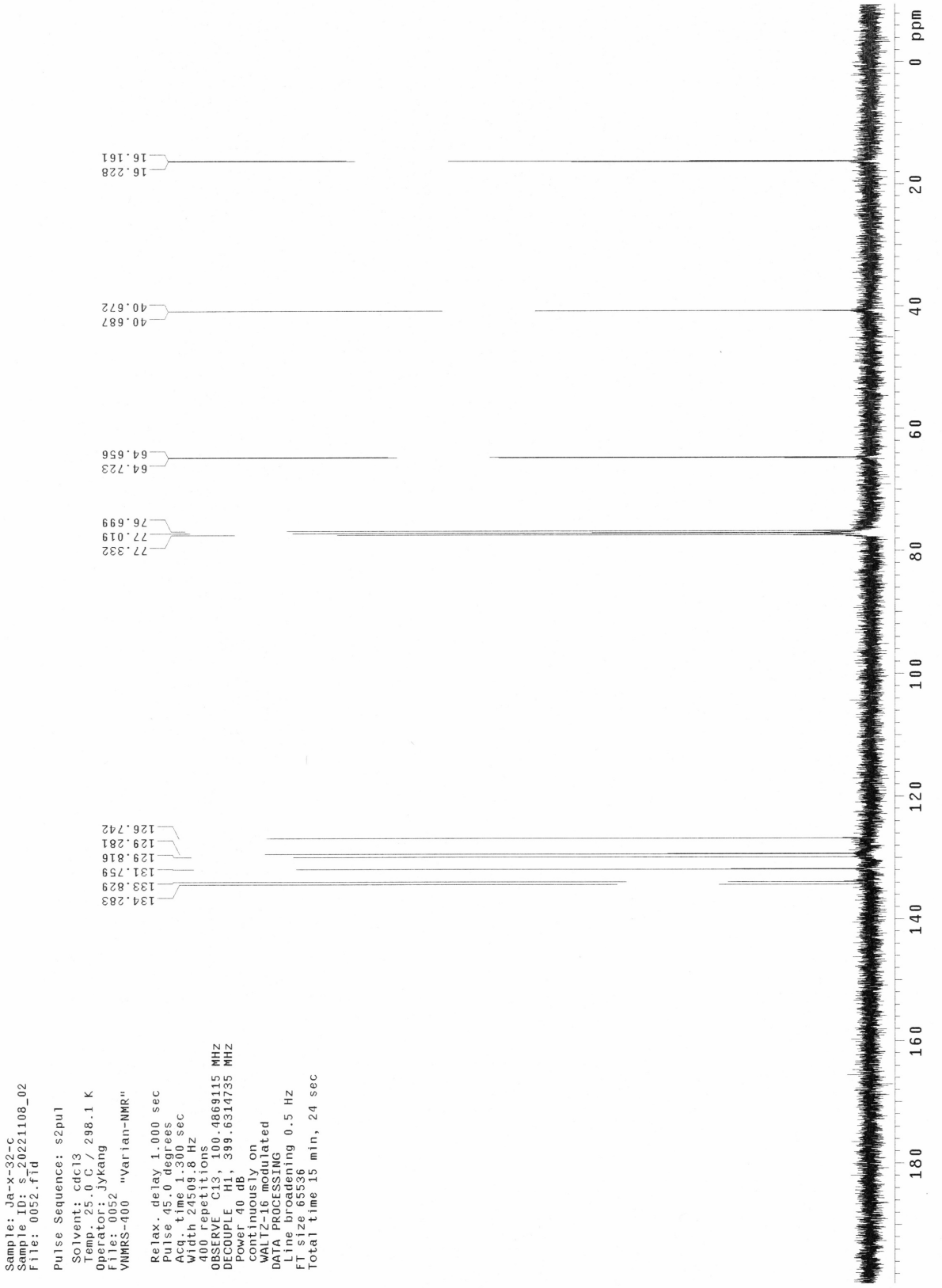

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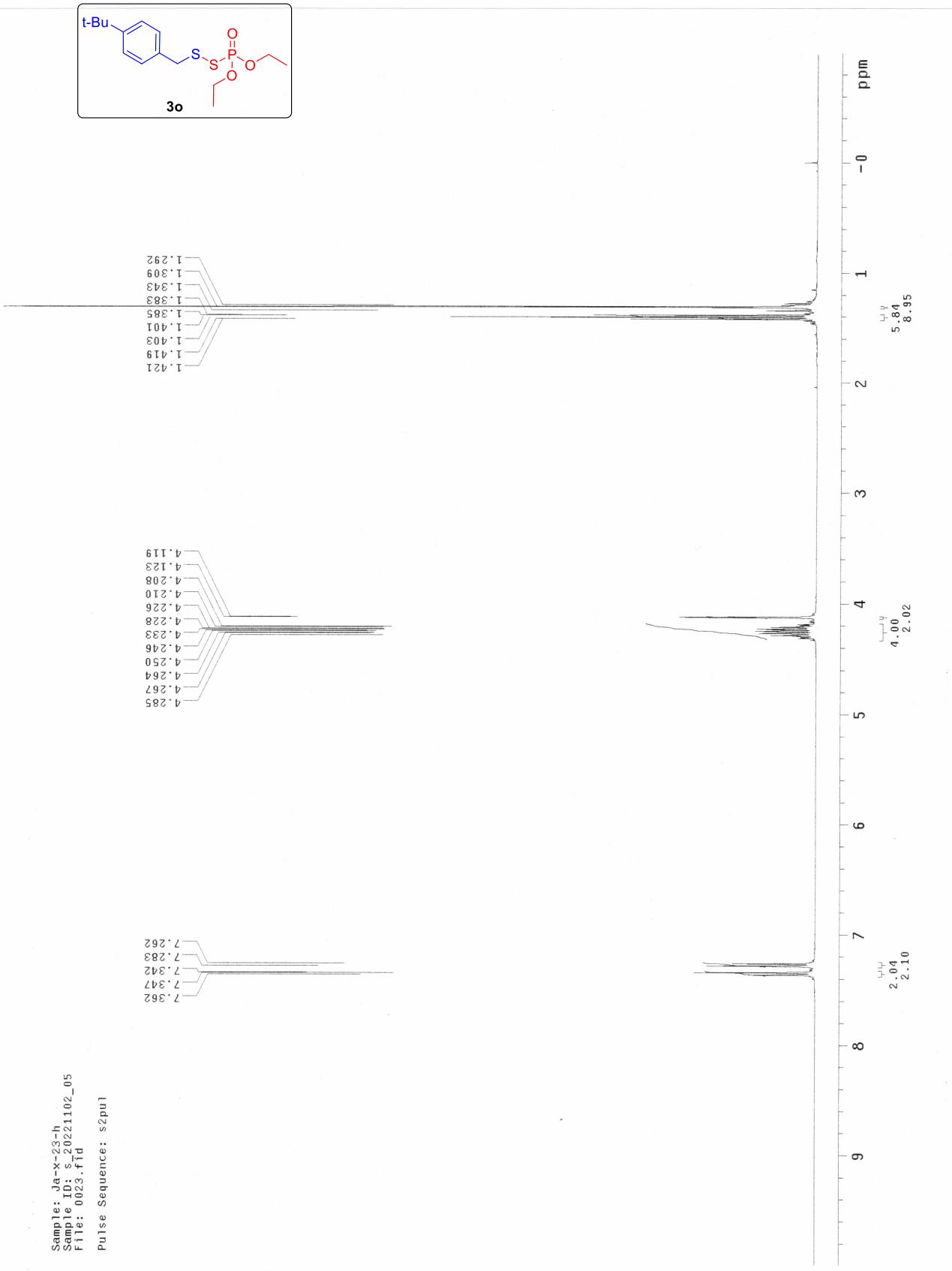
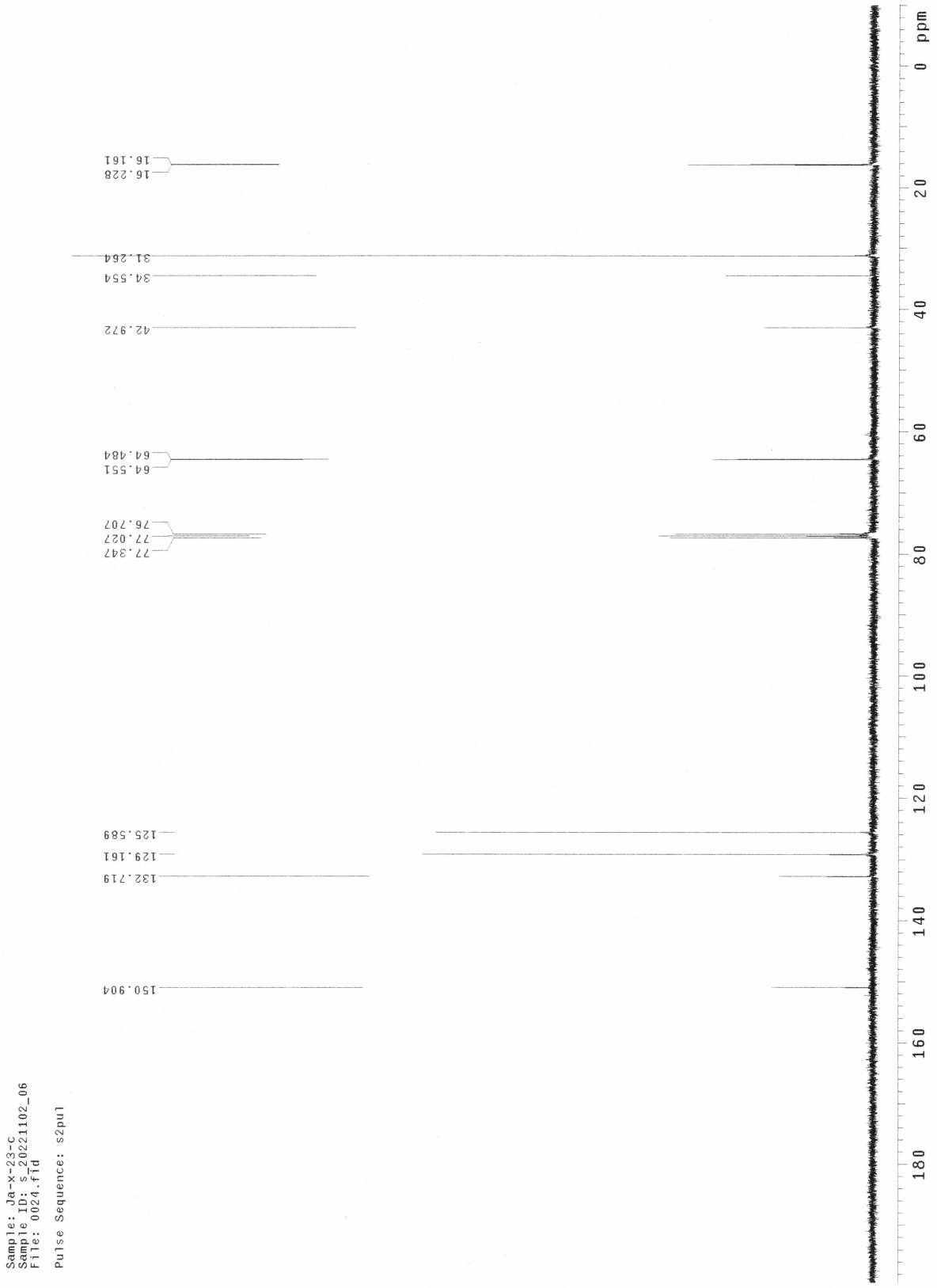
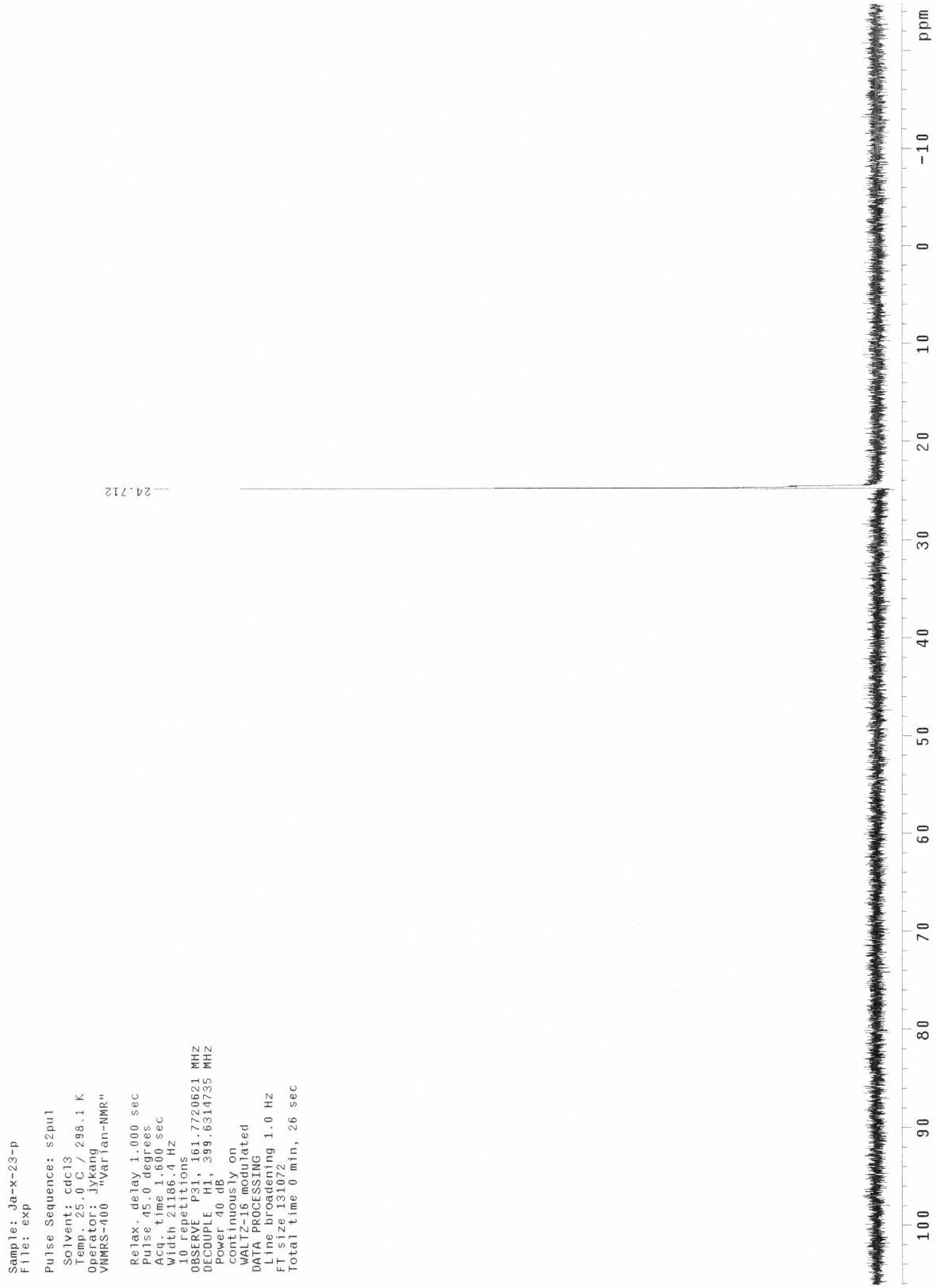
^{1}H NMR (400 MHz) in $CDCl_3$



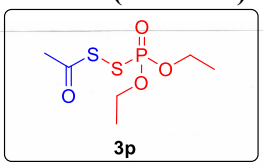
^{13}C NMR (100.5 MHz) in $CDCl_3$



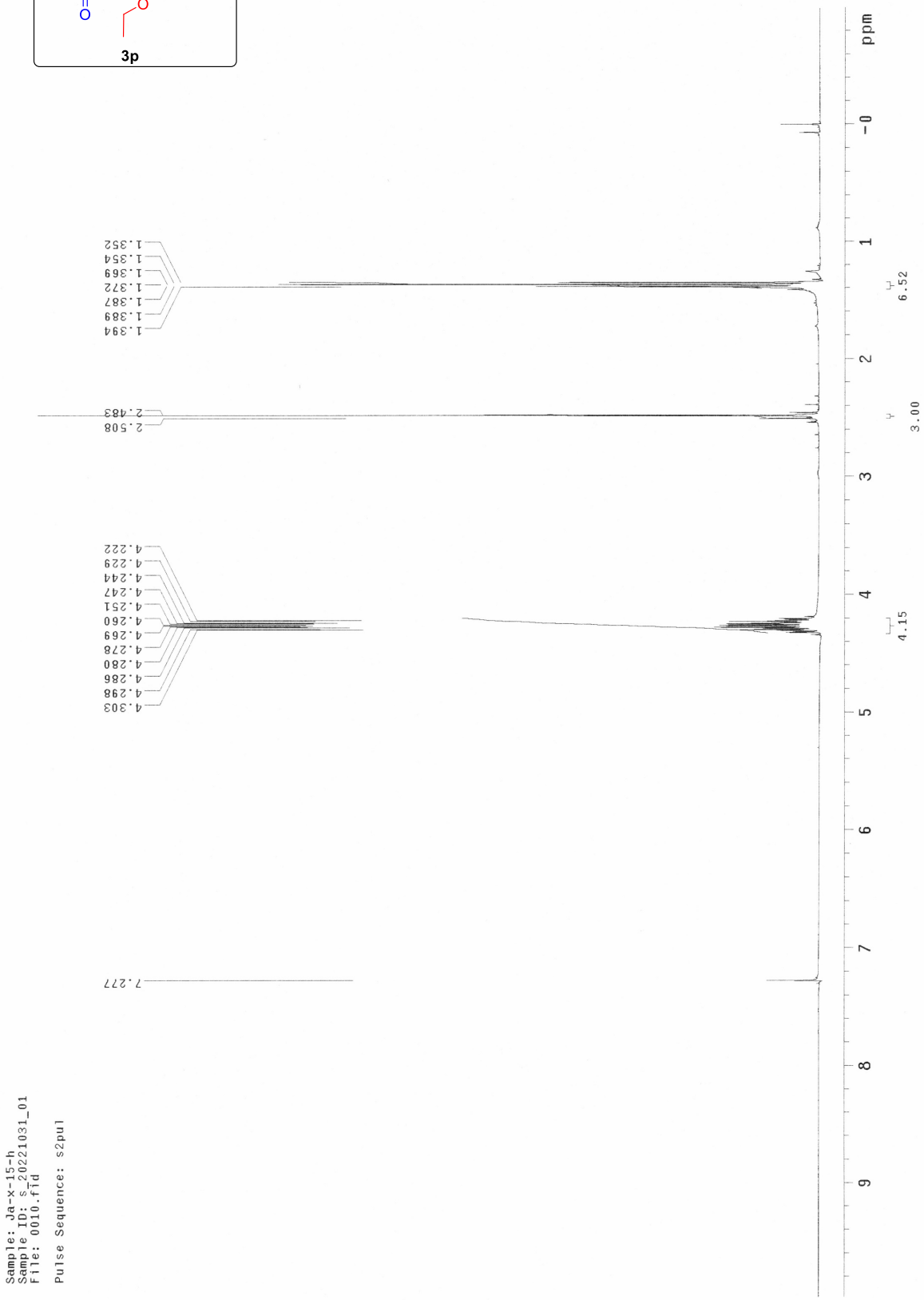
^{31}P NMR (162 MHz) in $CDCl_3$



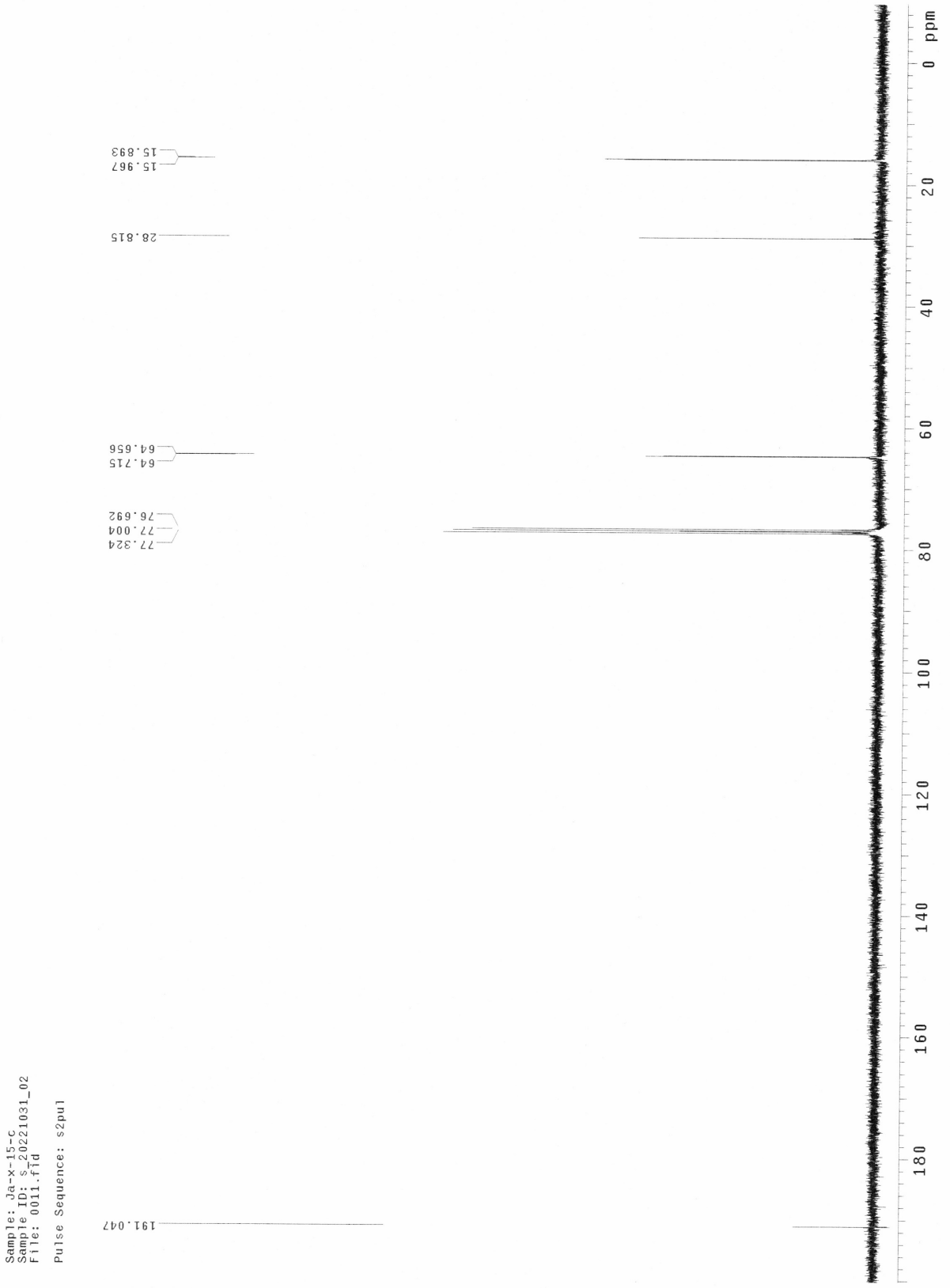
^{1}H NMR (400 MHz) in $CDCl_3$



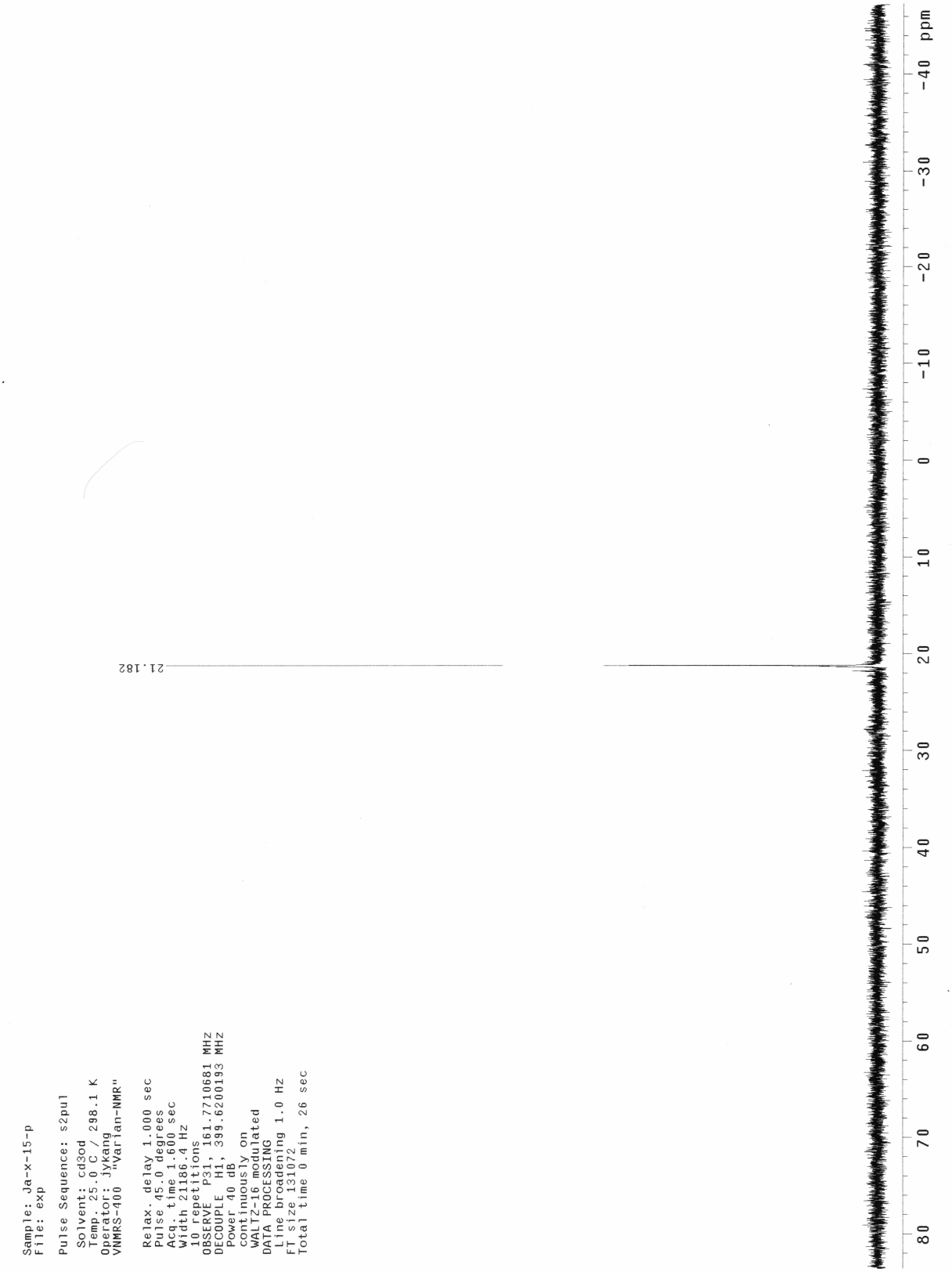
3p



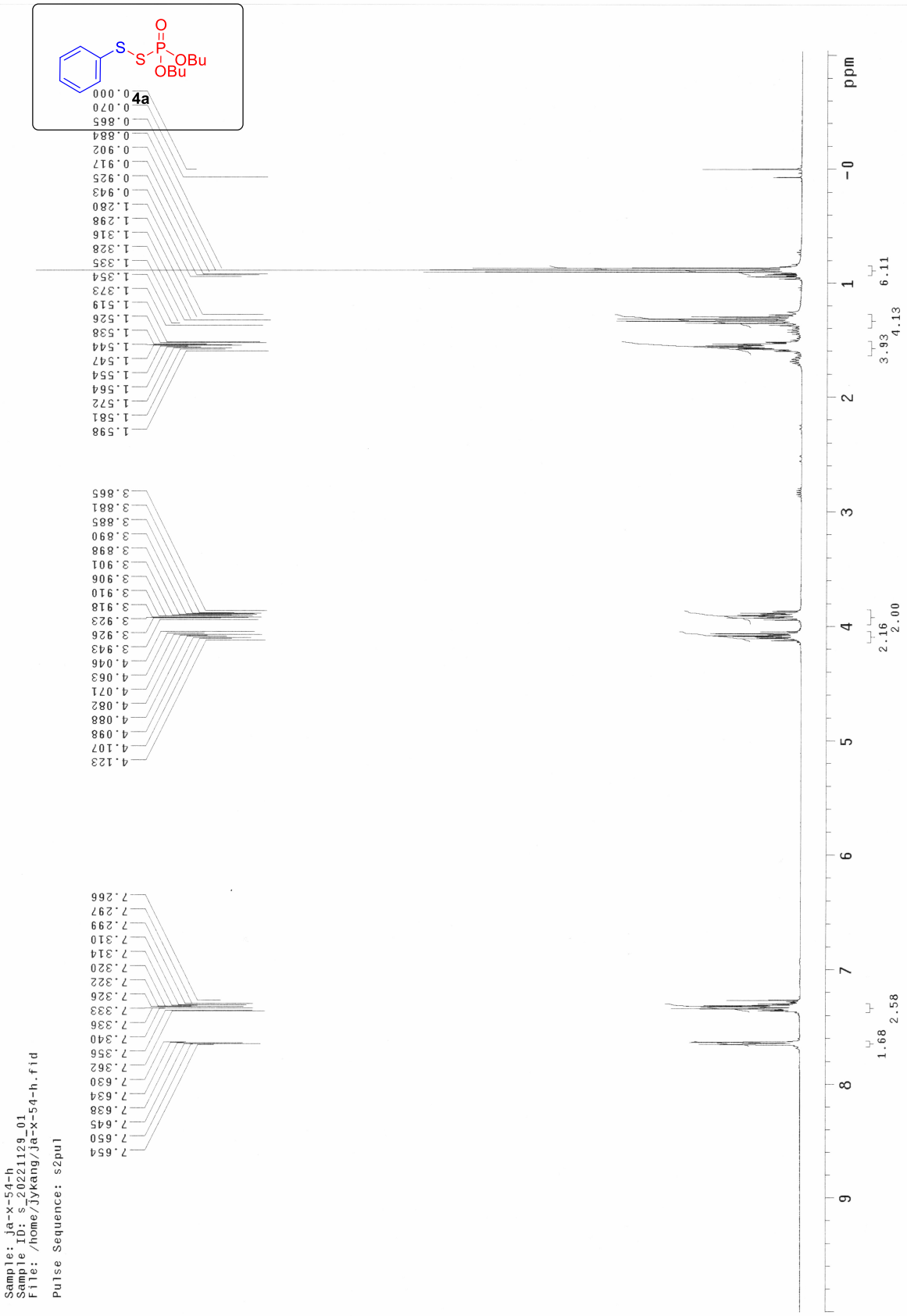
^{13}C NMR (100.5 MHz) in $CDCl_3$



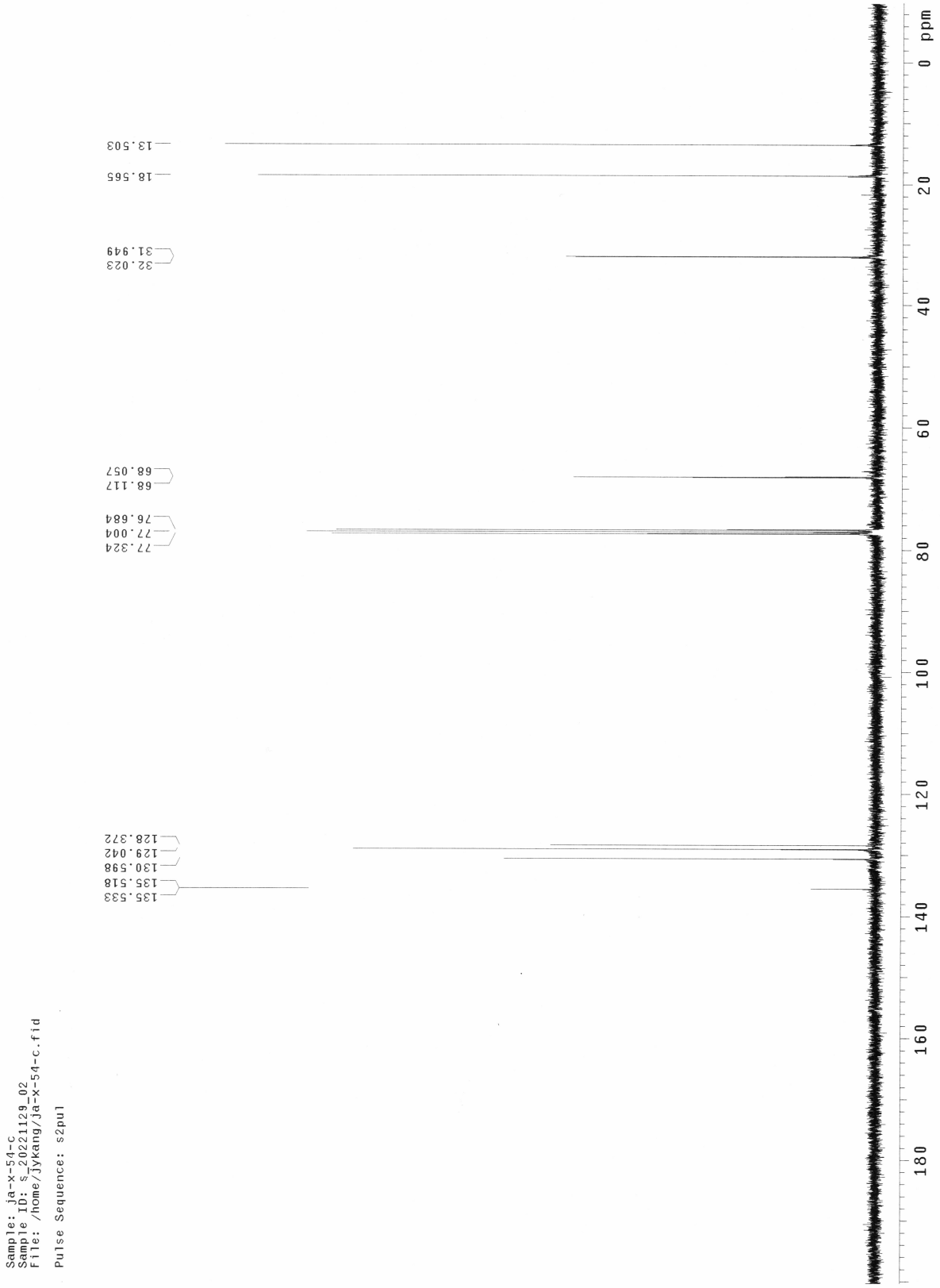
^{31}P NMR (162 MHz) in $CDCl_3$



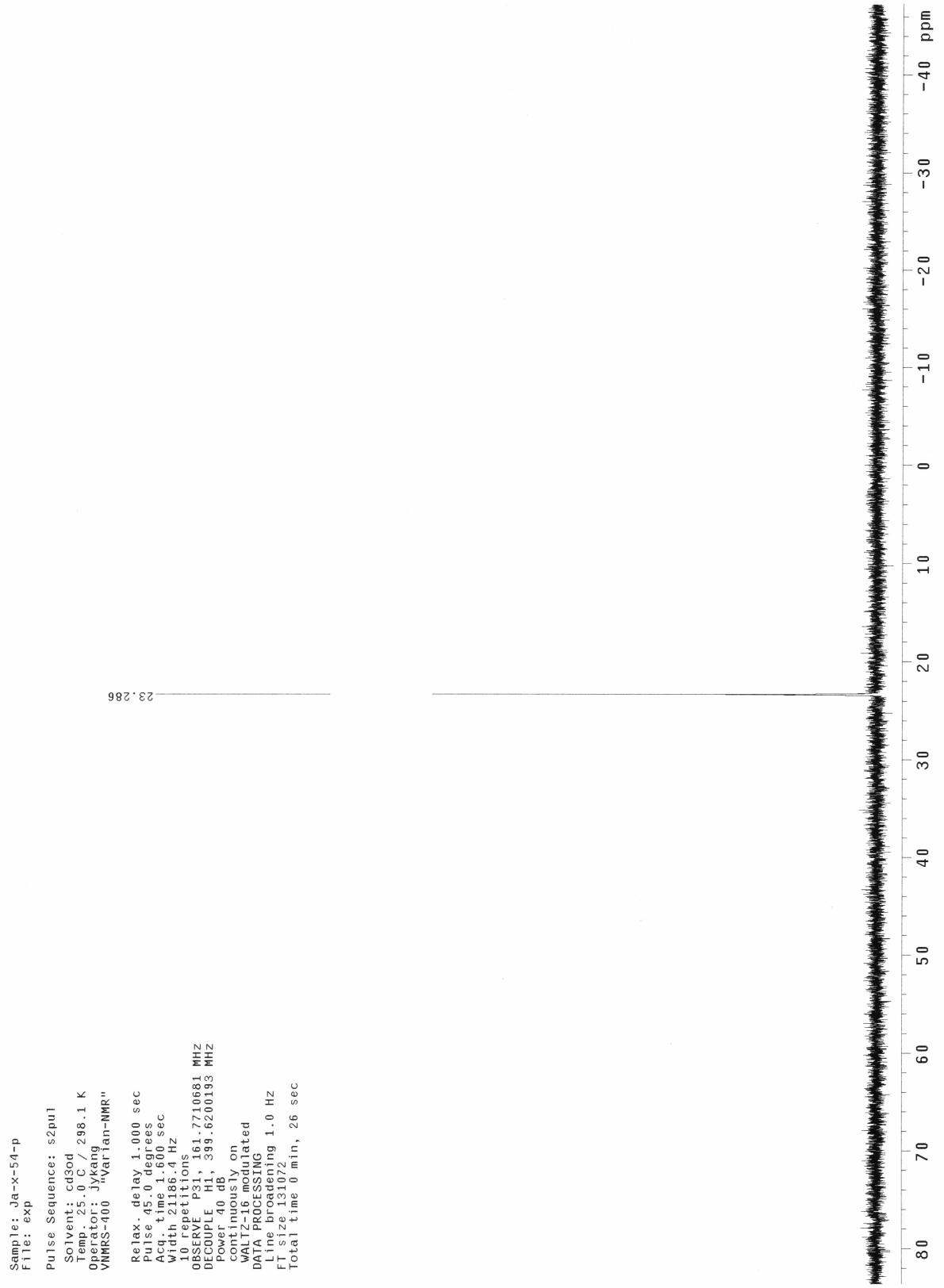
^{1}H NMR (400 MHz) in $CDCl_3$



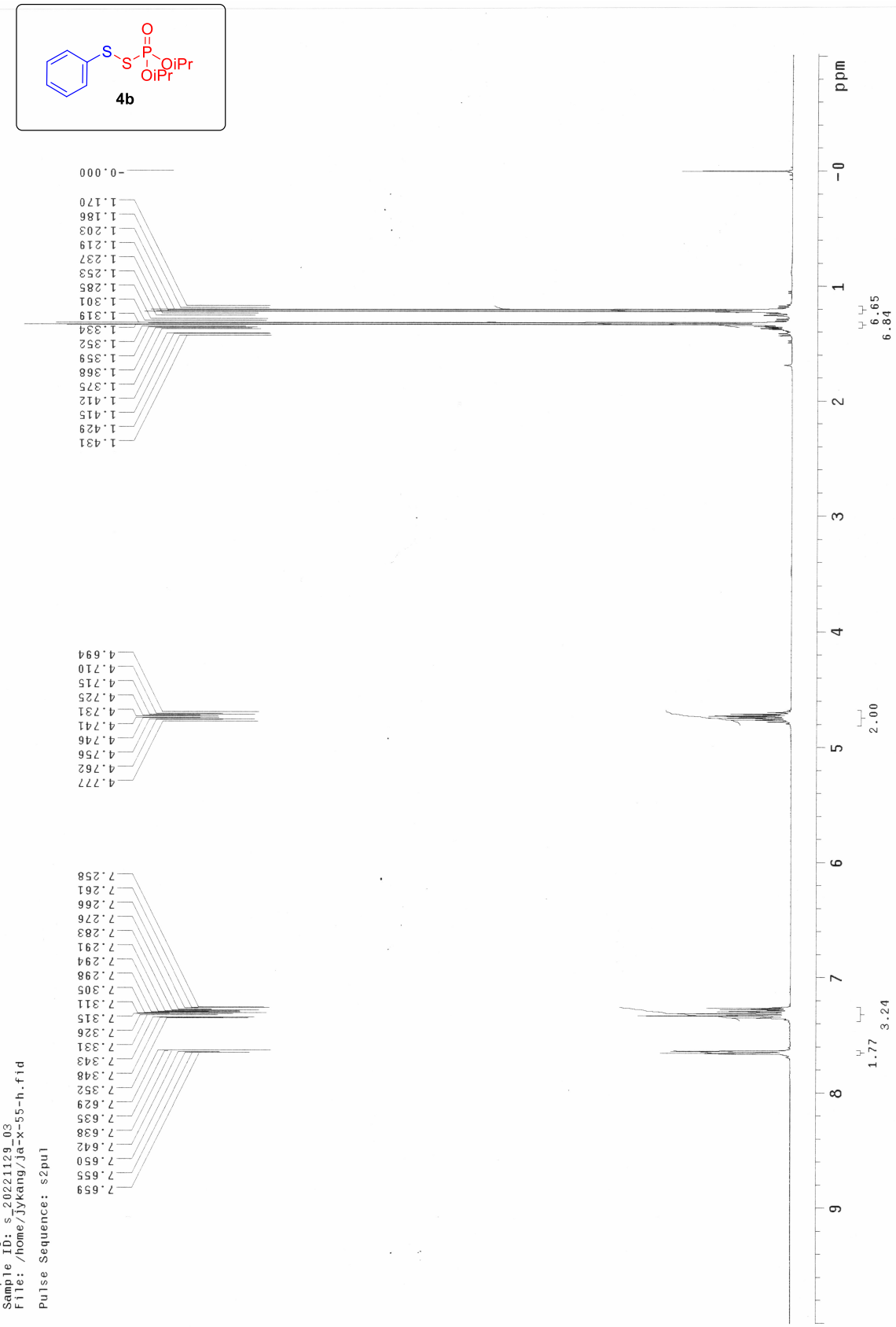
^{13}C NMR (100.5 MHz) in $CDCl_3$



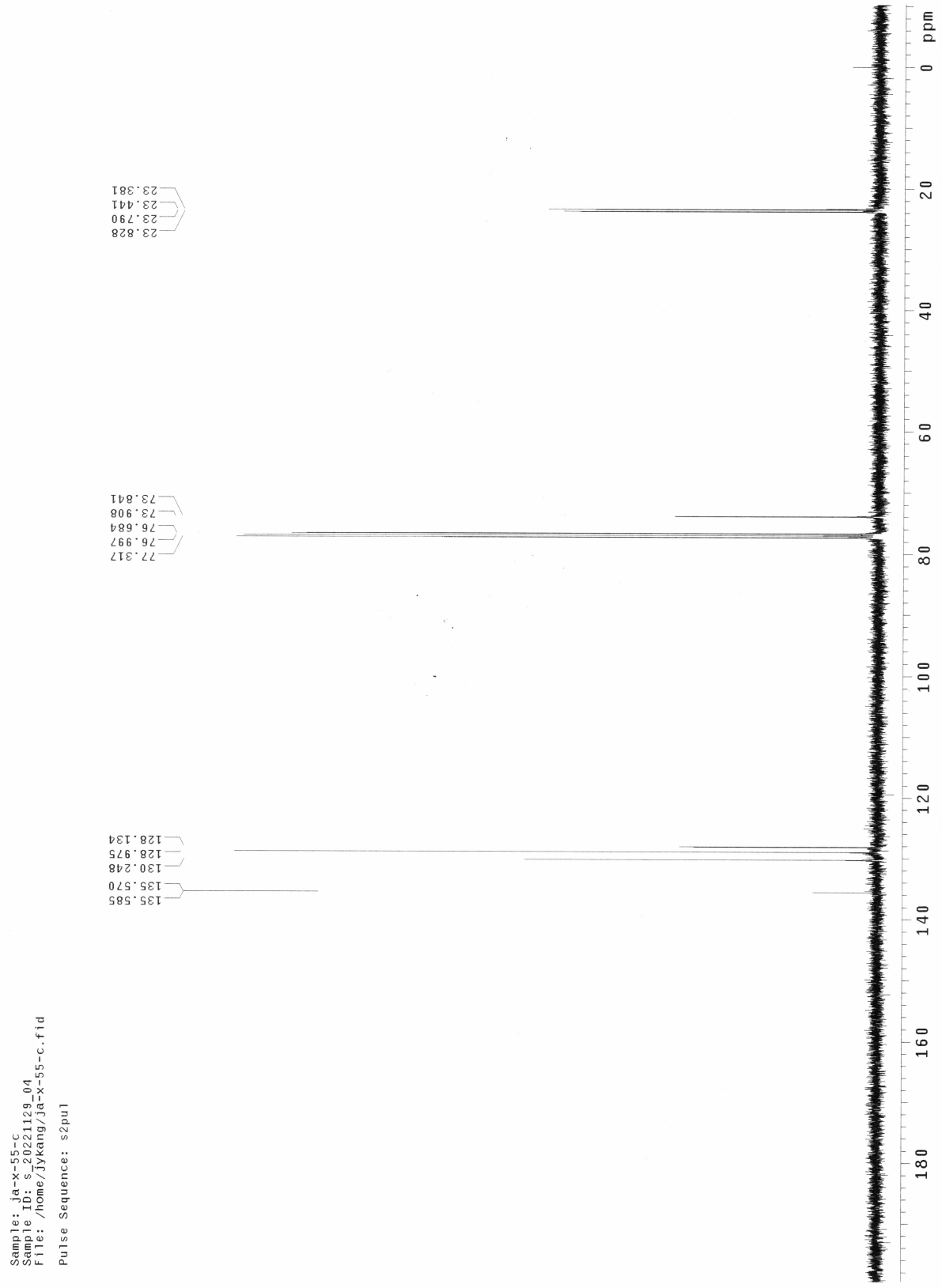
^{31}P NMR (162 MHz) in $CDCl_3$



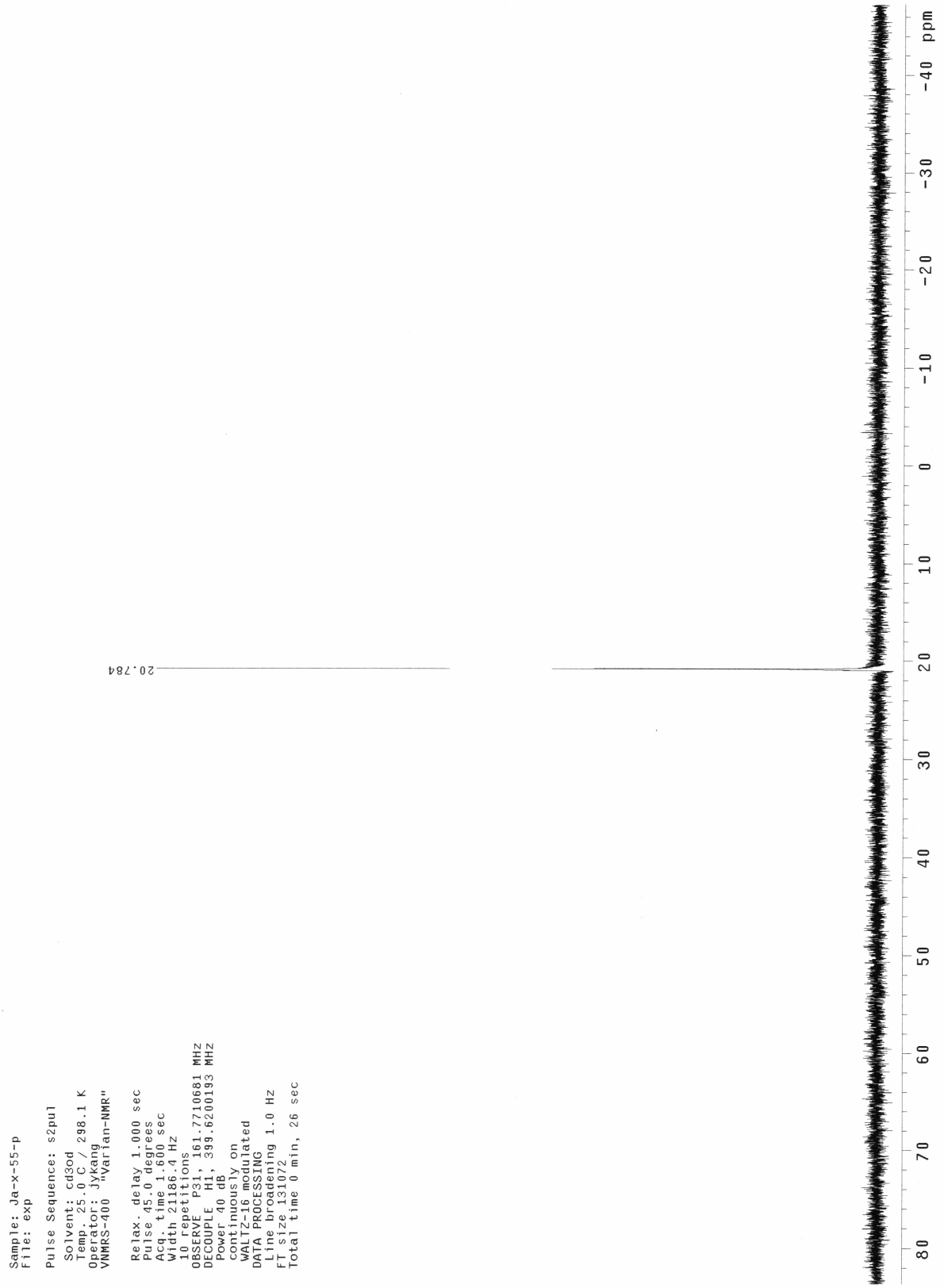
^{1}H NMR (400 MHz) in $CDCl_3$



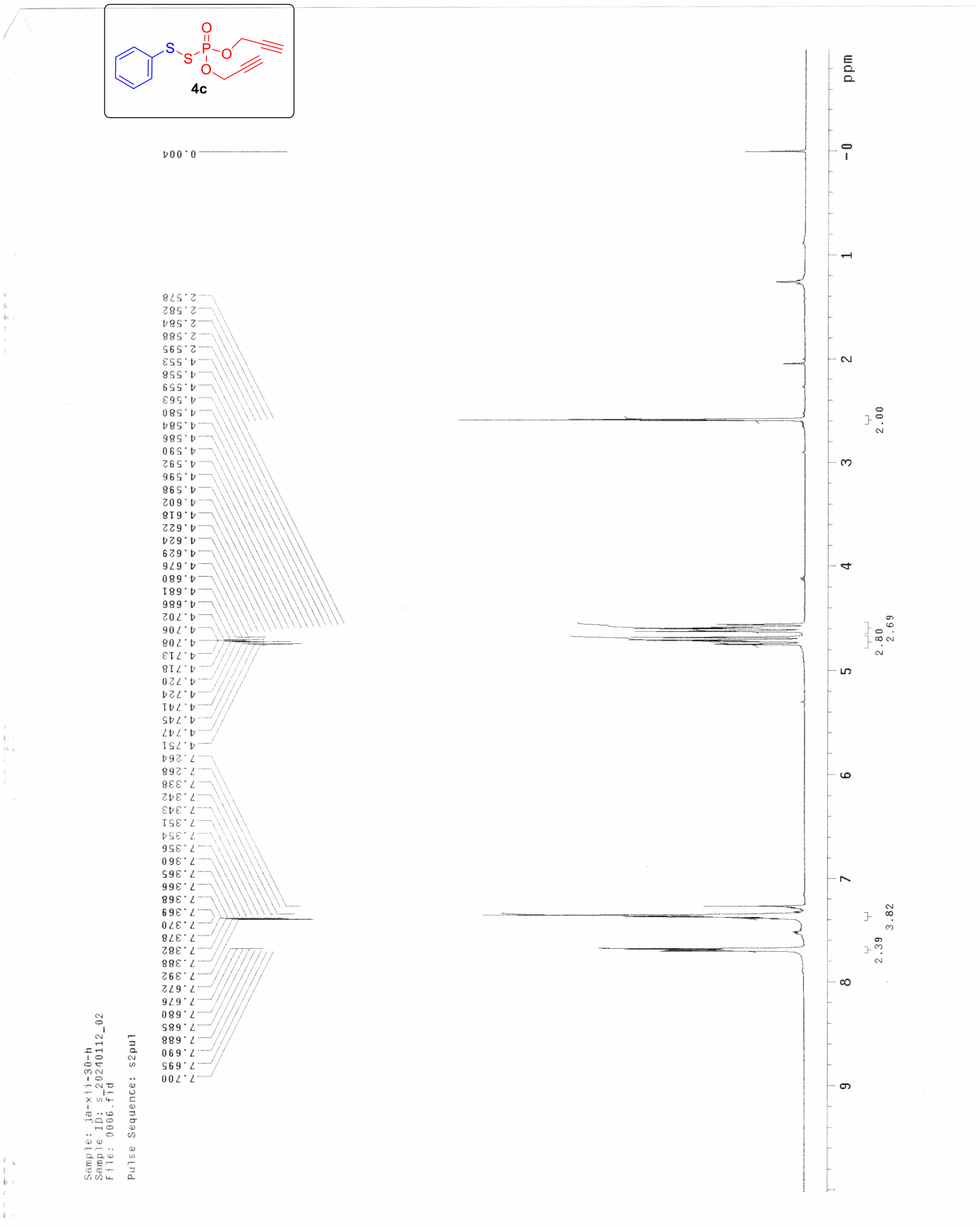
^{13}C NMR (100.5 MHz) in $CDCl_3$



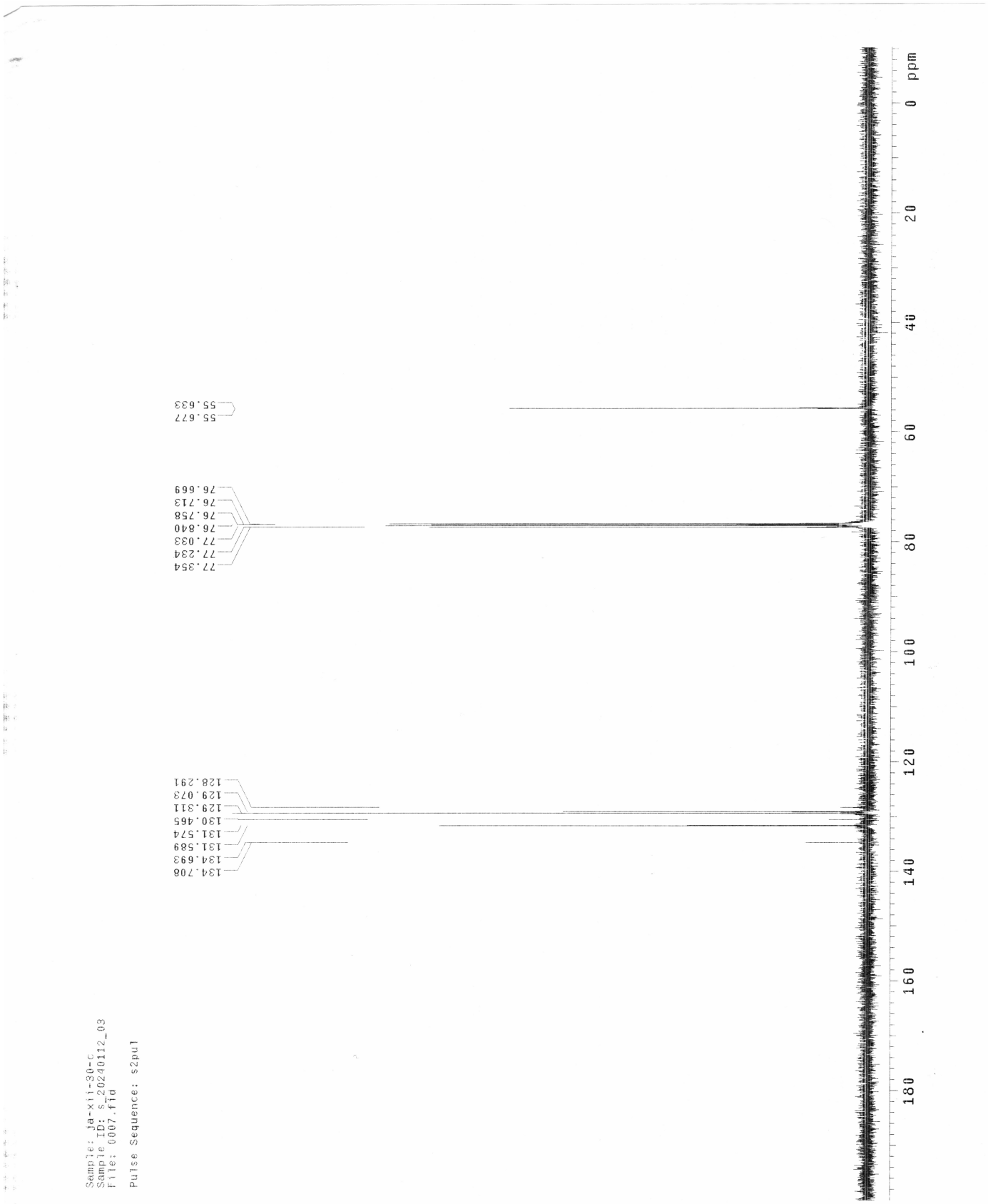
^{31}P NMR (162 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$

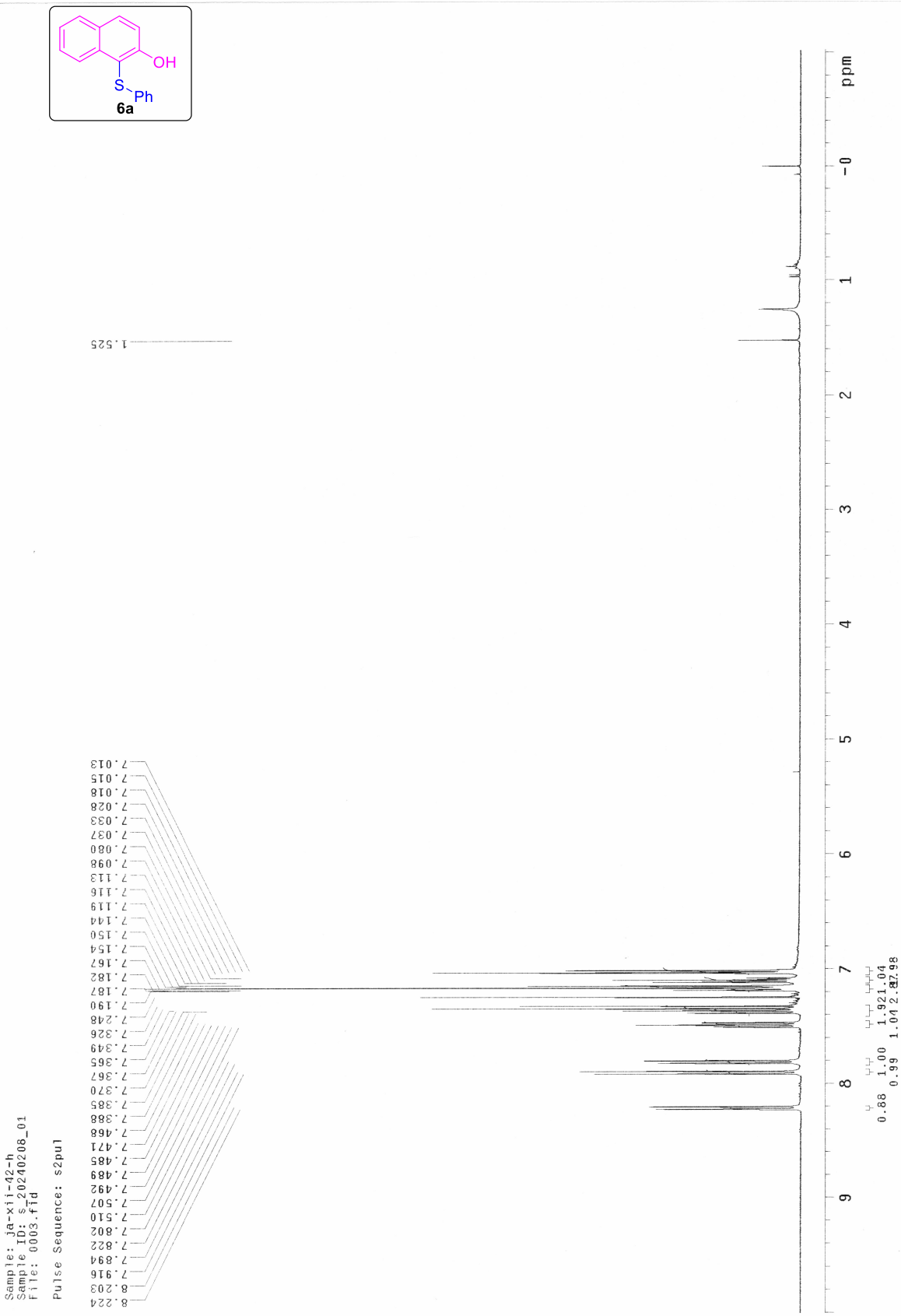


^{13}C NMR (100.5 MHz) in $CDCl_3$

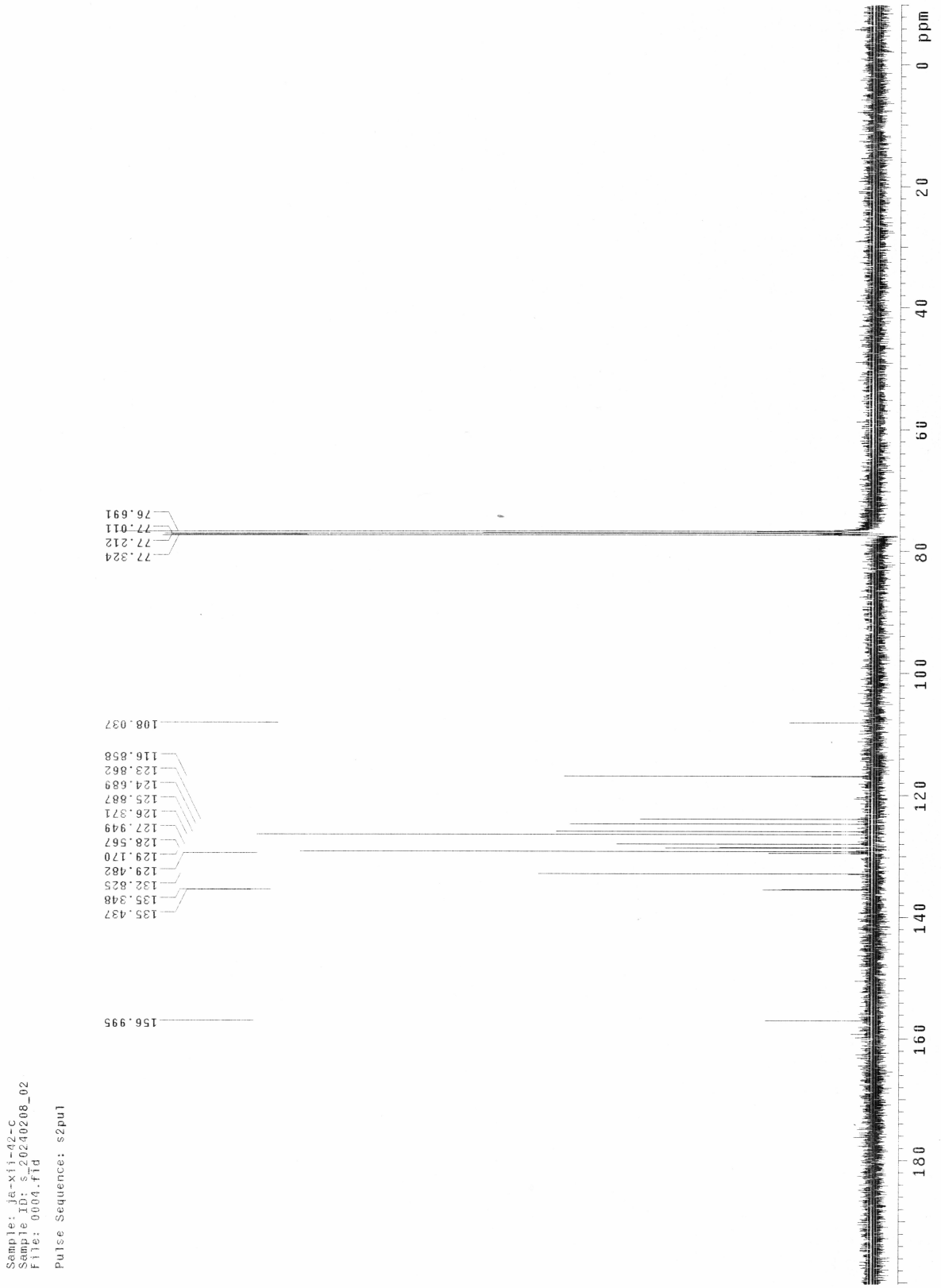


^{31}P NMR (162 MHz) in $CDCl_3$

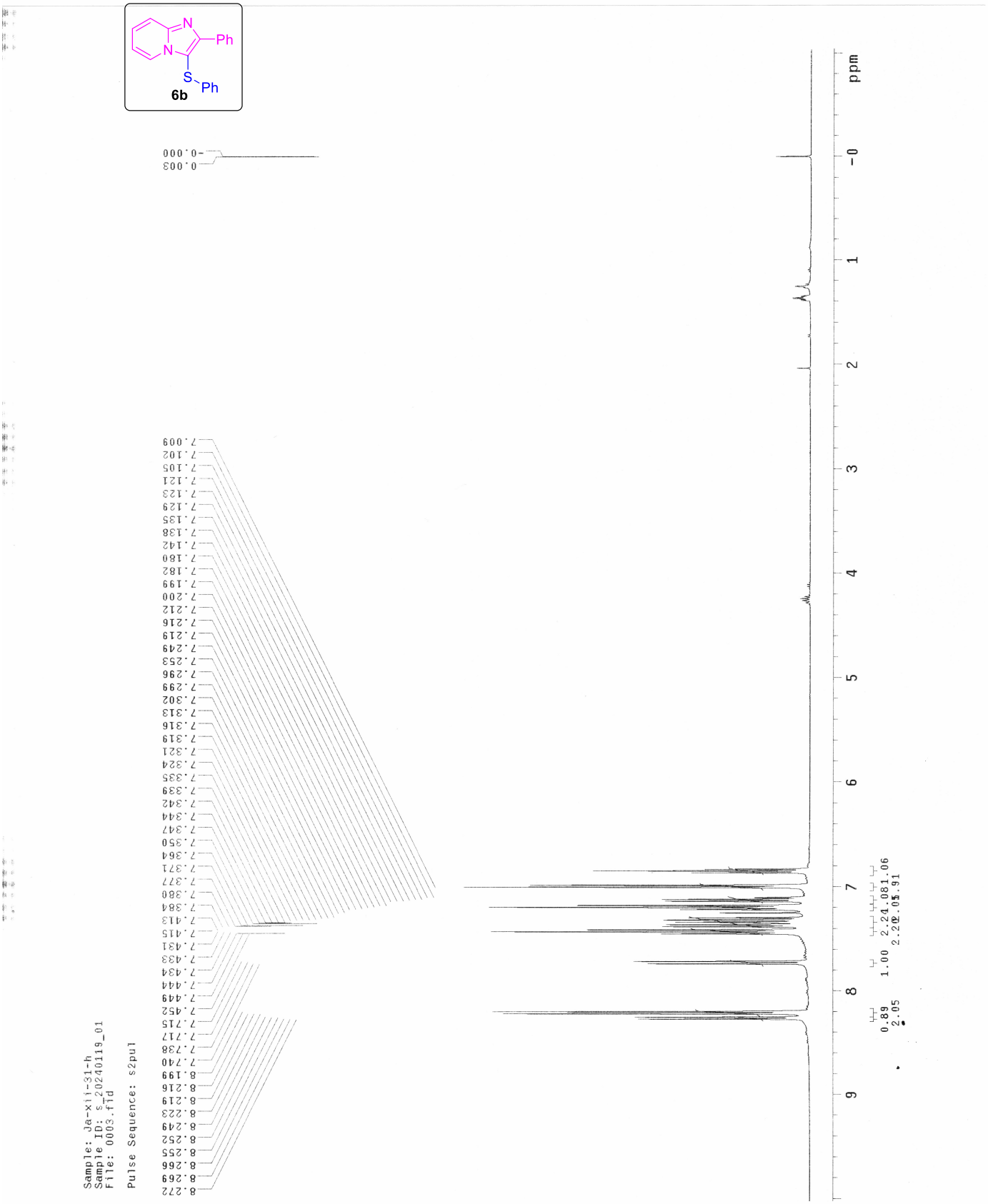
^{1}H NMR (400 MHz) in $CDCl_3$



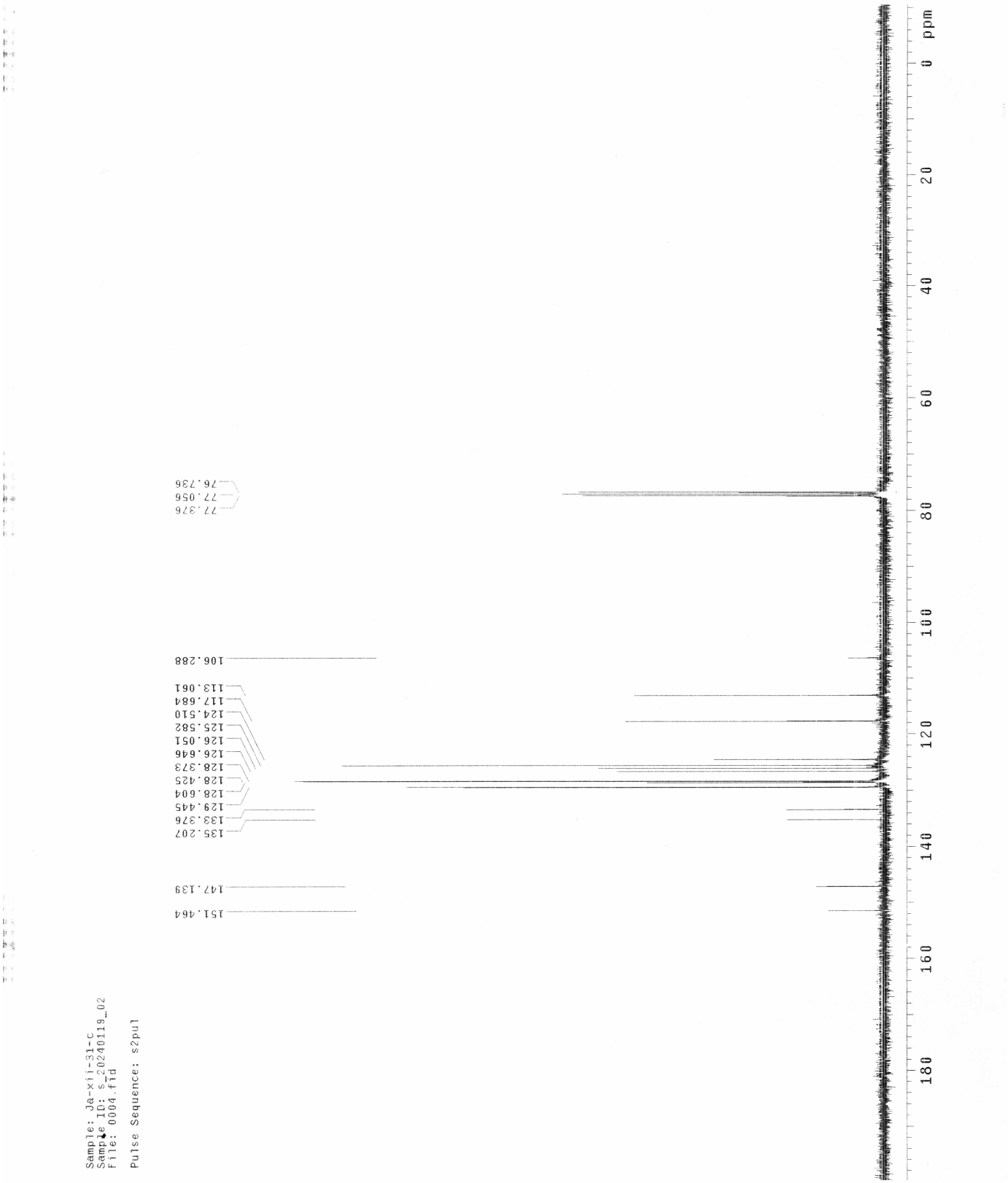
^{13}C NMR (100.5 MHz) in $CDCl_3$



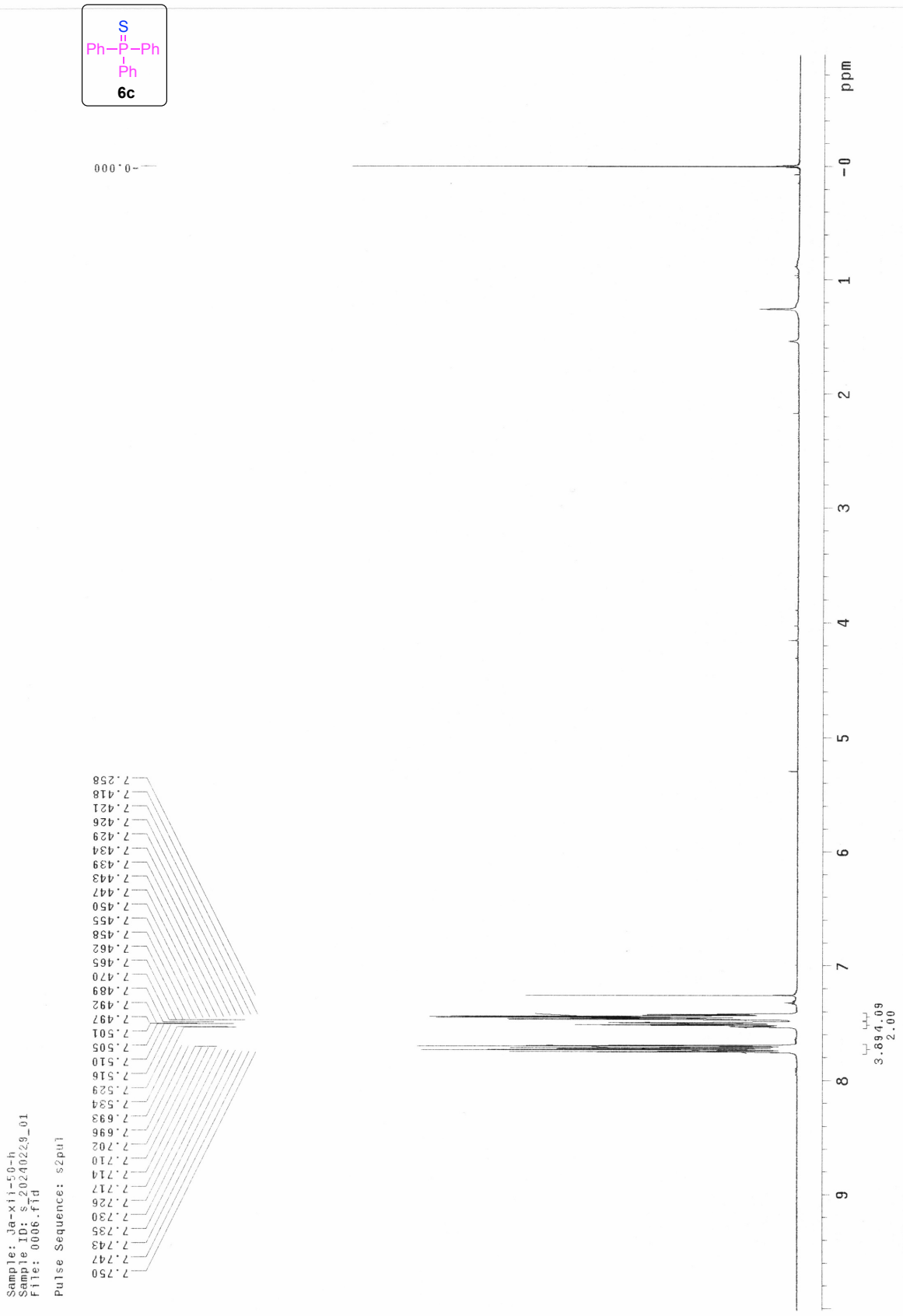
^{1}H NMR (400 MHz) in $CDCl_3$



^{13}C NMR (100.5 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$



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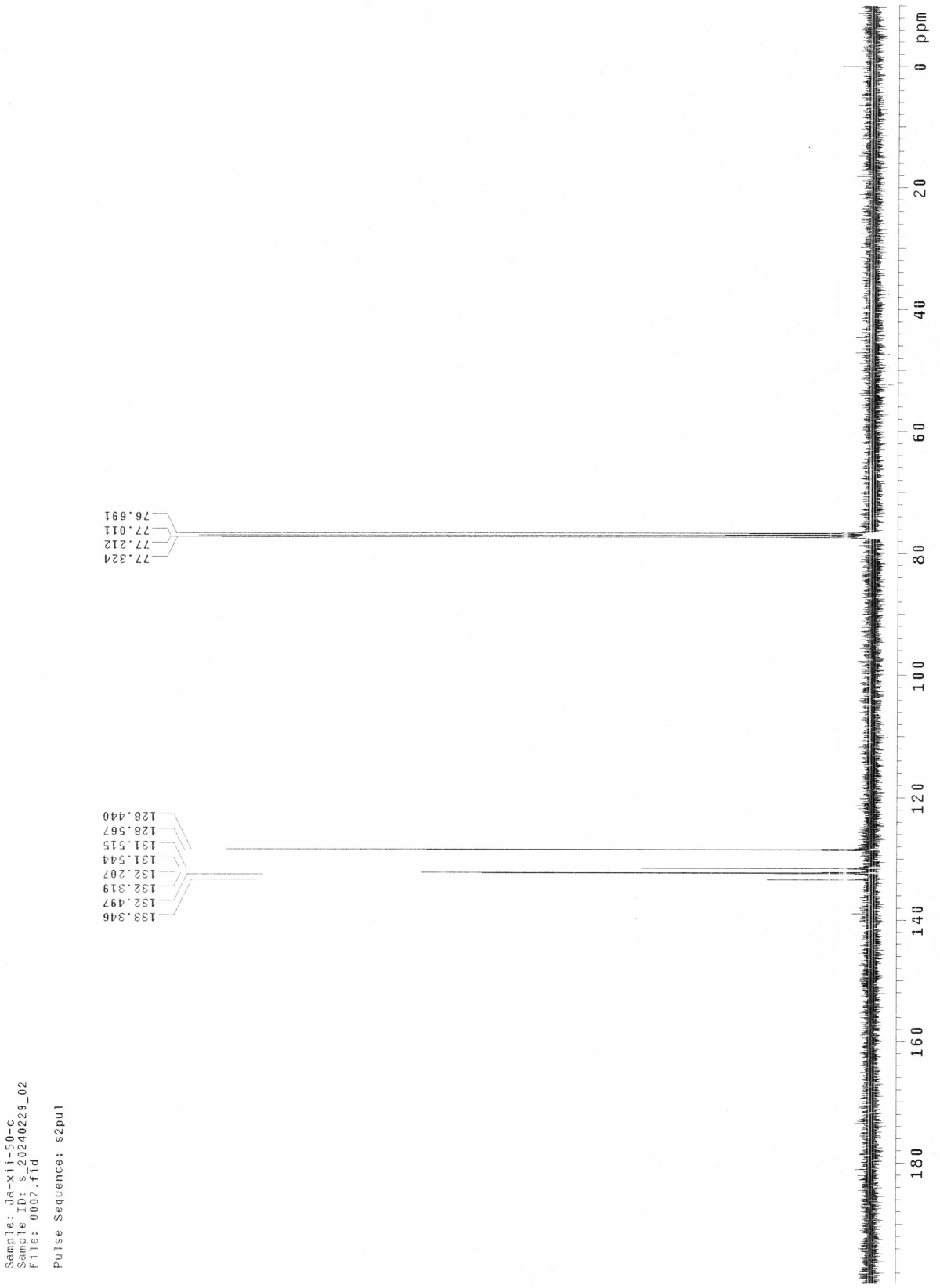
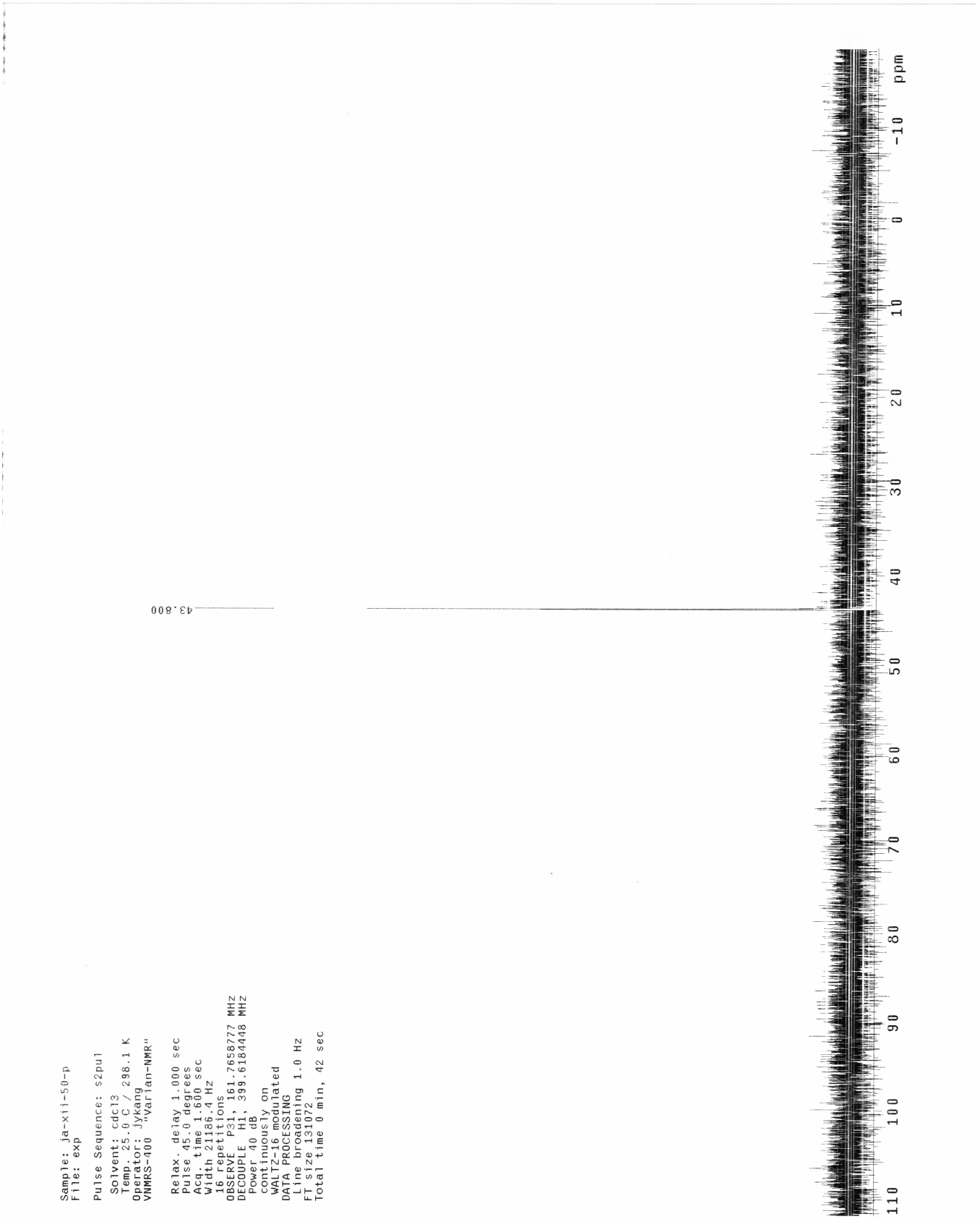
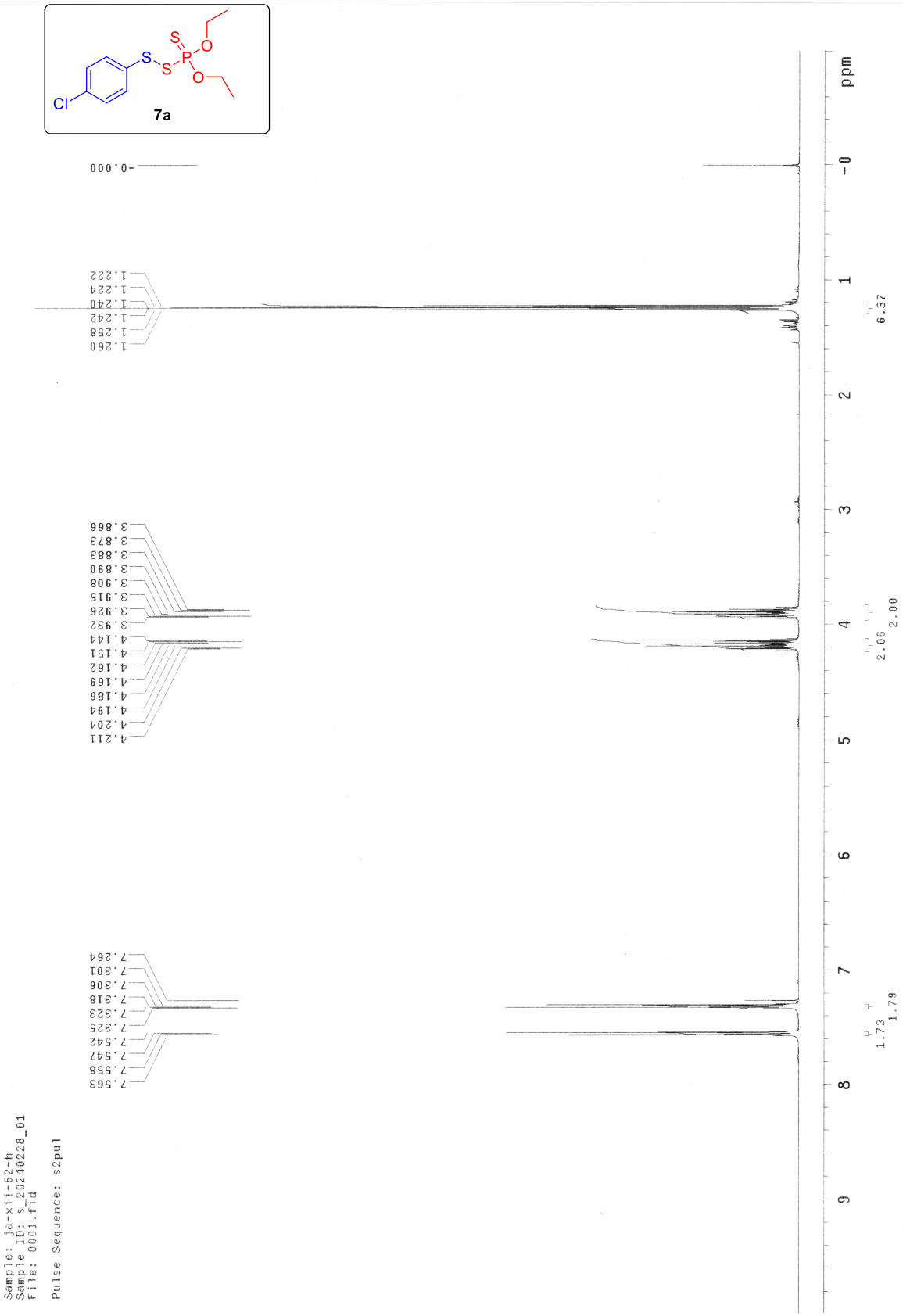


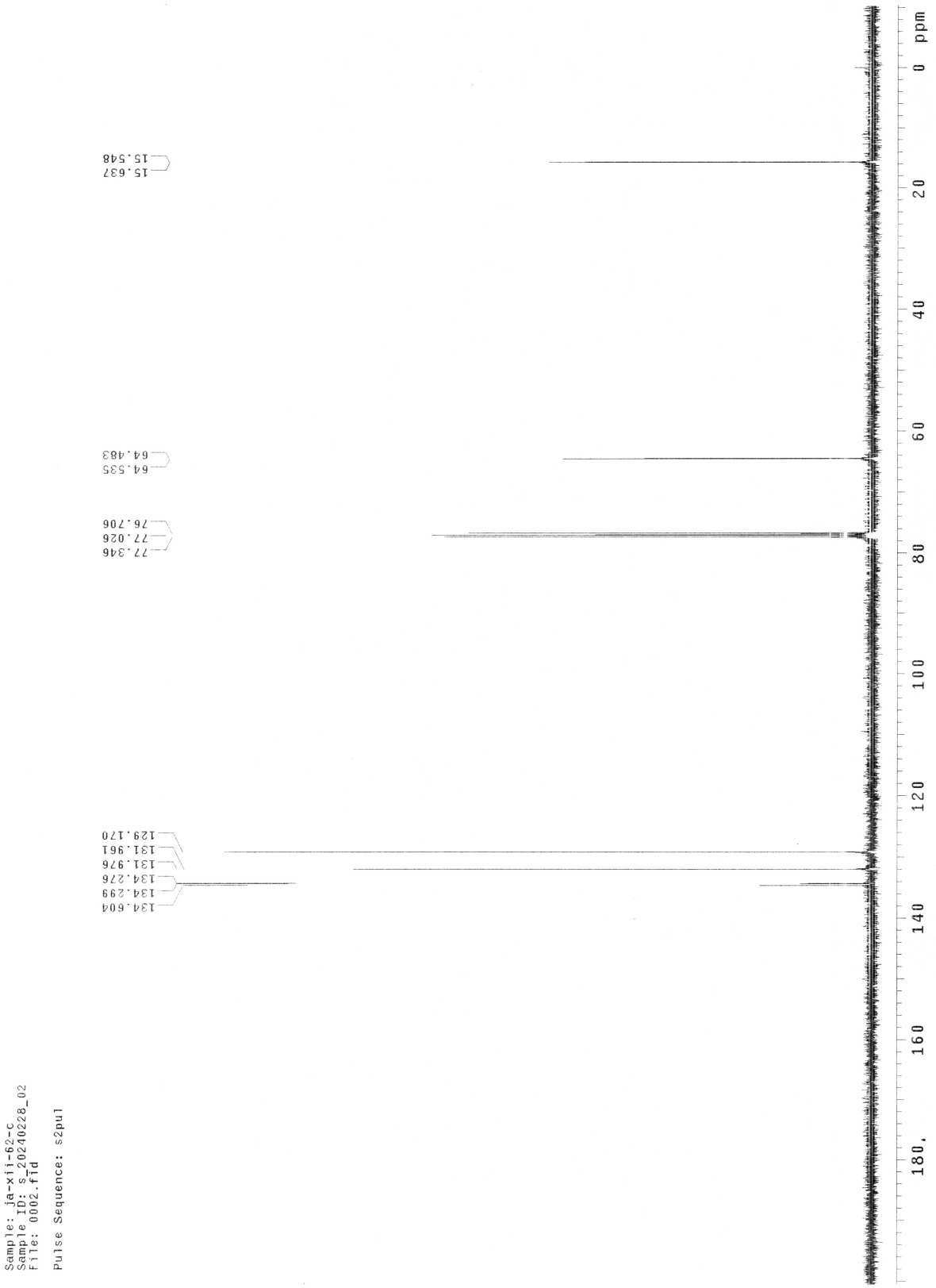
^{31}P NMR (162 MHz) in $CDCl_3$



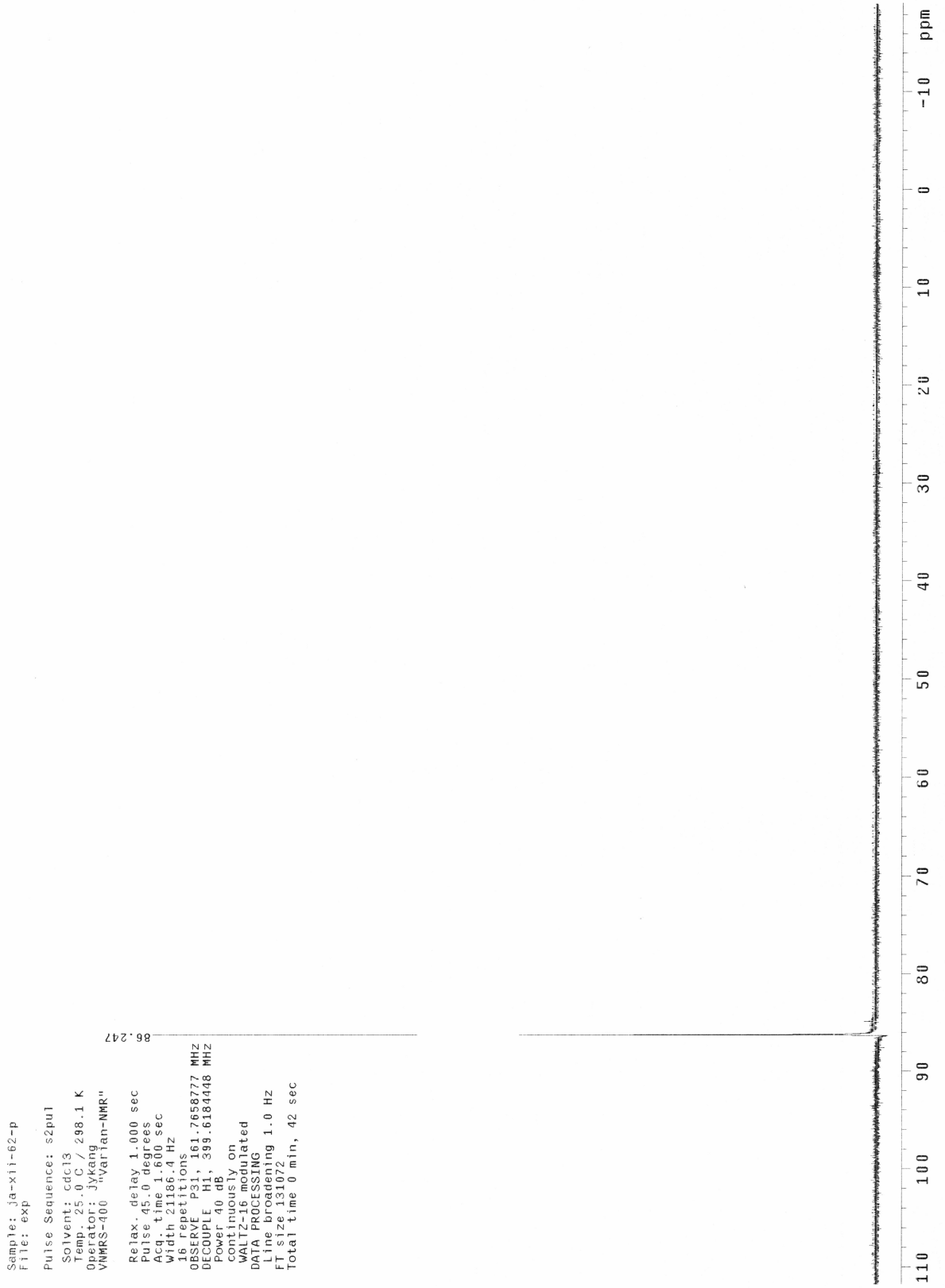
^{1}H NMR (400 MHz) in $CDCl_3$



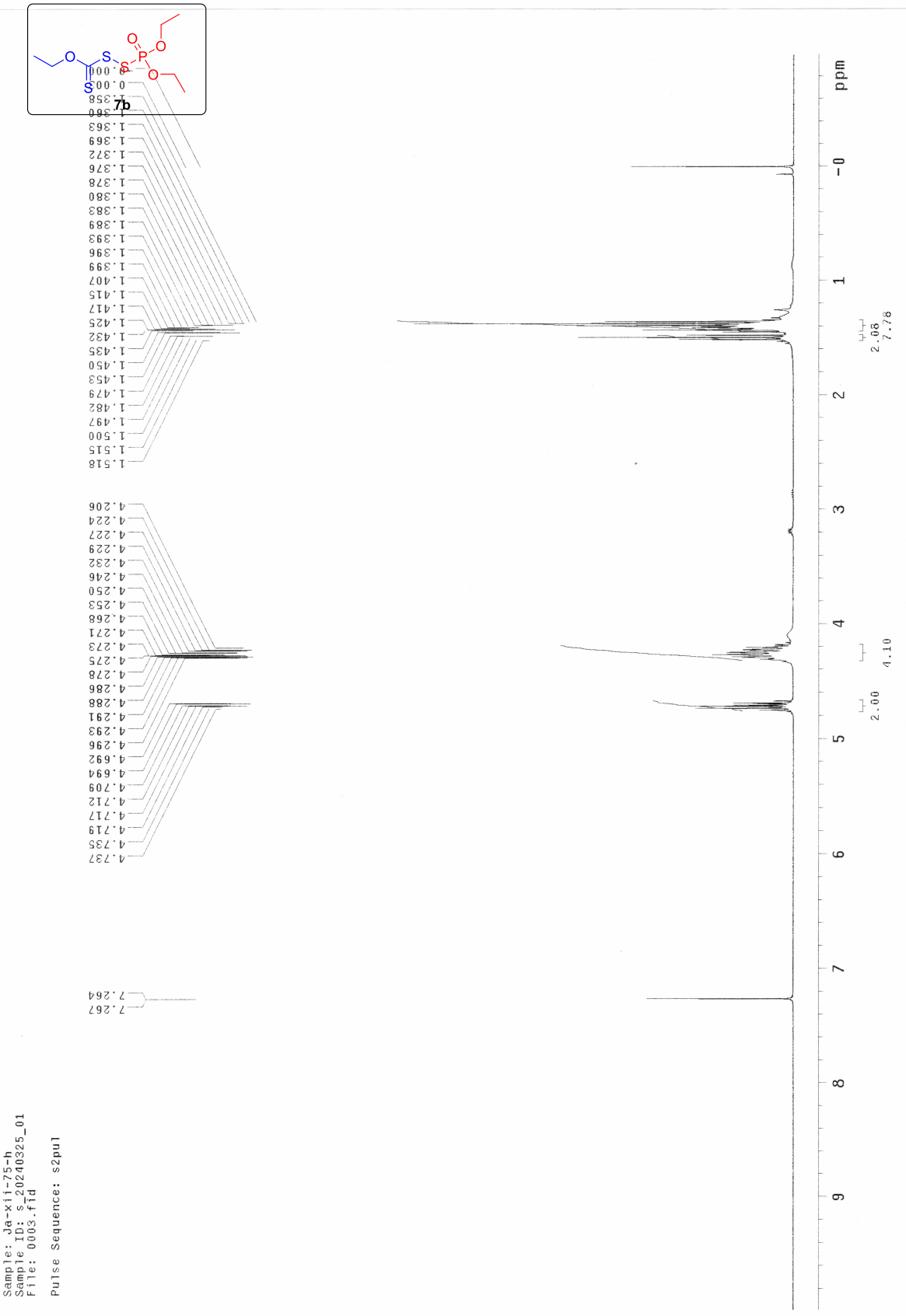
^{13}C NMR (100.5 MHz) in $CDCl_3$



^{31}P NMR (162 MHz) in $CDCl_3$



^{1}H NMR (400 MHz) in $CDCl_3$



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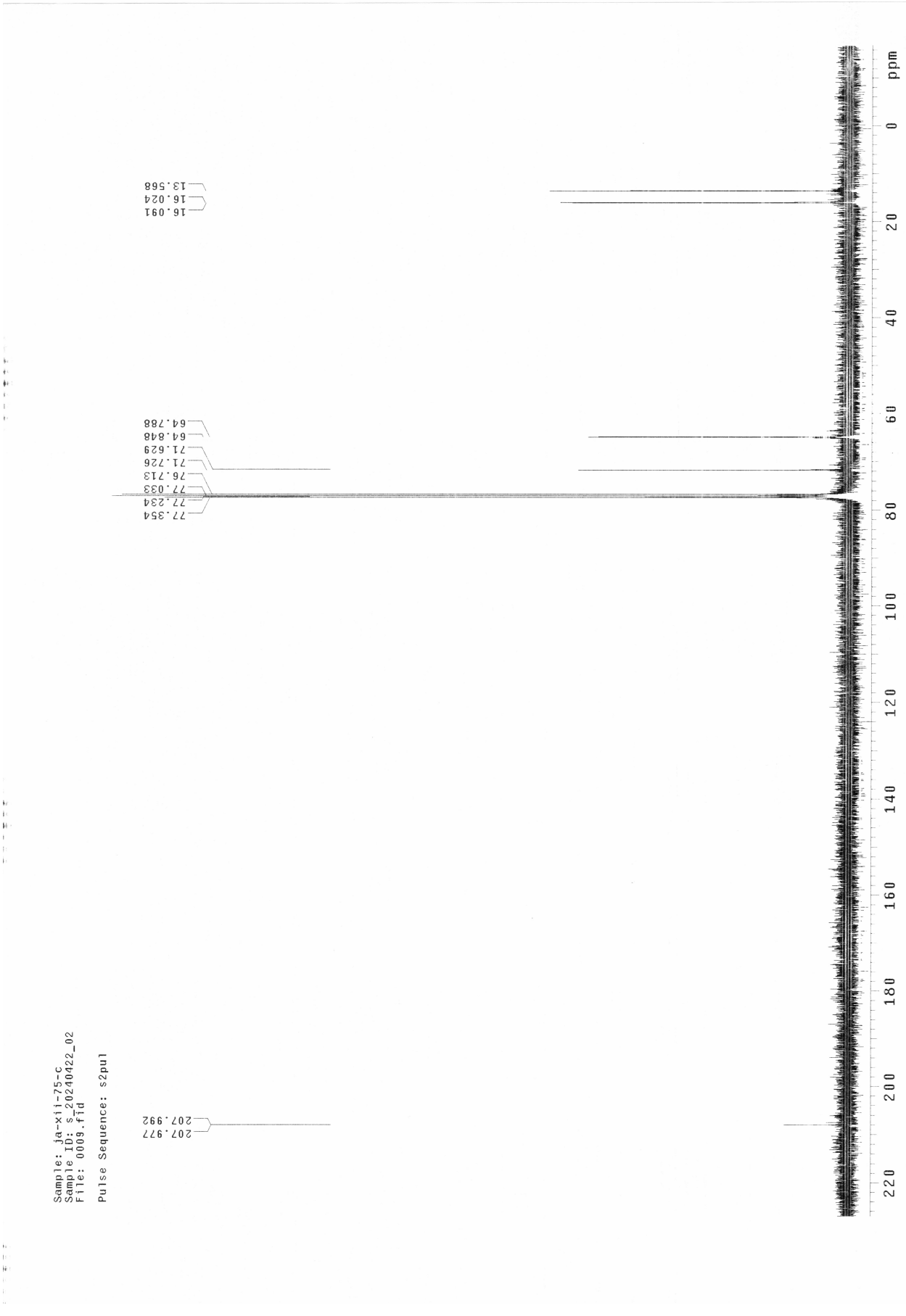

^{31}P NMR (162 MHz) in $CDCl_3$