



Supporting Information

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**Iridium-Catalyzed H/D Exchange at Vinyl Groups
without Olefin Isomerization**

Supporting Information

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General

Unless noted otherwise, all the manipulations were conducted inside an argon-filled dry box at room temperature. Glassware was dried at 130 °C for at least 4 hours. THF, Et₂O, toluene, benzene and pentane were collected from a solvent purification system containing a 1 m column of activated alumina under argon. Quantitative ¹H NMR spectra on deuterium exchange were obtained with a 90° pulse and a delay time of 5 *t*₁ on 500 MHz spectrometers. Chemical shifts were recorded relative to residual protiated solvents (C₆D₆: δ7.15). ¹³C NMR spectra were obtained at 125.8 MHz on a 500 MHz instrument, and chemical shifts were recorded relative to the solvent resonance (C₆D₆: δ128.0). Both ¹H NMR and ¹³C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ³¹P NMR spectra were obtained at 202.2 MHz, and chemical shifts are reported in parts per million downfield of 85% H₃PO₄.

The percentage of H/D exchange in a sample was based on a decrease in the integral of the ¹H NMR signals, as compared to the integral of the corresponding signals in the starting material. The ¹H NMR signals of interest were integrated against a resonance for hydrogens that do not undergo H/D exchange; to obtain these data on 1,3-dihalobenzenes and pyridine, about 3 mg of dry dioxane was added as an integration standard. The positions of deuterium incorporation were confirmed by ²H NMR spectroscopy.

Materials

Unless noted otherwise, reagents were purchased from commercial suppliers. Liquid substrates were purged with argon for at least 10 min in a vial and then dried over activated 4 Å molecular sieves for at least 2 days in a glove box before use. Solid samples were evacuated and refilled with argon when imported into the glove box. 1-Allyl-1-aminomethylcyclohexane,¹ 2,5-dimethyl-1-hexen-5-ol,² iridium complexes (D'BPP)Ir(H)(NH₂) **1**,³ **2**,⁴ **4**,⁵ **5**,⁶ and (D'BPP)RhHCl⁷ were synthesized according to reported procedures. Dry C₆D₆ was distilled from sodium/benzophenone ketyl, degassed by three cycles of freeze-thaw and stored in the glove box. 2,5-Dimethylpyrrole was freshly distilled under argon before use. Silica gel 60 with 230-400 mesh was purchased from EMD Chemicals (lot TA1165285303; pH 6.8).

Synthesis of (D'BPP)Rh(NH₃) **3**

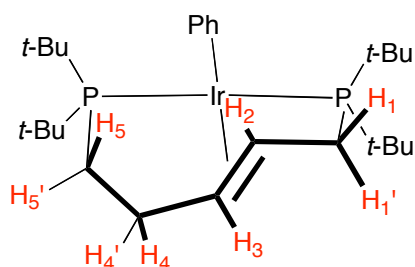
In an argon-filled dry box, solid KHMDS (44 mg, 0.22 mmol) was added to a suspension of (D'BPP)RhHCl (100 mg, 0.20 mmol) in dry pentane (3 mL) in a 20 mL vial fitted with a cap containing a Teflon-lined septum. The stirred yellow suspension was then purged with excess, dry ammonia gas. After stirring for 5 min under the ammonia atmosphere, the yellow suspension was filtered through a Gelman Acrodisc containing a 0.2 µm PTEE membrane, and was washed with pentane. The yellow filtrate was concentrated to about 2 mL and stored at -30 °C overnight to give 65% yield of orange needles of pure **3** (60 mg). ¹H NMR (500 MHz, C₆D₁₂) _ 1.98-1.82 (m, 3H), 1.74-1.56 (m, 5H), 1.30 (t, *J* = 5.5 Hz, 18H), 1.26 (t, *J* = 5.5 Hz, 18H), 1.36-1.06 (m, 4H; overlapping with the triplets at _ 1.30 and _ 1.26); ¹³C NMR (500 MHz, C₆D₁₂) _ 42.5 (d, *J* = 29.4 Hz), 41.2 (t, *J* = 8.3 Hz, two superimposed quaternary carbons of the *tert*-butyl groups), 36.2 (m), 35.0 (m), 30.8 (t, *J* = 3.7 Hz), 30.4 (t, *J* = 4.6 Hz); ³²P NMR (500 MHz, C₆D₁₂) _ 81.3 (d, *J* = 184.6 Hz). Anal. Calcd for C₂₁H₄₈NP₂Rh: C, 52.61; H, 10.09; N, 2.92. Found: C, 53.01; H, 10.35; N, 3.12.

General Procedure for the Catalytic H/D Exchange

Unless otherwise stated, in an argon-filled glove box, a screw-capped NMR tube was charged with the substrate (0.20 mmol), C₆D₆ (0.50 mL), and finally iridium catalyst **1** (5.6 mg, 0.010 mmol). The tube was tightly capped and then vigorously shaken to give an orange solution. After standing for an indicated period of time at room temperature or 50 °C, the reaction mixture was exposed to air and passed through a short plug of silica gel with C₆D₆ washings to remove iridium complexes. The filtrate was pure by ¹H and ¹³C NMR spectroscopy in all cases, except for the exchanged product of 1-aminomethyl-1-allylcyclohexane. This product contained a majority of the iridium catalyst, but these signals did not interfere with integration of the vinylic hydrogens. ¹H, ²H and ¹³C NMR spectra of the deuterated products are provided as part of supporting materials.

The reactions with cyclohexene and methylenecyclohexane were conducted in sealed tubes. For 2,5-dimethylpyrrole, the percentage of deuterium incorporation was recorded before filtration through a silica gel plug because some deuterium was lost during filtration. The exchange with tiamulin was conducted with 5% catalyst **1** on a 0.1 mmol scale; the exchange with Altrenogest was conducted with 10% **1** on a 0.1 mmol scale; and the exchange with forskolin was conducted with 10% **1** on a 0.018 mmol scale.

Synthesis of [(*t*-Bu)₂PCH₂CH₂CH=CHCH₂P(*t*-Bu)₂][IrPh] **7**



In an argon-filled dry box, (D'BPP)IrH₄ **2** (56 mg, 0.10 mmol) was stirred with 2-norbornene (47 mg, 0.50 mmol) in 2.0 mL of dry C₆H₆ at room temperature for 12 h. The solvent was then slowly evaporated under vacuum to give a quantitative yield of the desired product **7** as an orange powder (63 mg). The complex is insoluble in C₆D₁₂ in the absence of trace C₆H₆. The proton and carbon signals were assigned with the aid of a combination of DEPT-135, COSY, C-H HMQC and selective ³¹P-decoupled ¹H NMR spectroscopy. ¹H NMR (500 MHz, C₆D₁₂; additional C₆H₆ peak at δ 7.25) δ 7.60 (br s, **H_{ortho}**), 7.37 (br s, **H'_{ortho}**), 6.86 (t, J = 7.2 Hz, **2H_{meta}**), 6.48 (d, J = 6.3 Hz, **H_{para}**), 3.54 (dd, J = 9.7, 6.1 Hz, **H3**), 3.08 (m, **H1**), 2.58 (ddd, J = 15.2, 7.4, 2.0 Hz, **H1'**), 2.01 (m, **H4**), 1.92 (m, 1H, **H2**), 1.76 (m, **H5'**), 1.34-1.24 (m, **H4'**, overlapping with *CMe*₃ at δ 1.28), 1.28 (d, J = 11.8 Hz, 9H, *CMe*₃), 1.25 (d, J = 12.6 Hz, 9H, *CMe*₃), 1.19 (d, J = 12.4 Hz, 9H, *CMe*₃), 1.13-1.00 (m, **H5**, overlapping with *CMe*₃ at δ 1.04), 1.04 (d, J = 12.0 Hz, 9H, *CMe*₃); ¹³C NMR (500 MHz, C₆D₁₂; additional C₆H₆ peak at δ 128.7) δ 170.7 (s, **C_{ipso}**), 140.8 (br s, **C_{ortho}**), 139.0 (br s, **C'_{ortho}**), 126.7 (br s, **C_{meta}**), 120.7 (s, **C_{para}**), 66.1 (s, **C3**), 37.2 (d, J = 16.6 Hz, *CMe*₃), 35.6 (d, J = 20.5 Hz, *CMe*₃), 34.4 (d, J = 14.7 Hz, *CMe*₃), 34.1 (s, *CMe*₃), 33.1 (d, J = 25.4 Hz, **C1**), 30.8 (d, J = 3.9 Hz, *CMe*₃), 30.5 (two overlapping *CMe*₃ peaks), 30.3 (d, J = 3.7 Hz, **C2**), 30.0 (d, J = 3.9 Hz, *CMe*₃), 29.3 (d, J = 9.8 Hz, **C4**), 22.9 (d, J = 22.5 Hz, **C5**); ³²P NMR (500 MHz, C₆D₁₂) δ 65.7 (d, J = 340.3

Hz), -33.5 (d, $J = 340.3$ Hz). Anal. Calcd for $C_{27}H_{49}IrP_2$: C, 51.65; H, 7.87. Found: C, 51.88; H, 8.06.

H/D exchange of $[(t\text{-Bu})_2PCH_2CH_2CH=CHCH_2P(t\text{-Bu}_2)]IrPh$ **7** with C_6D_6

In an argon-filled dry box, $[(t\text{-Bu})_2PCH_2CH_2CH=CHCH_2P(t\text{-Bu}_2)]IrPh$ **7** (7.0 mg, 0.011 mmol) was dissolved in 0.70 mL of C_6D_{12} in a screw-capped NMR tube. Then C_6D_6 (18 mg, 0.21 mmol) was added and mixed well by vigorous shaking. After 5 min at room temperature, a 1H NMR spectrum was acquired. The Ir-Ph and C-3 hydrogens were >95% deuterated. After an additional 5 min, a second 1H NMR spectrum was acquired. An identical 1H NMR spectrum was obtained, indicating that the exchange has reached equilibrium. The positions of deuteration were confirmed by 2H NMR spectroscopy.

The solvents of the above deuterated sample were evaporated under vacuum, and the yellow solid residue $d_6\text{-7}$ was then dissolved in 0.70 mL of C_6D_{12} and C_6H_6 (45 mg, 0.63 mmol). After 5 min at room temperature a 1H NMR spectrum was acquired. Greater than 95% 1H signal intensity of the Ir-Ph and C-3 hydrogens was observed. The loss of deuterium at the Ir-Ph and C-3 positions was confirmed by 2H NMR spectroscopy.

Comparison of $(D^tBPP)Ir(H)(NH_2)$ **1** and $[(t\text{-Bu})_2PCH_2CH_2CH=CHCH_2P(t\text{-Bu}_2)]IrPh$ **7** as catalysts in H/D exchange of *t*-butylethylene.

$(D^tBPP)Ir(H)(NH_2)$ **1** (5.7 mg, 0.010 mmol) or $[(t\text{-Bu})_2PCH_2CH_2CH=CHCH_2P(t\text{-Bu}_2)]IrPh$ **7** (6.3 mg, 0.010 mmol) was dissolved in 0.5 mL of C_6D_6 in a screw-capped NMR tube. *t*-Butylethylene (17 mg, 0.20 mmol) was introduced via a microsyringe, and the resulting orange solution was shaken vigorously. Aliquots were removed at intervals from the reaction mixture in the glove box and quenched by passing through a plug of silica gel with C_6D_6 in air. The extent of substrate deuteration was determined by quantitative 1H NMR spectroscopy (see attached 1H NMR spectra). After 20 min at room temperature, the resting state of the catalyst in the reactions initiated by **1** was determined to be a 4.5:1 mixture of **1** and **7** by ^{31}P NMR spectroscopy. The resting state of the catalyst in reactions initiated with **7** after 2 h at room temperature was determined by ^{31}P NMR spectroscopy to be **7**.

References

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Supporting Information

Part II. ^1H , ^2H and ^{13}C NMR Spectra

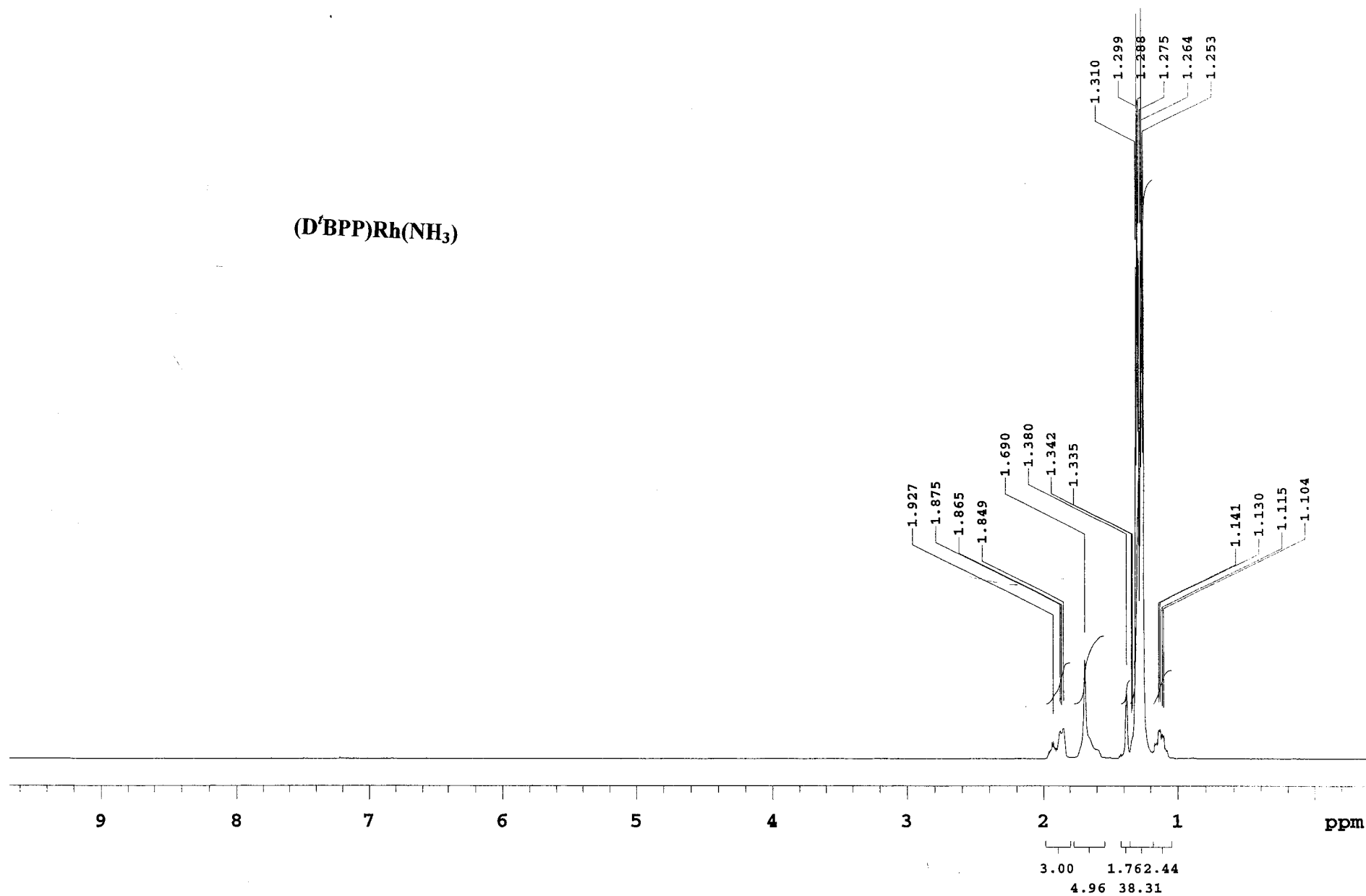
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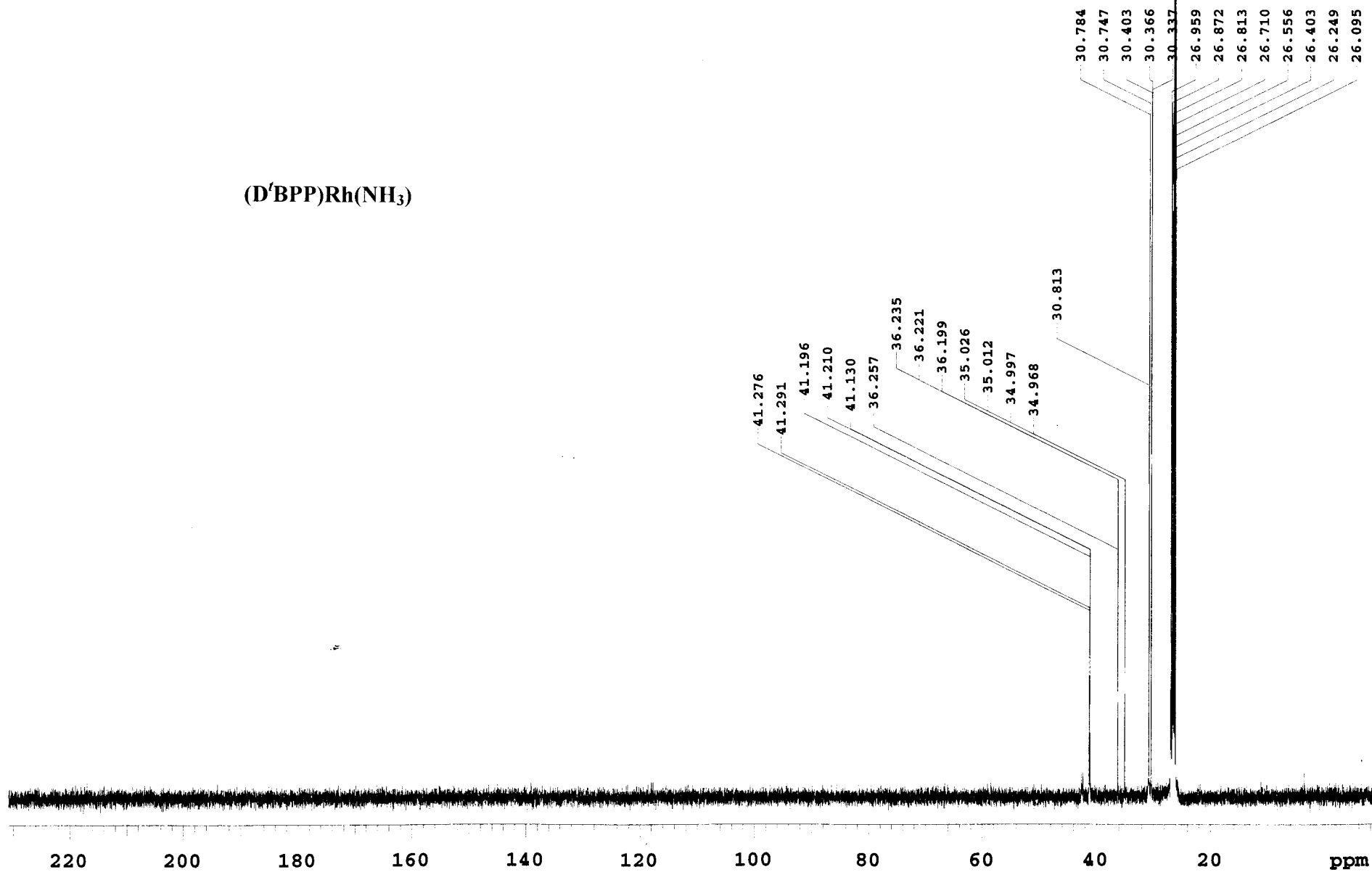
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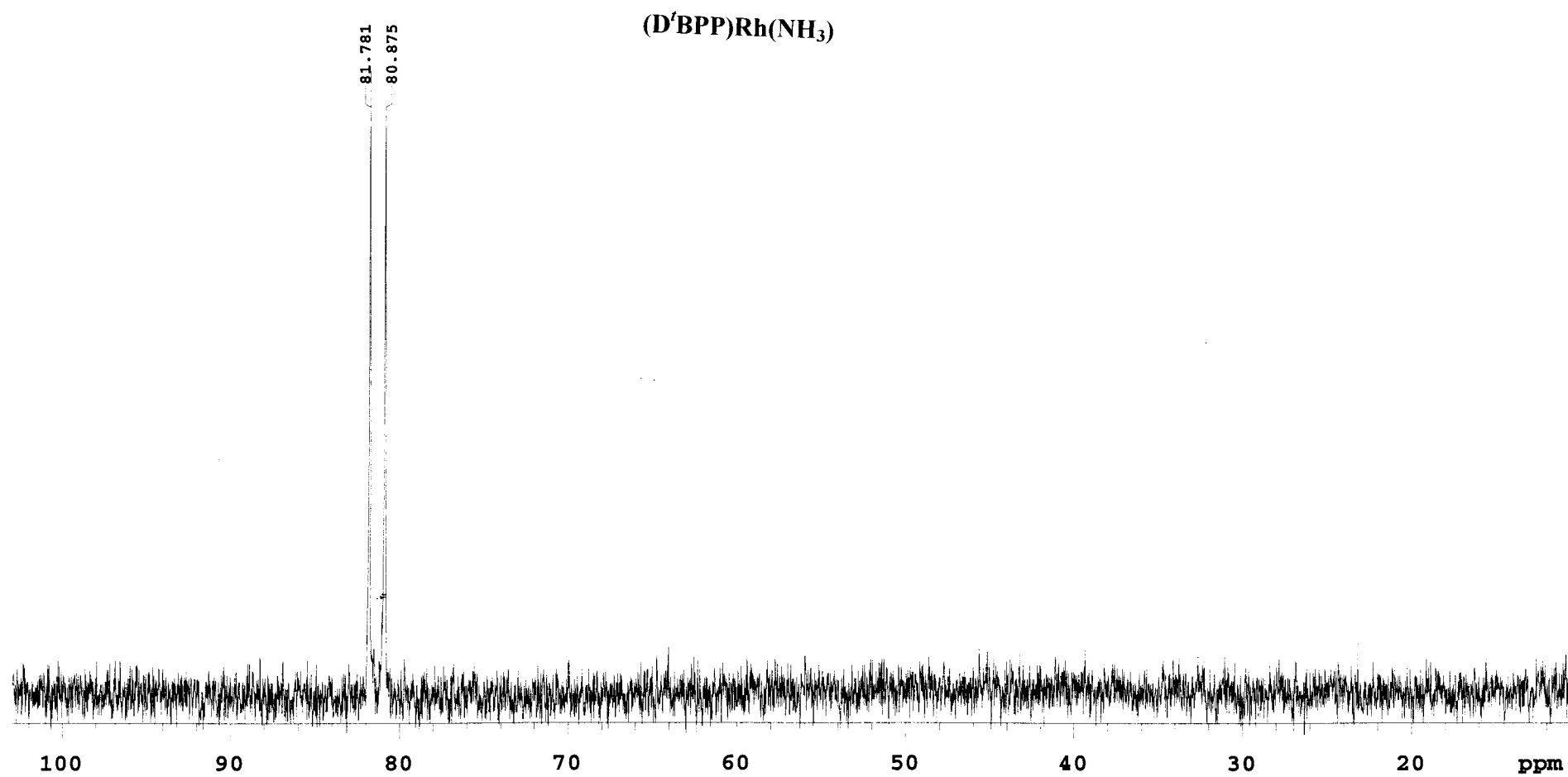
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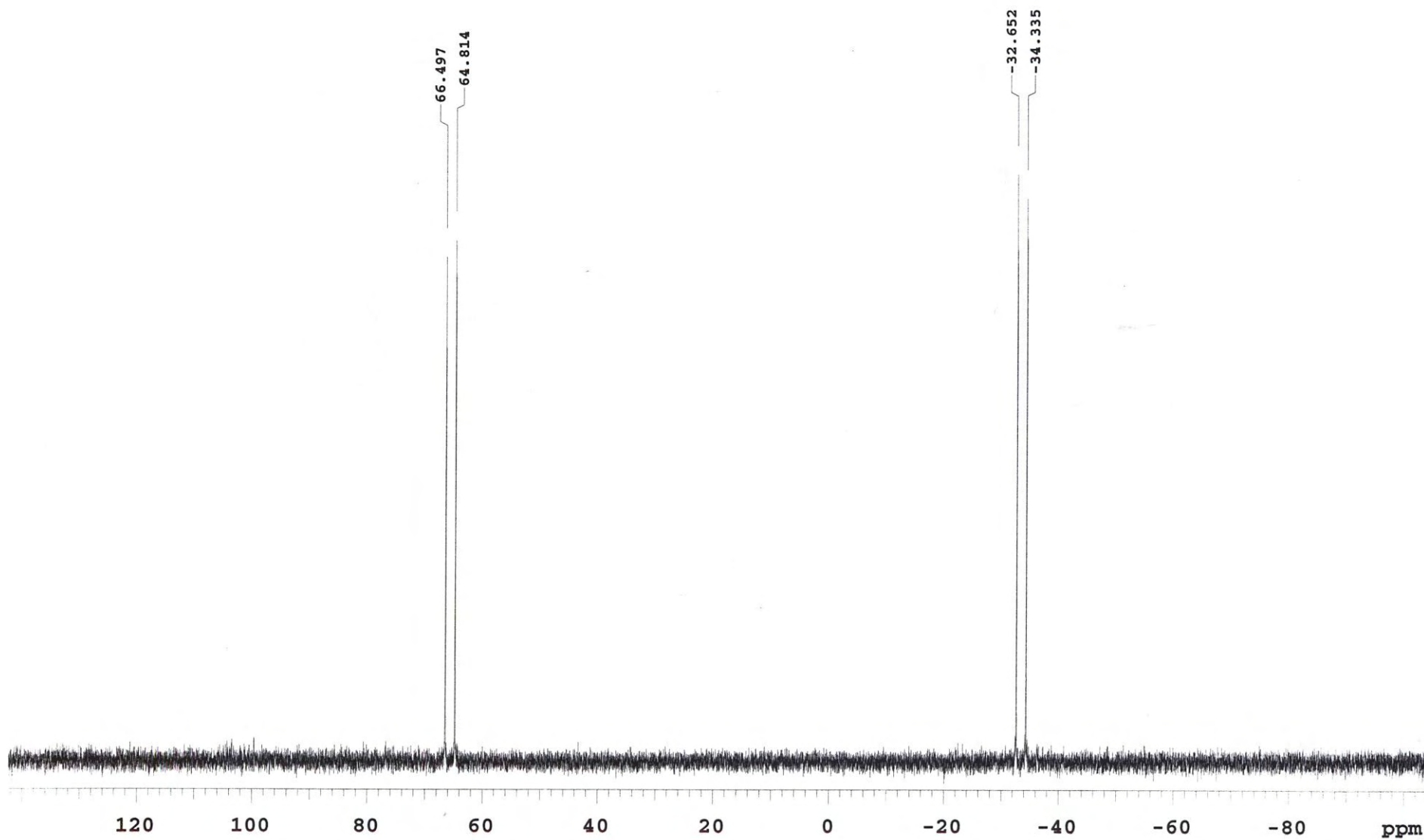
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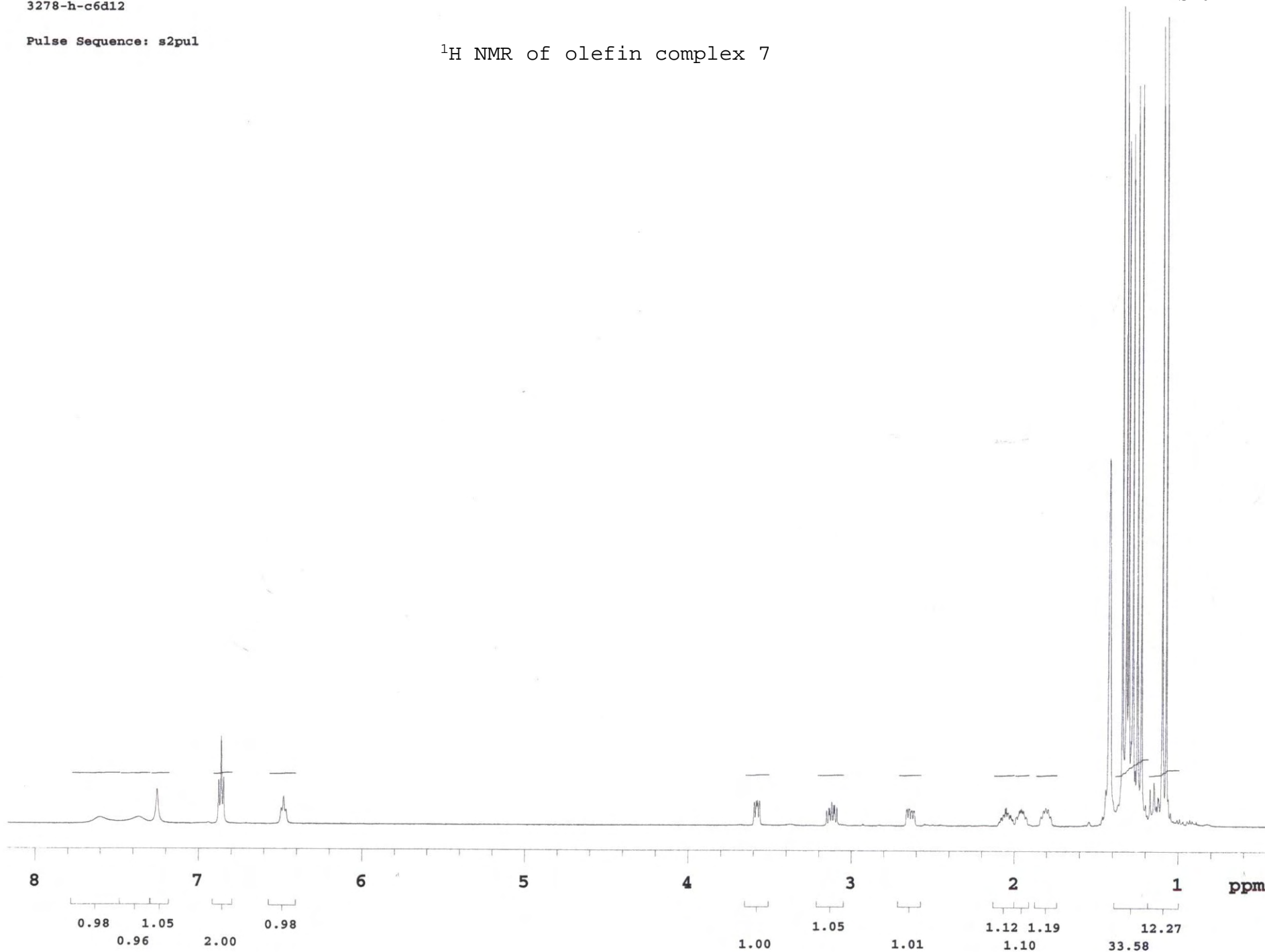
 ^{31}P NMR of olefin complex 7

3278-h-c6d12

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^1H NMR of olefin complex 7

S10

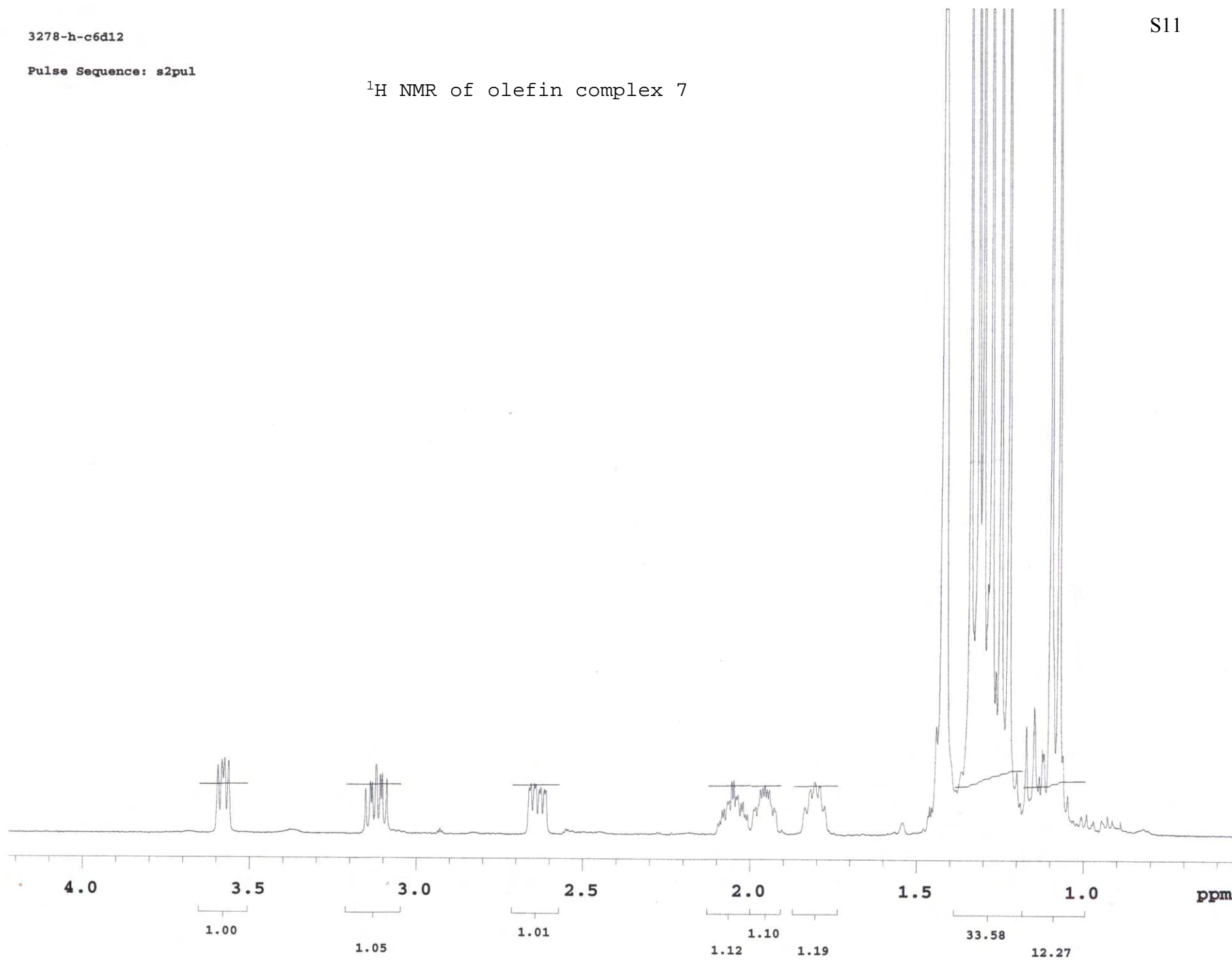


3278-h-c6d12

S11

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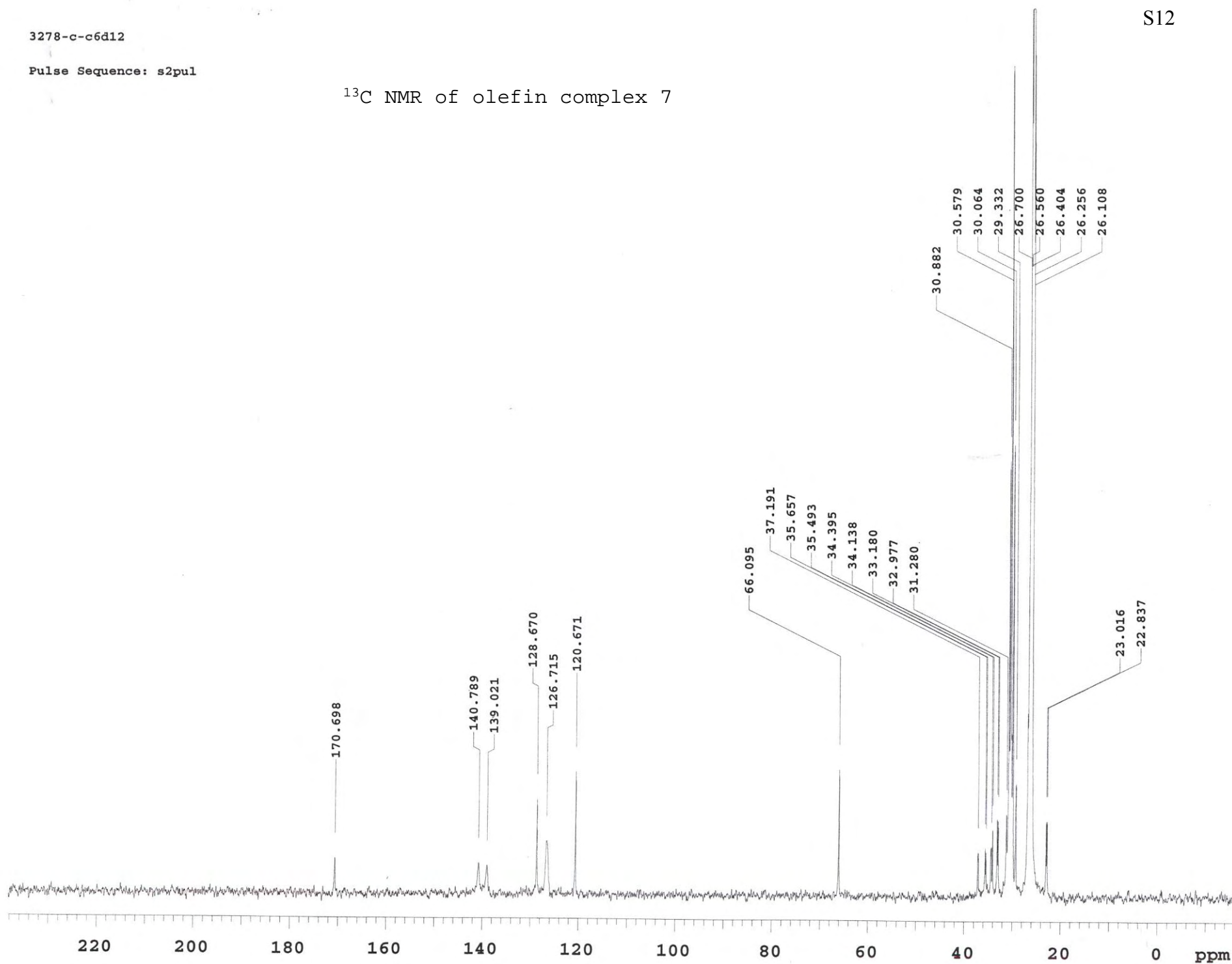


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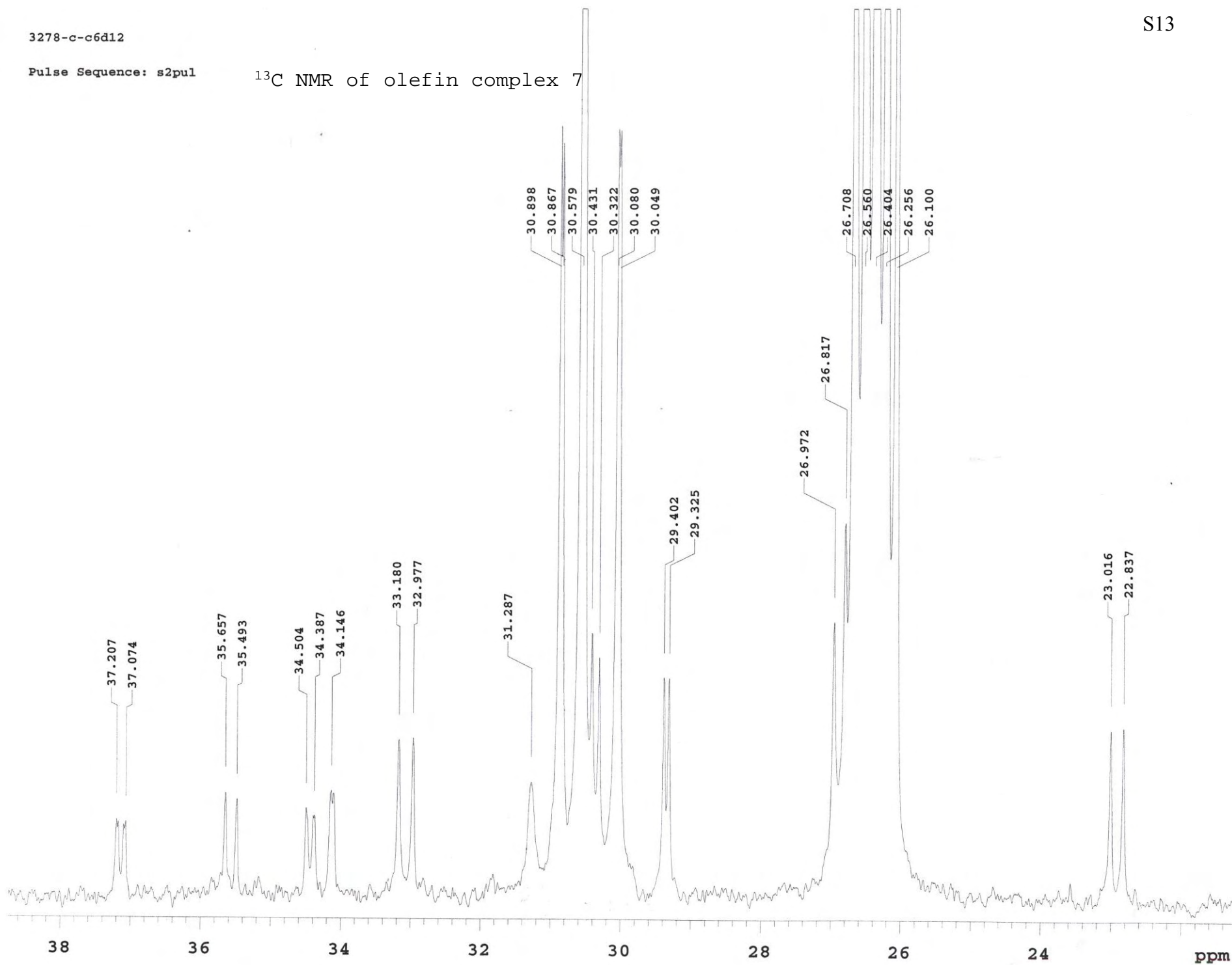
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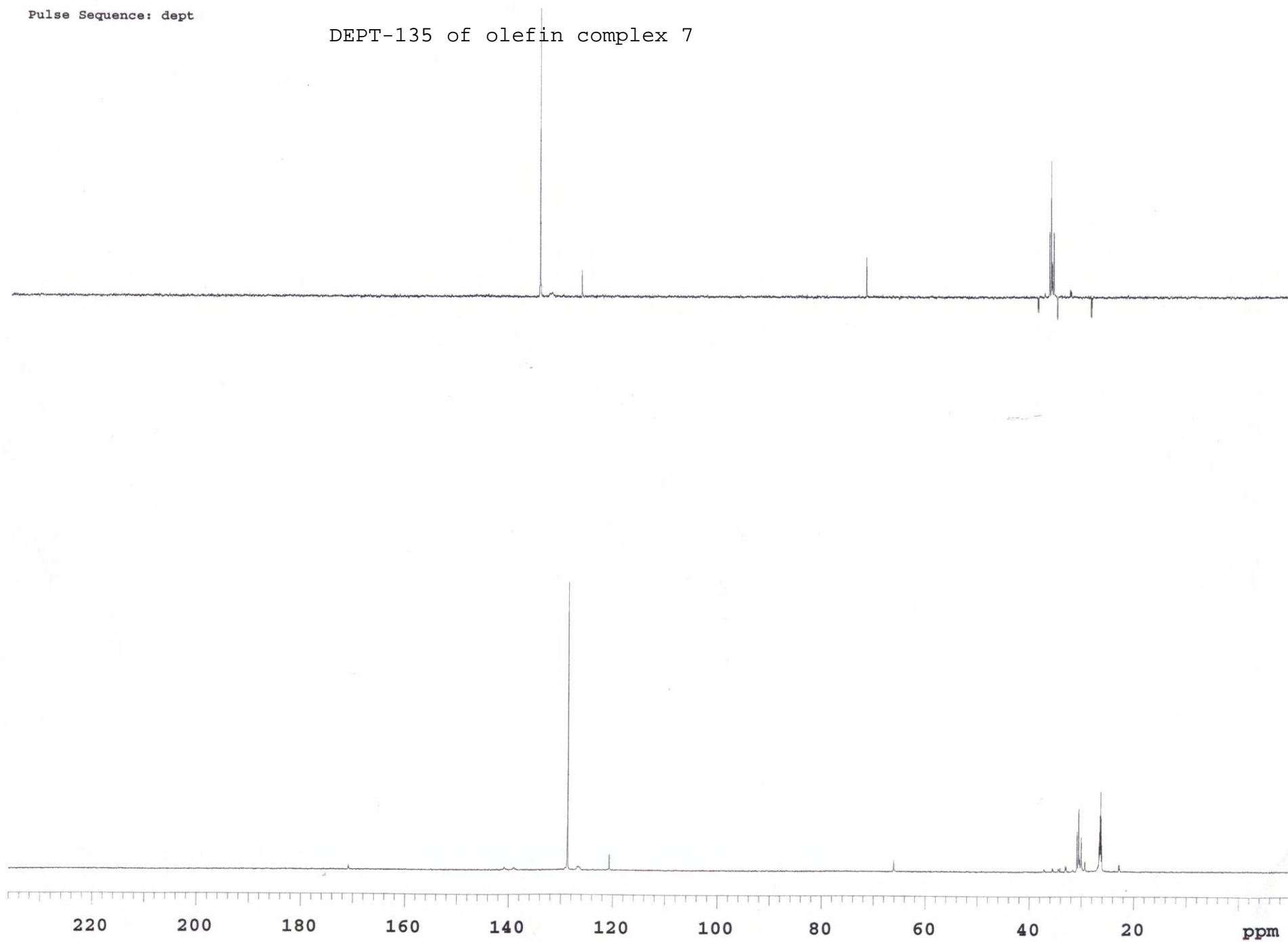
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 ^{13}C NMR of olefin complex 7

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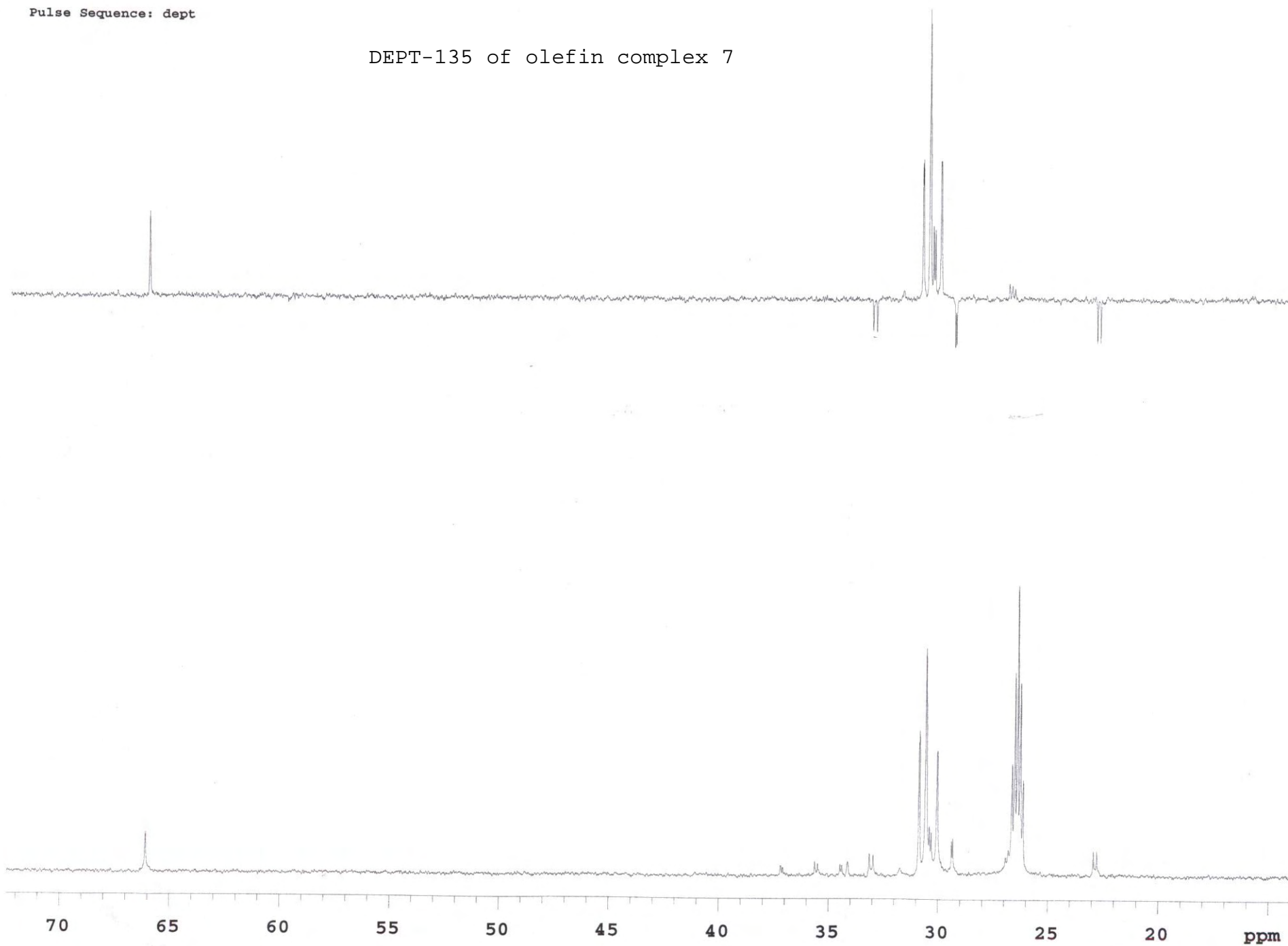
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DEPT-135 of olefin complex 7



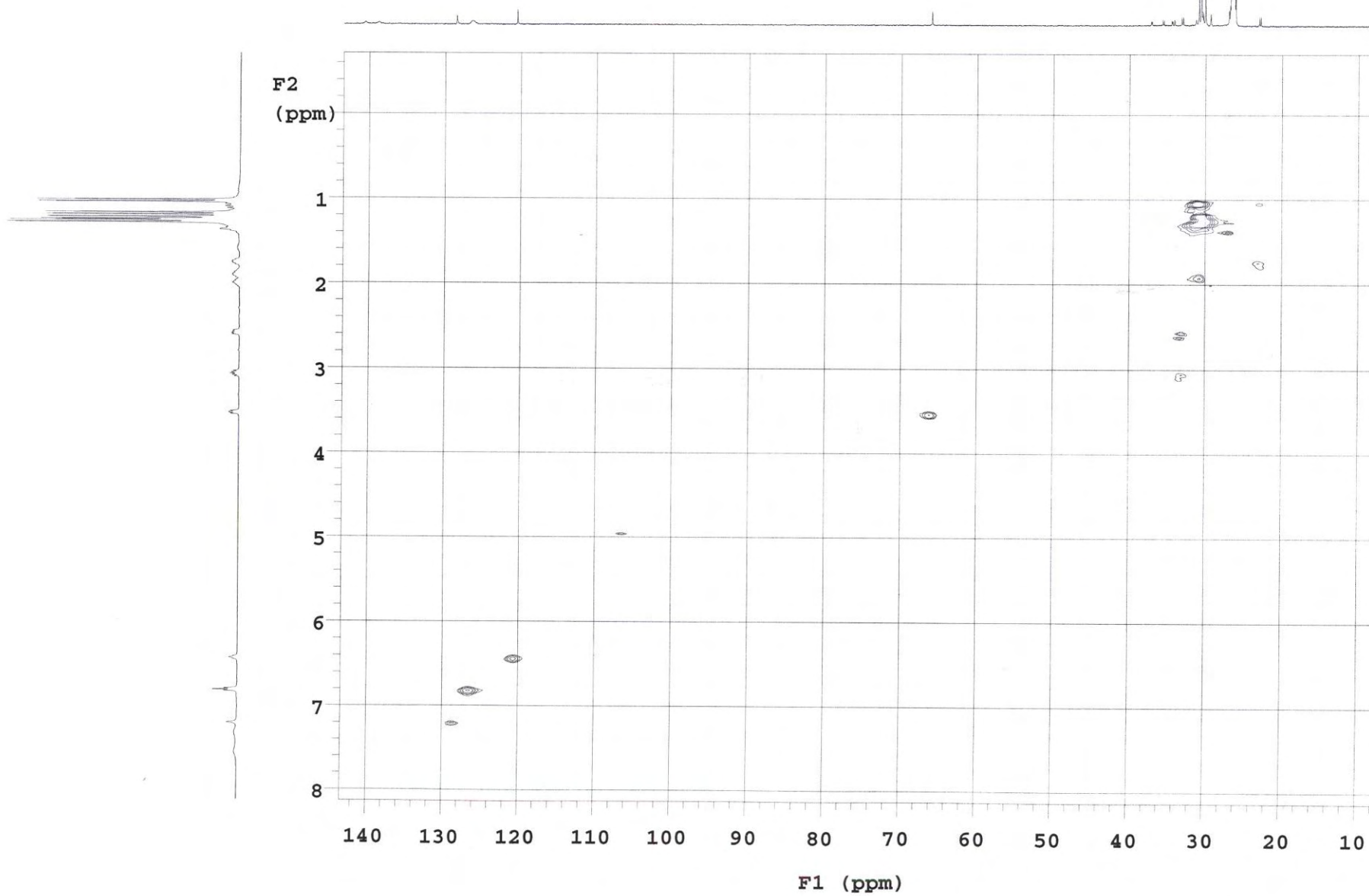
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DEPT-135 of olefin complex 7



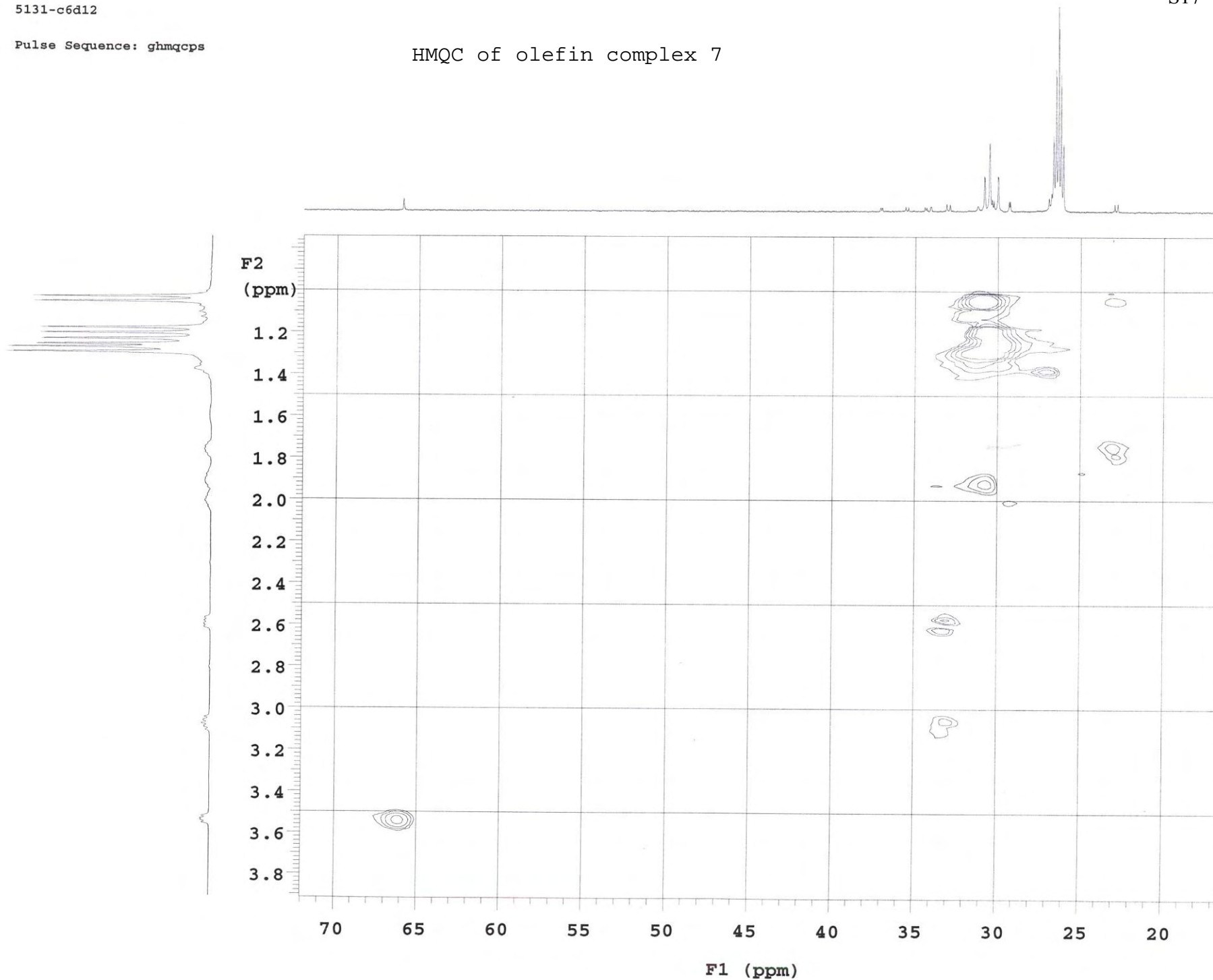
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HMQC of olefin complex 7



Pulse Sequence: ghmqcps

HMQC of olefin complex 7



STANDARD PROTON PARAMETERS

Pulse Sequence: gcosy

Solvent: cyclohexane

Ambient temperature

INOVA-500 "ui500nb"

Relax. delay 1.000 sec

Acq. time 0.126 sec

Width 4070.8 Hz

2D Width 4070.8 Hz

4 repetitions

169 increments

OBSERVE H1, 500.0706944 MHz

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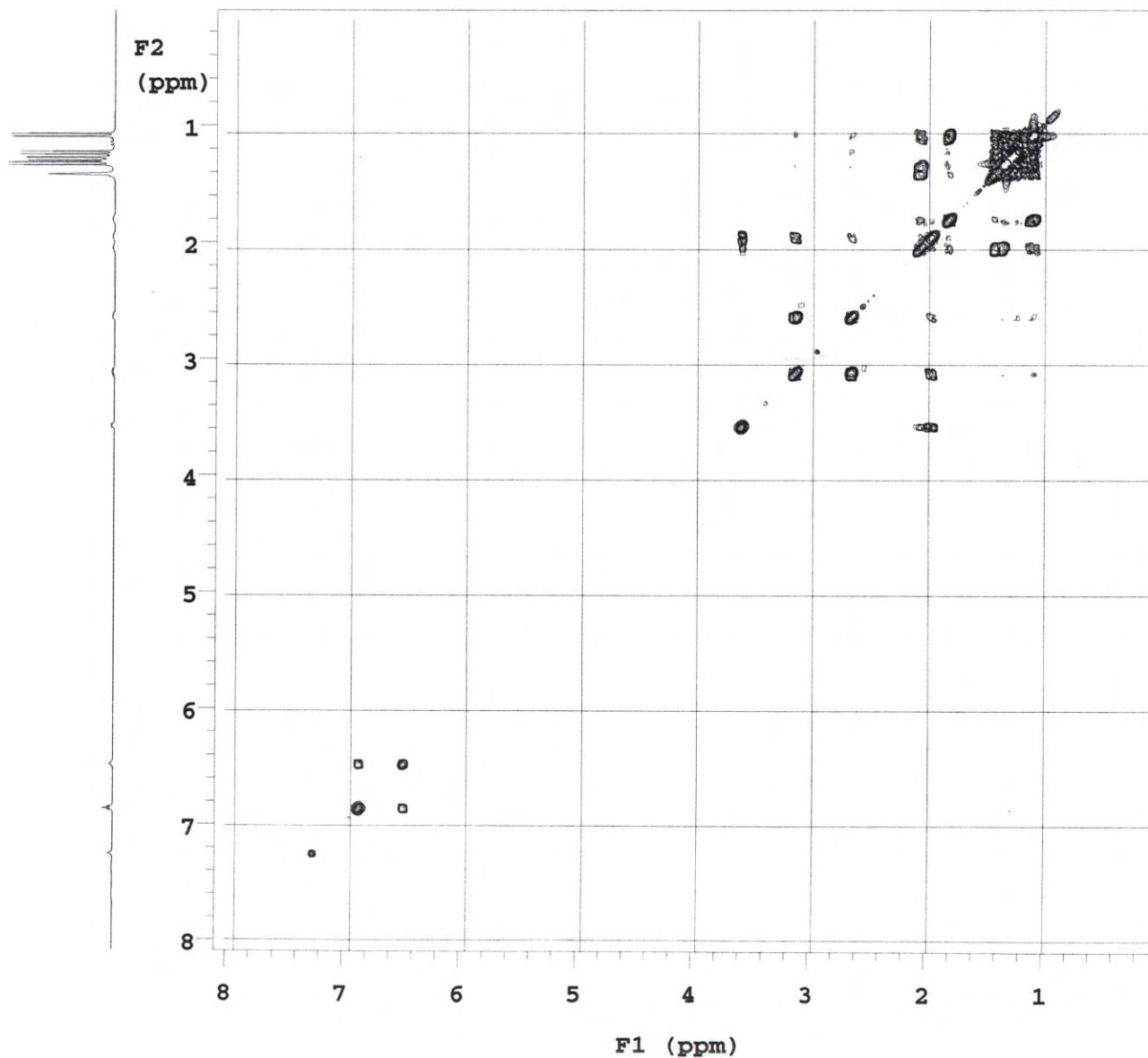
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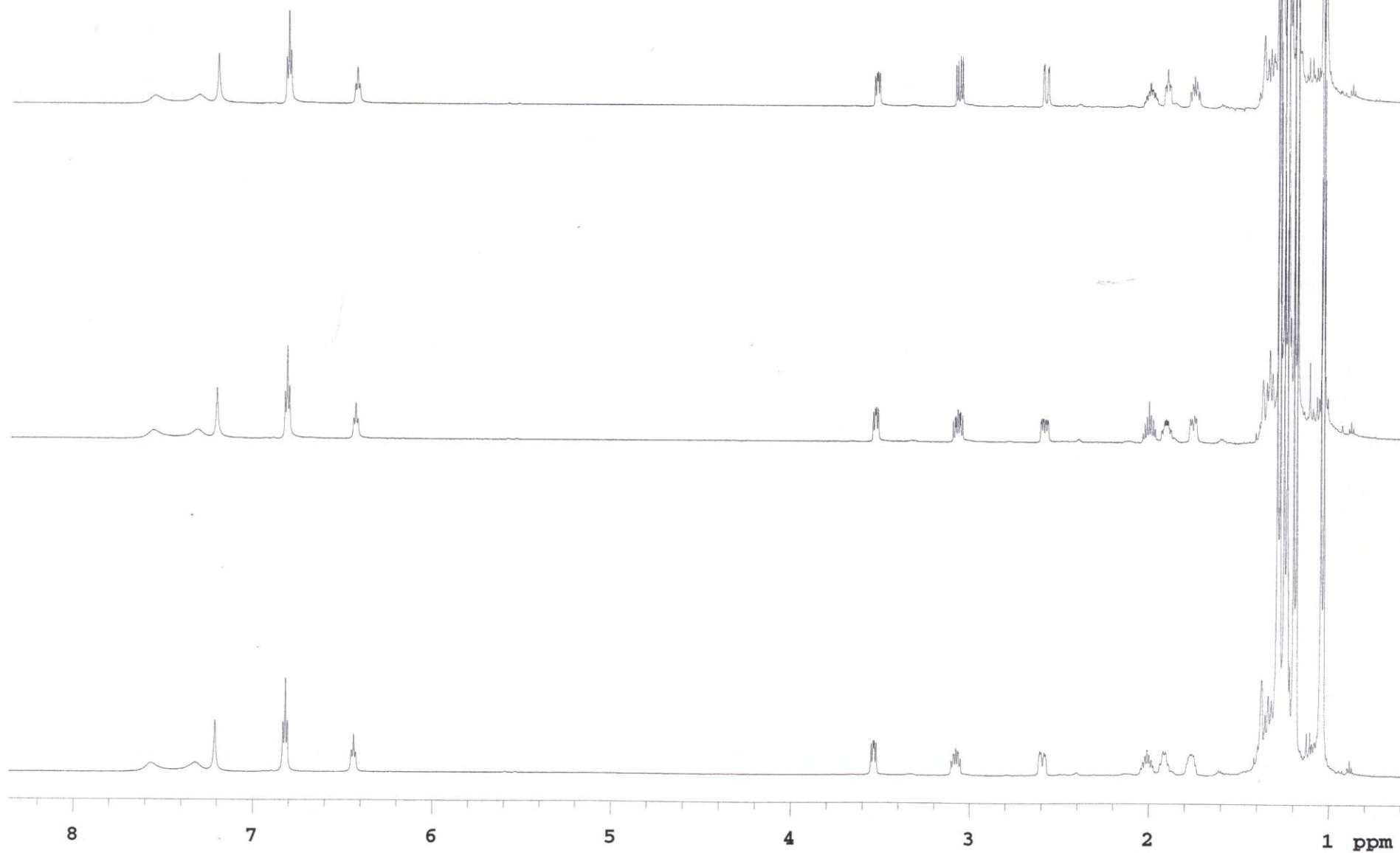
COSY of olefin complex 7



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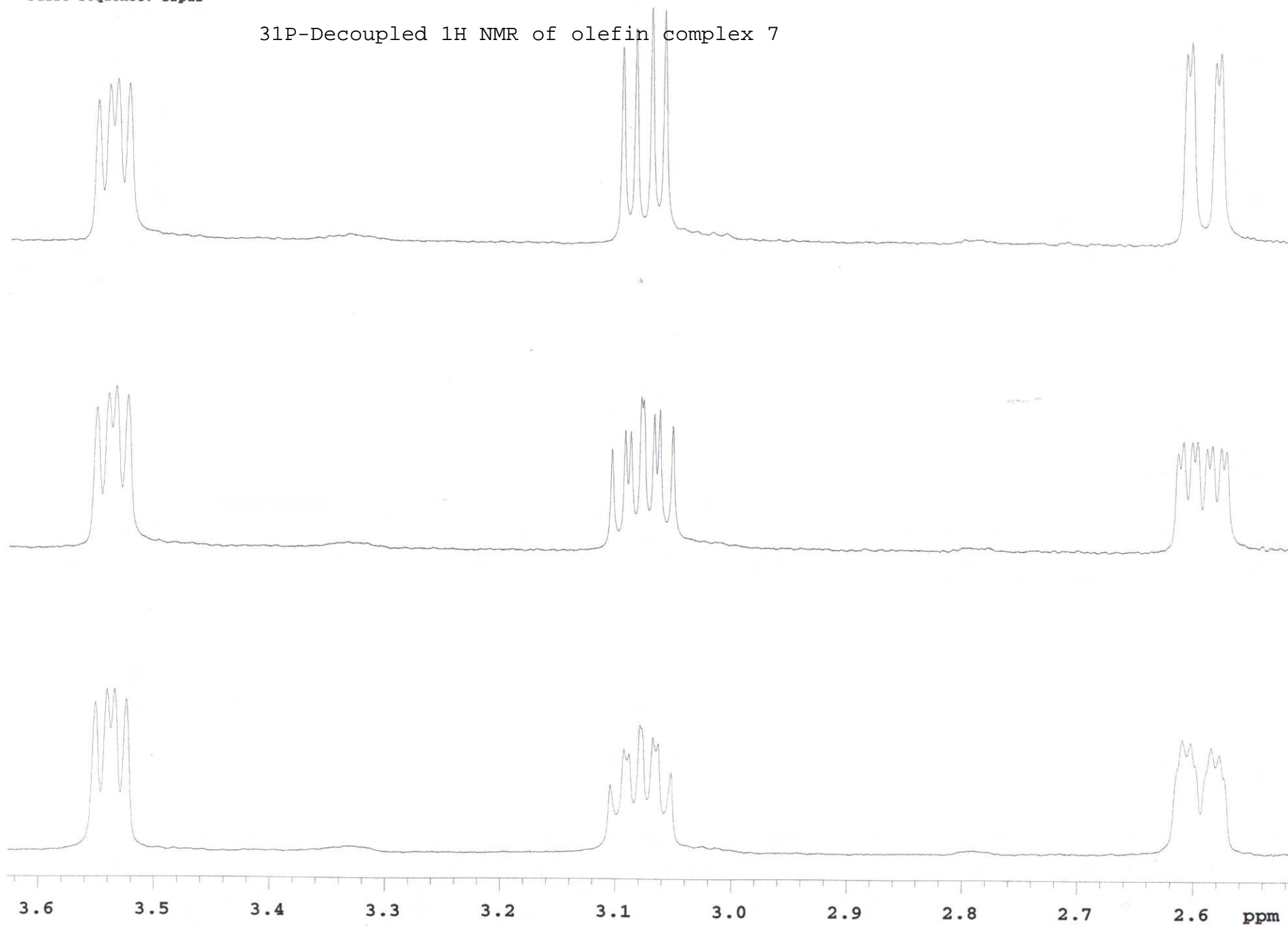
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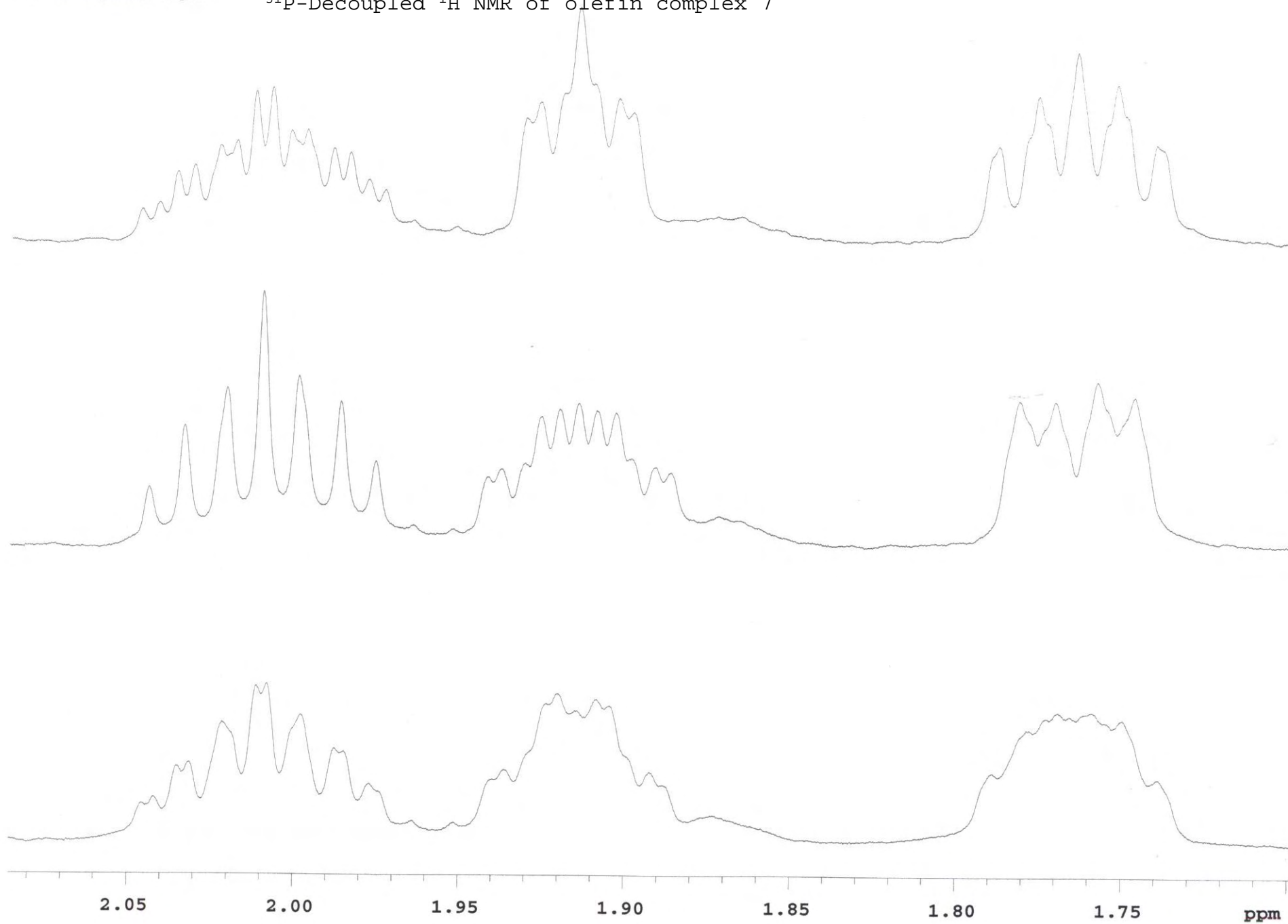
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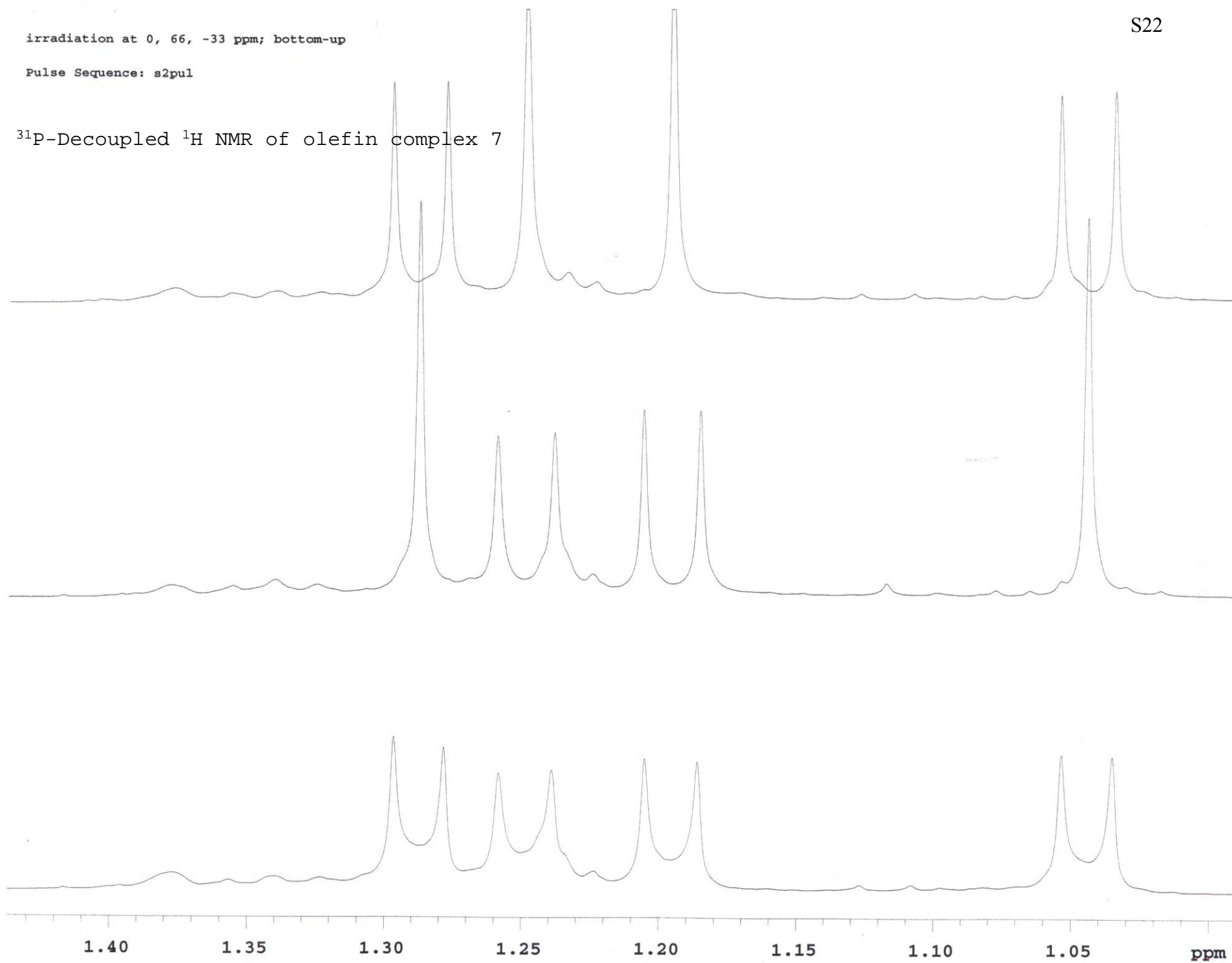
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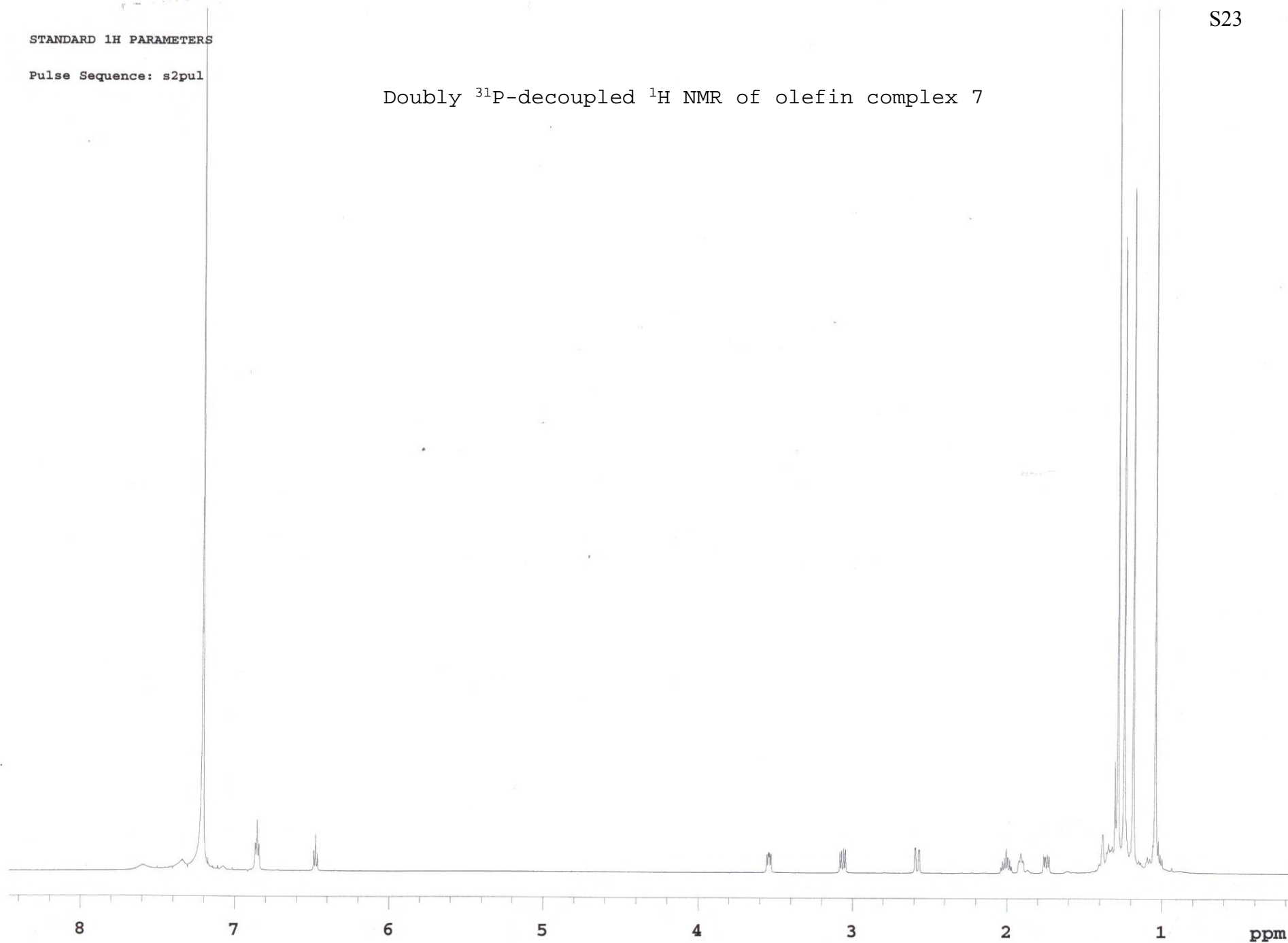
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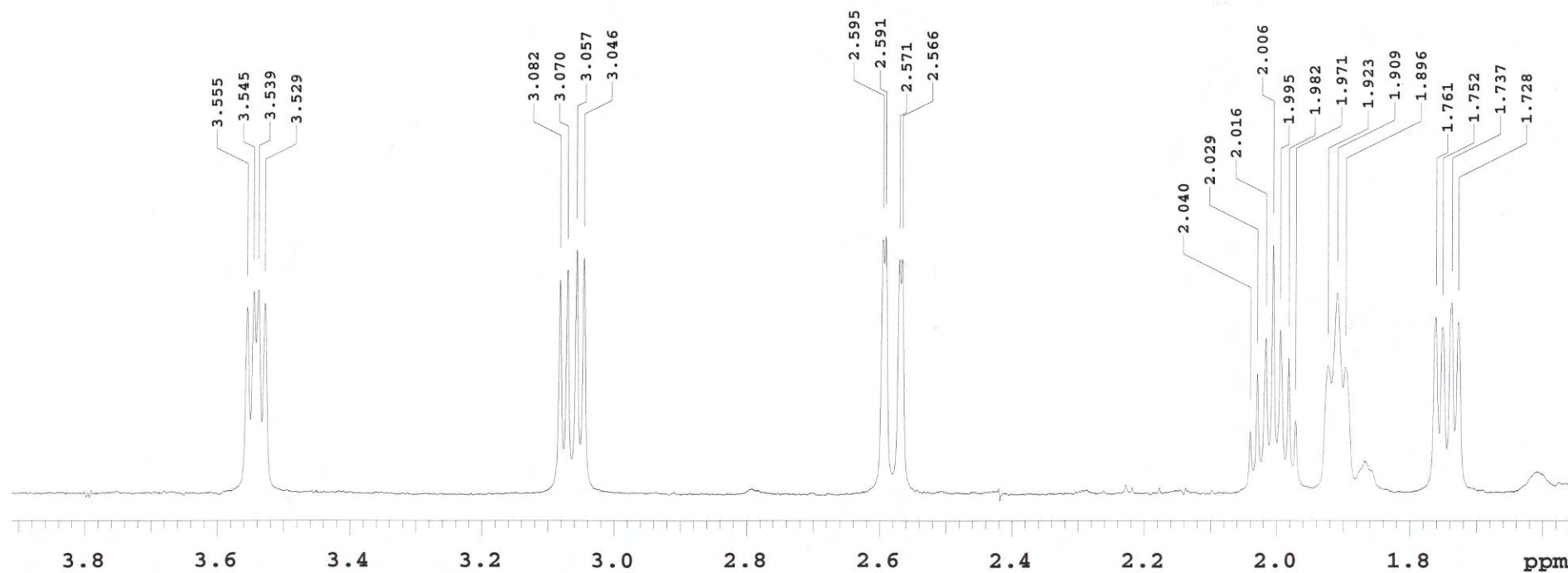
STANDARD 1H PARAMETERS

Pulse Sequence: s2pul

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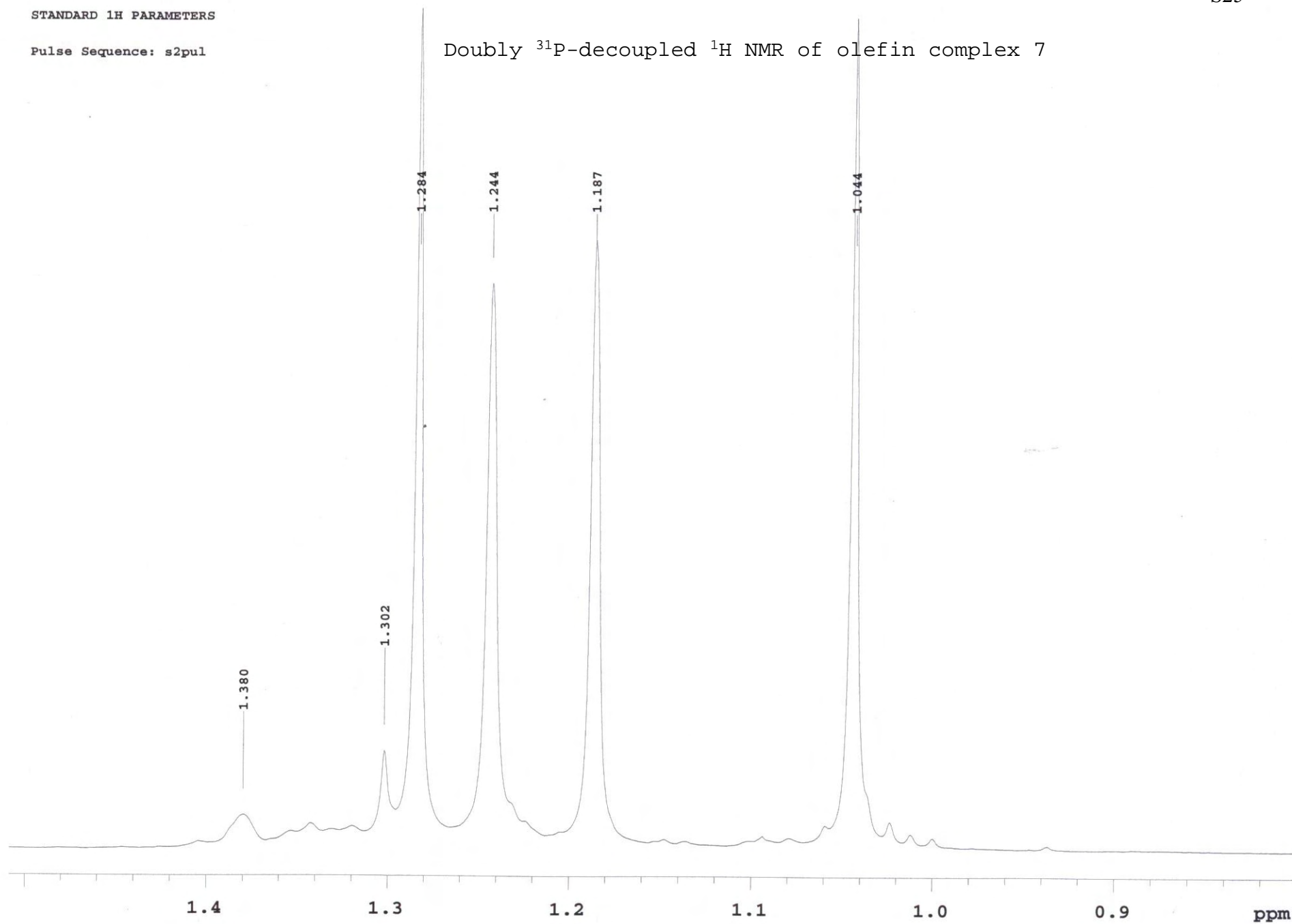
STANDARD 1H PARAMETERS

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Doubly ^{31}P -decoupled ^1H NMR of olefin complex 7

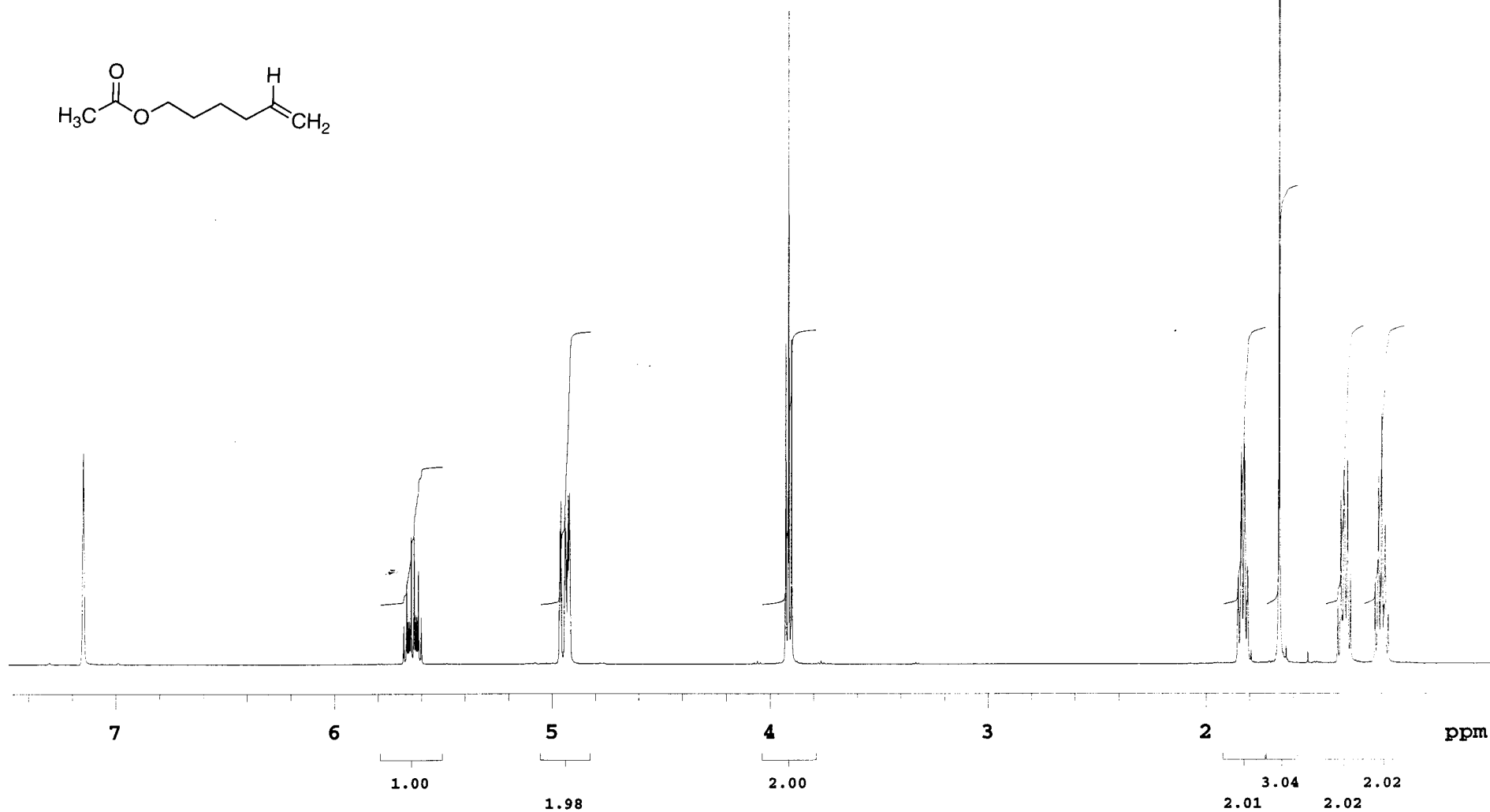
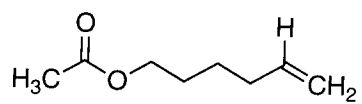
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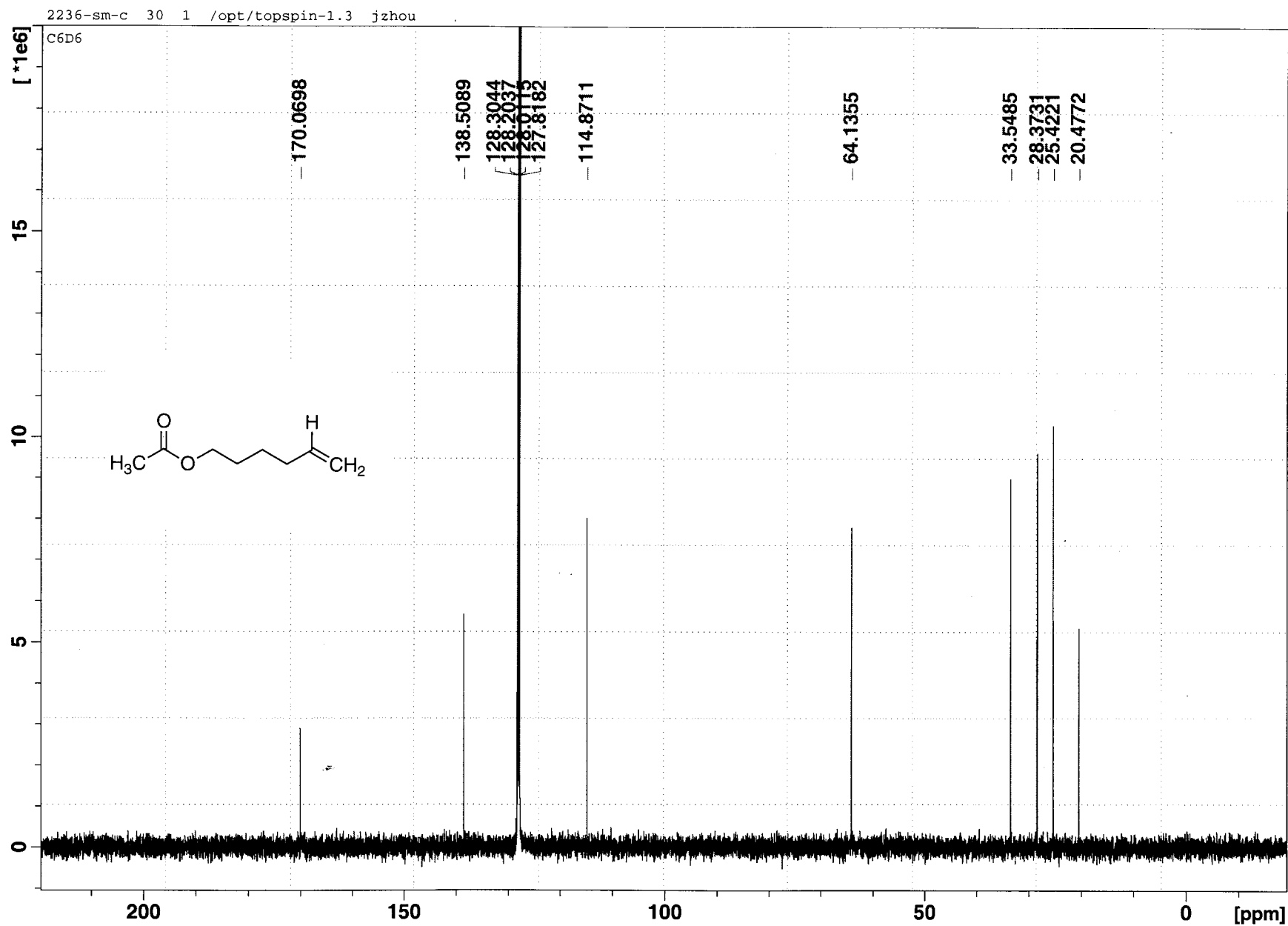
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Doubly ^{31}P -decoupled ^1H NMR of olefin complex 7

3084sm-h

Pulse Sequence: s2pul





3089-10h

Pulse Sequence: s2pul

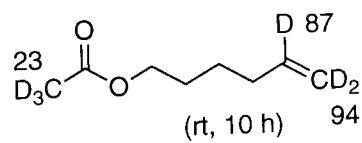
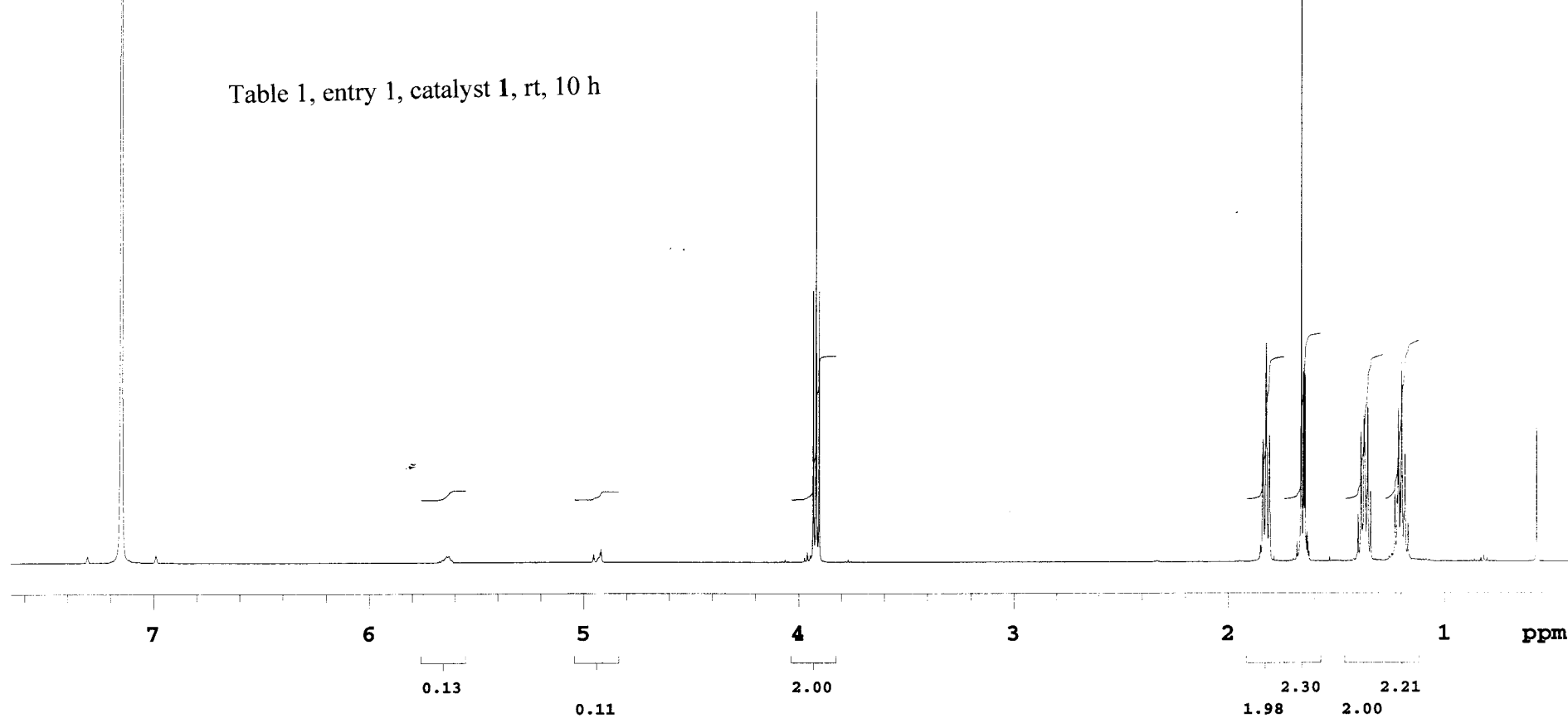
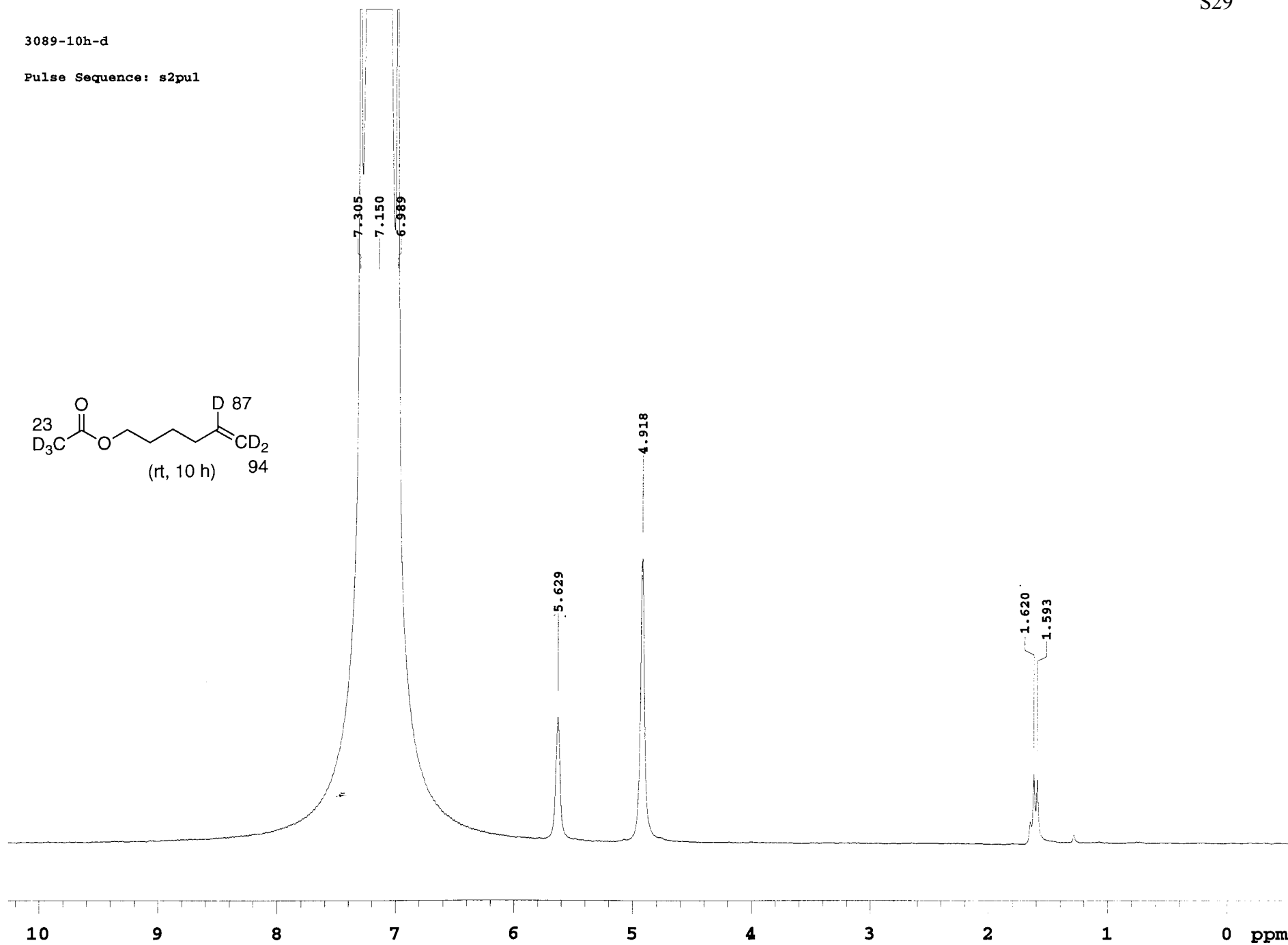


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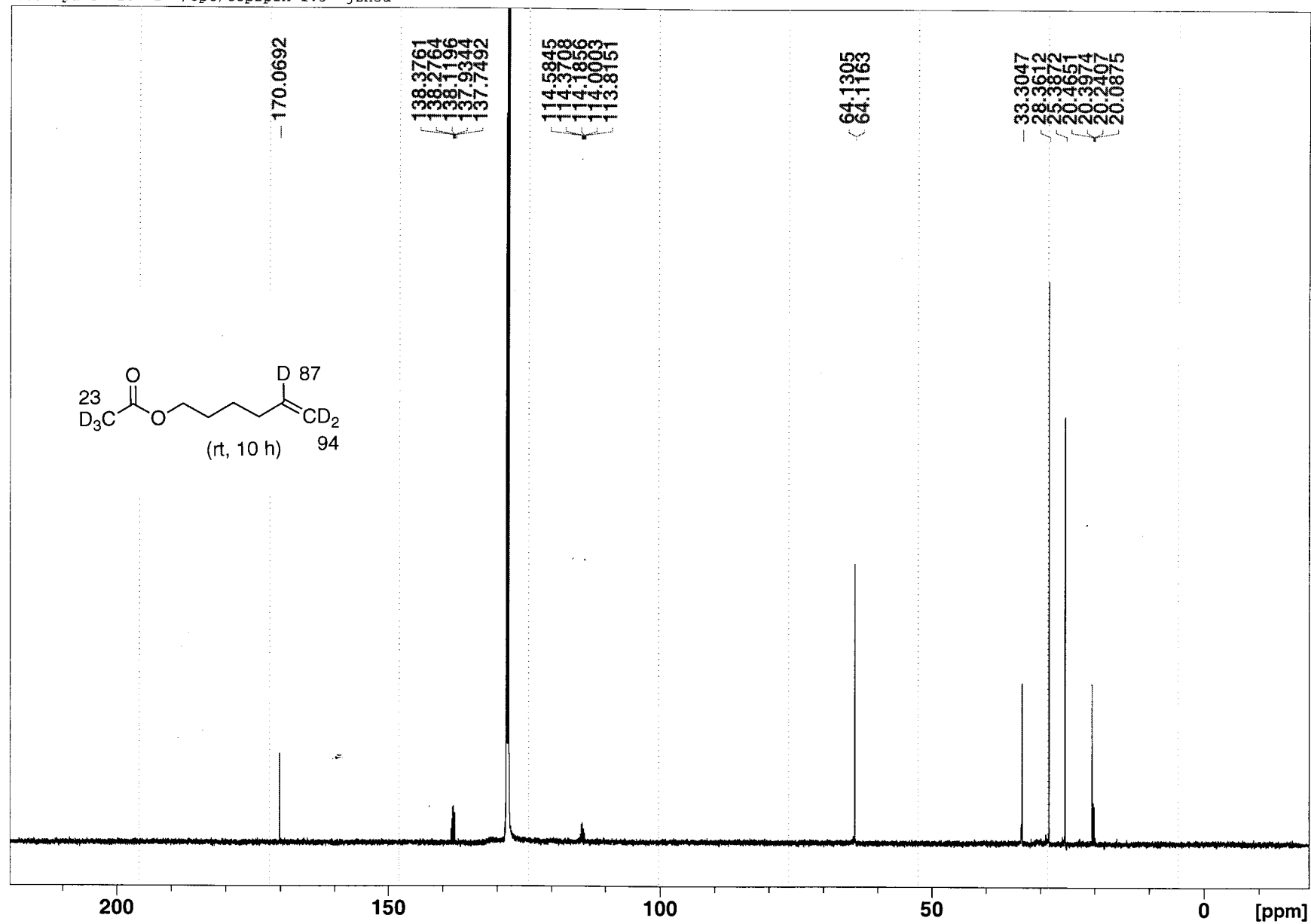


3089-10h-d

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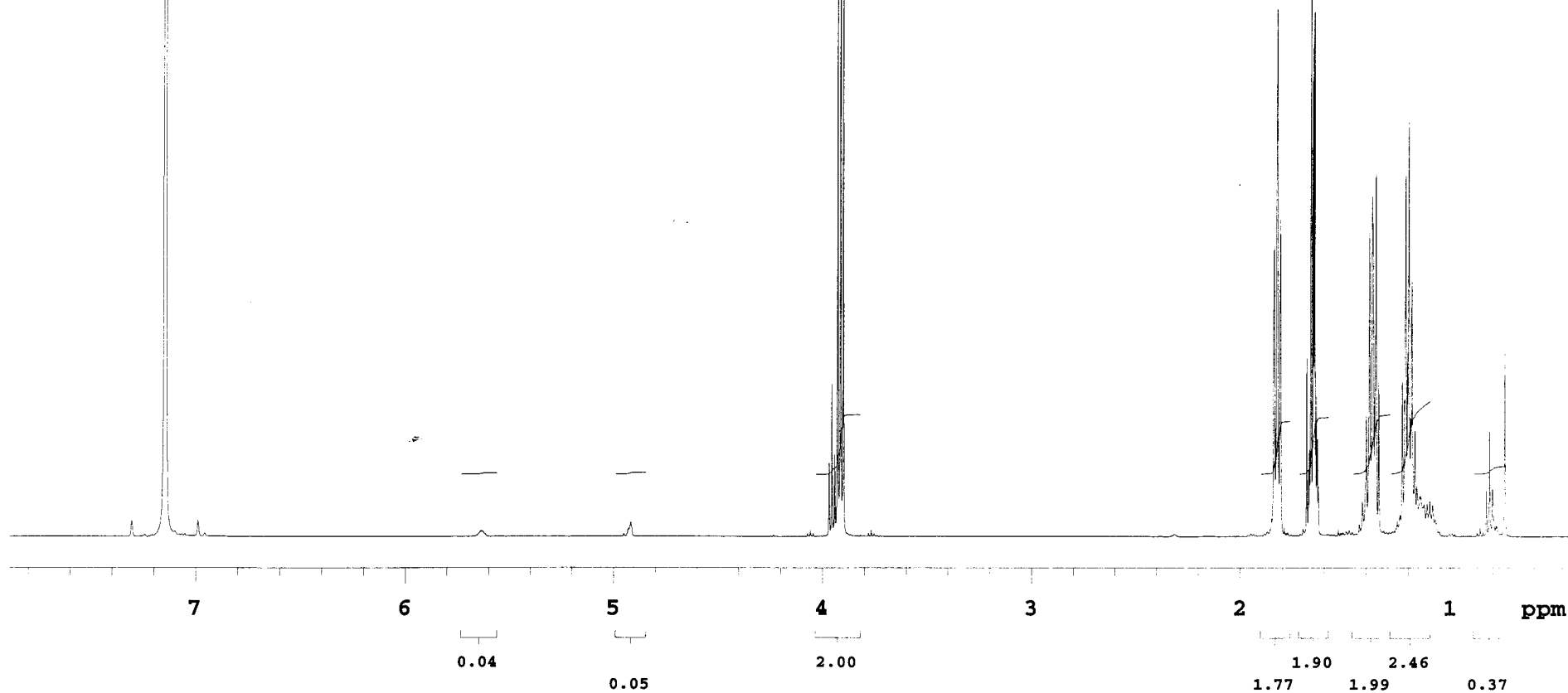


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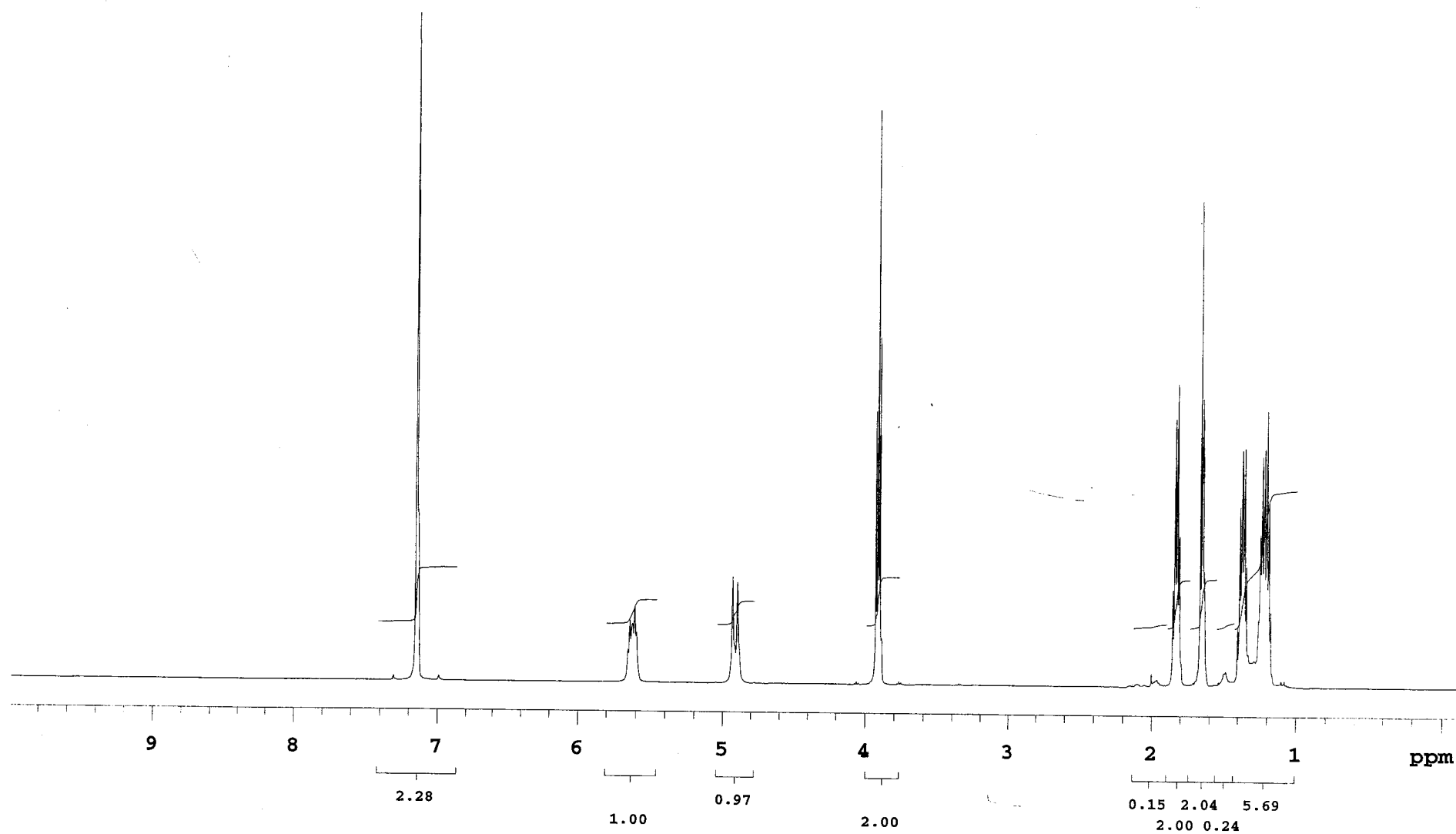
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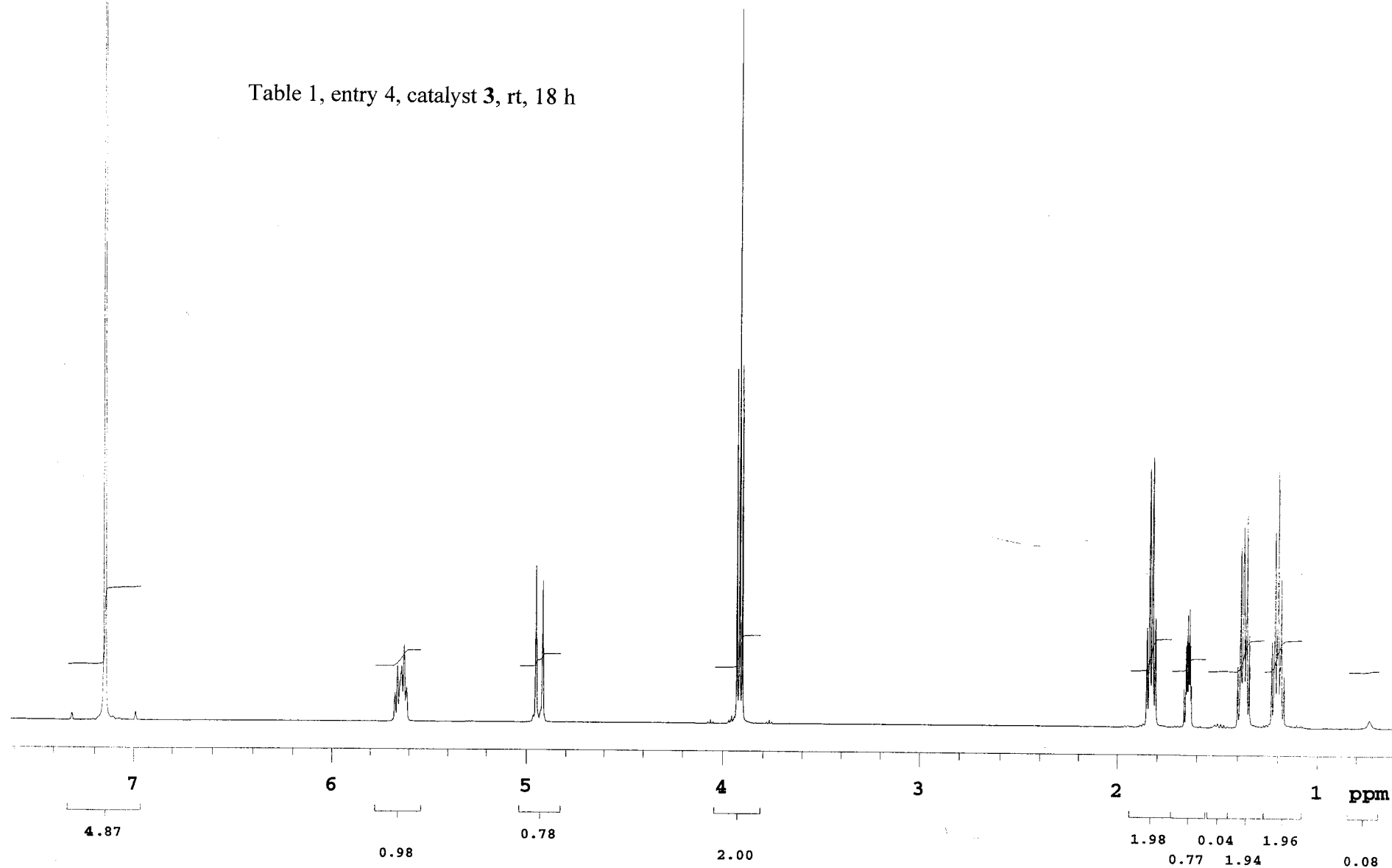
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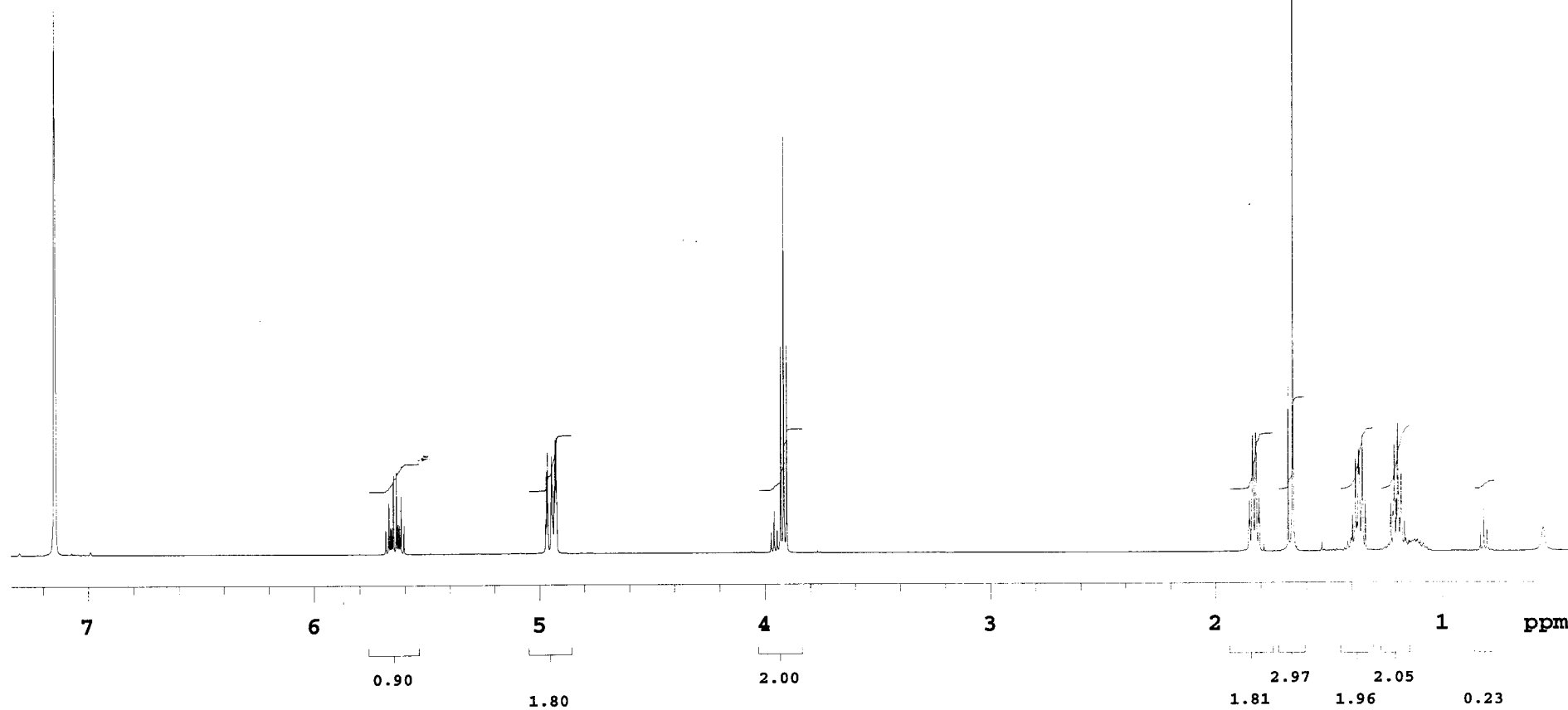
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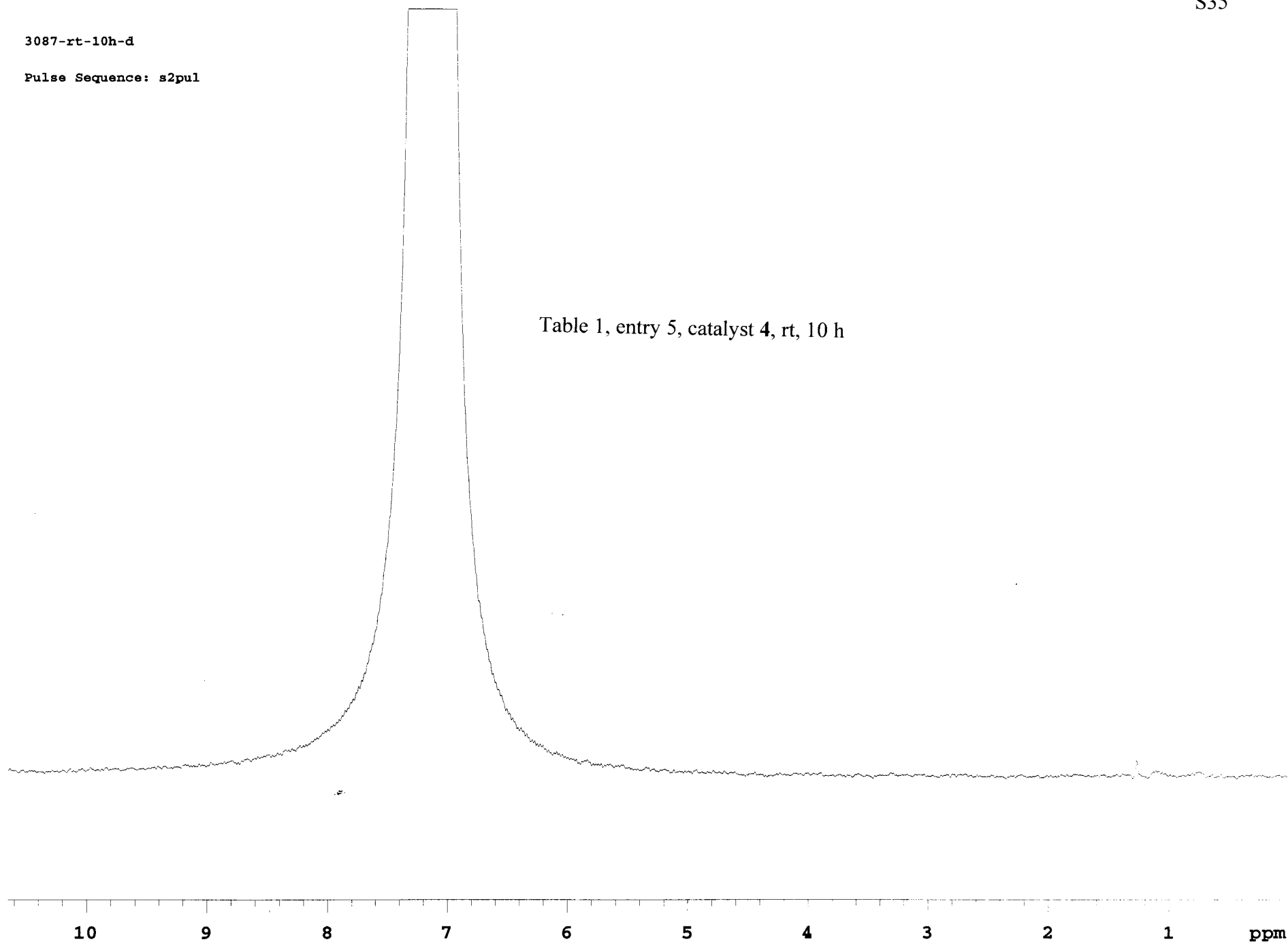
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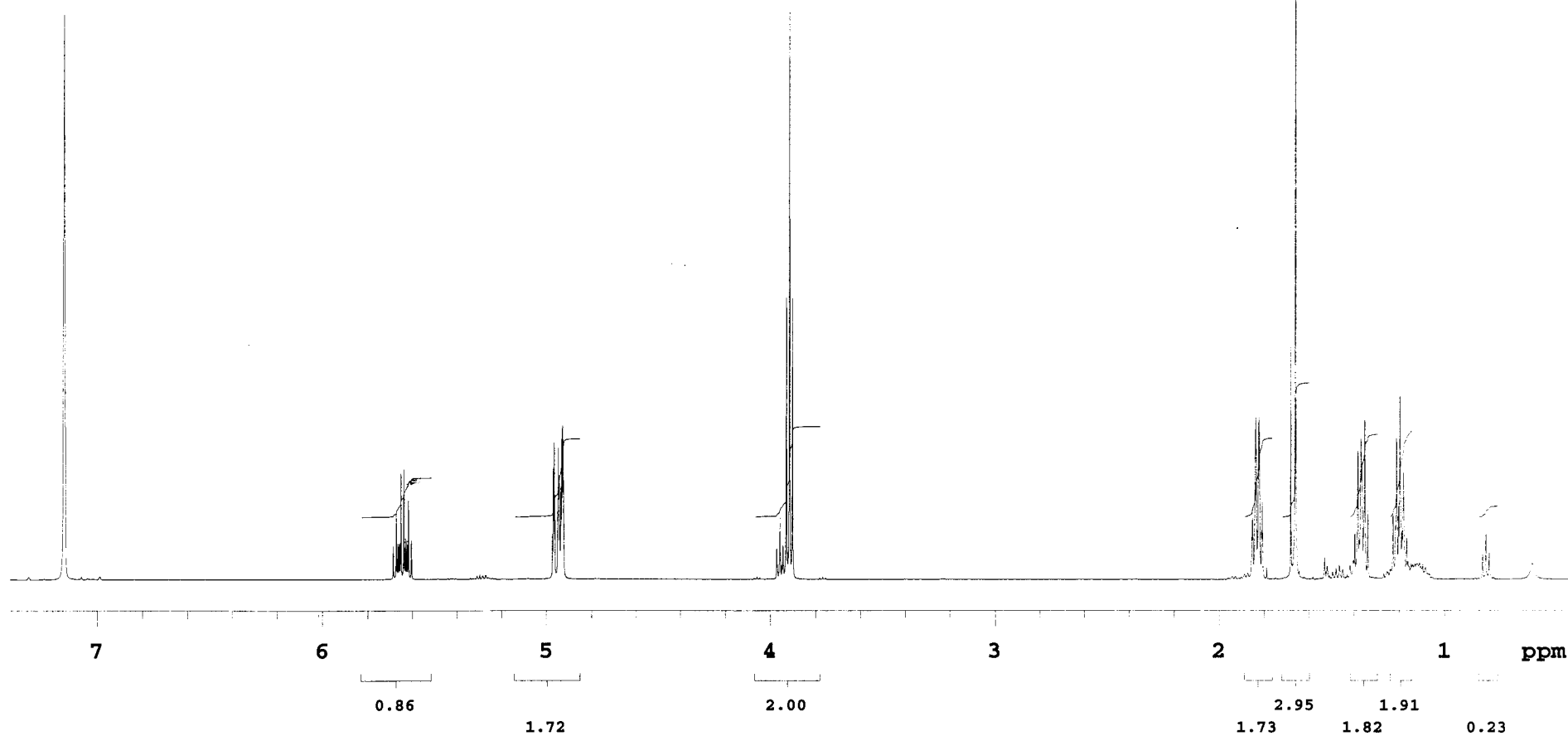
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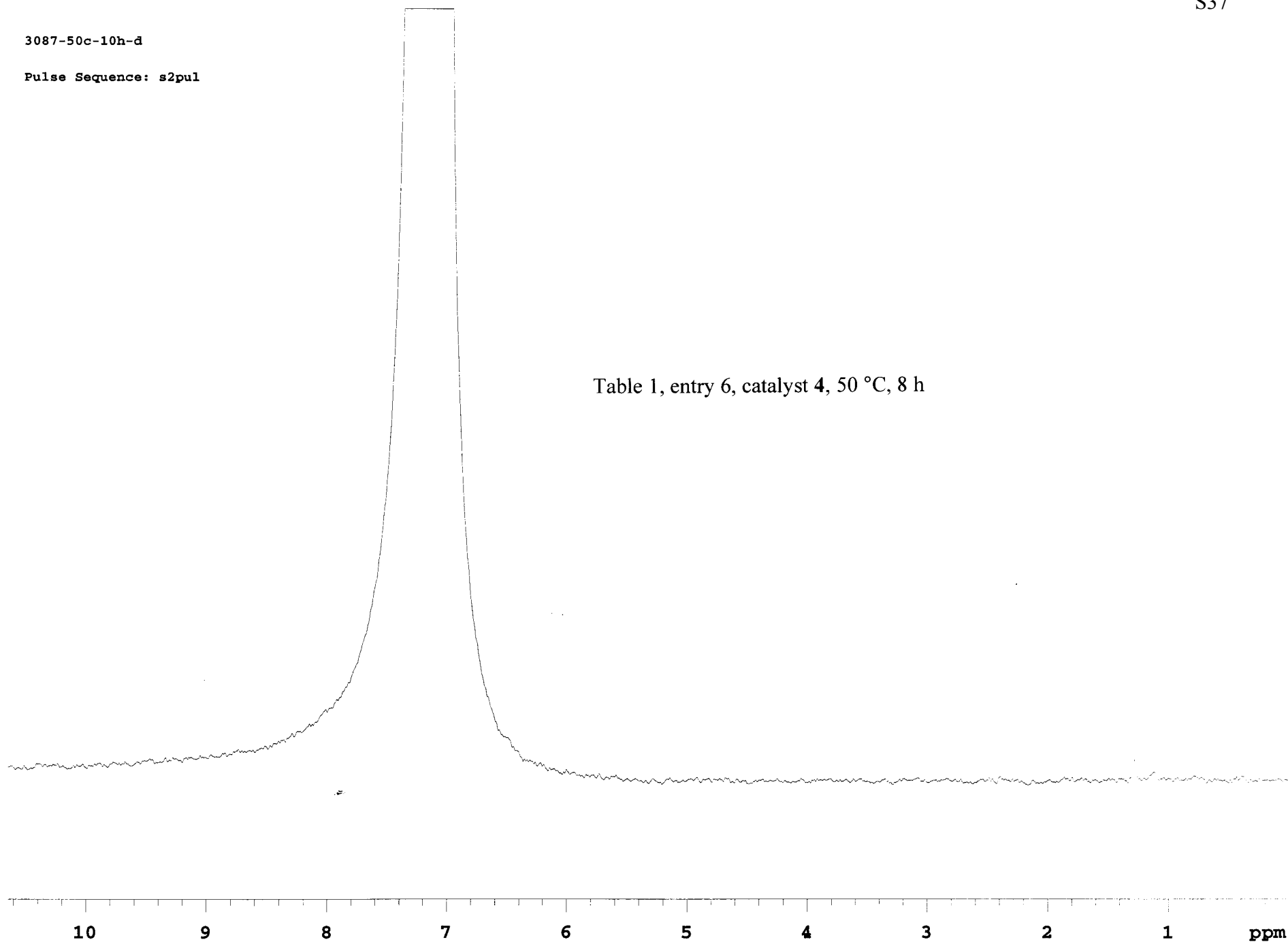
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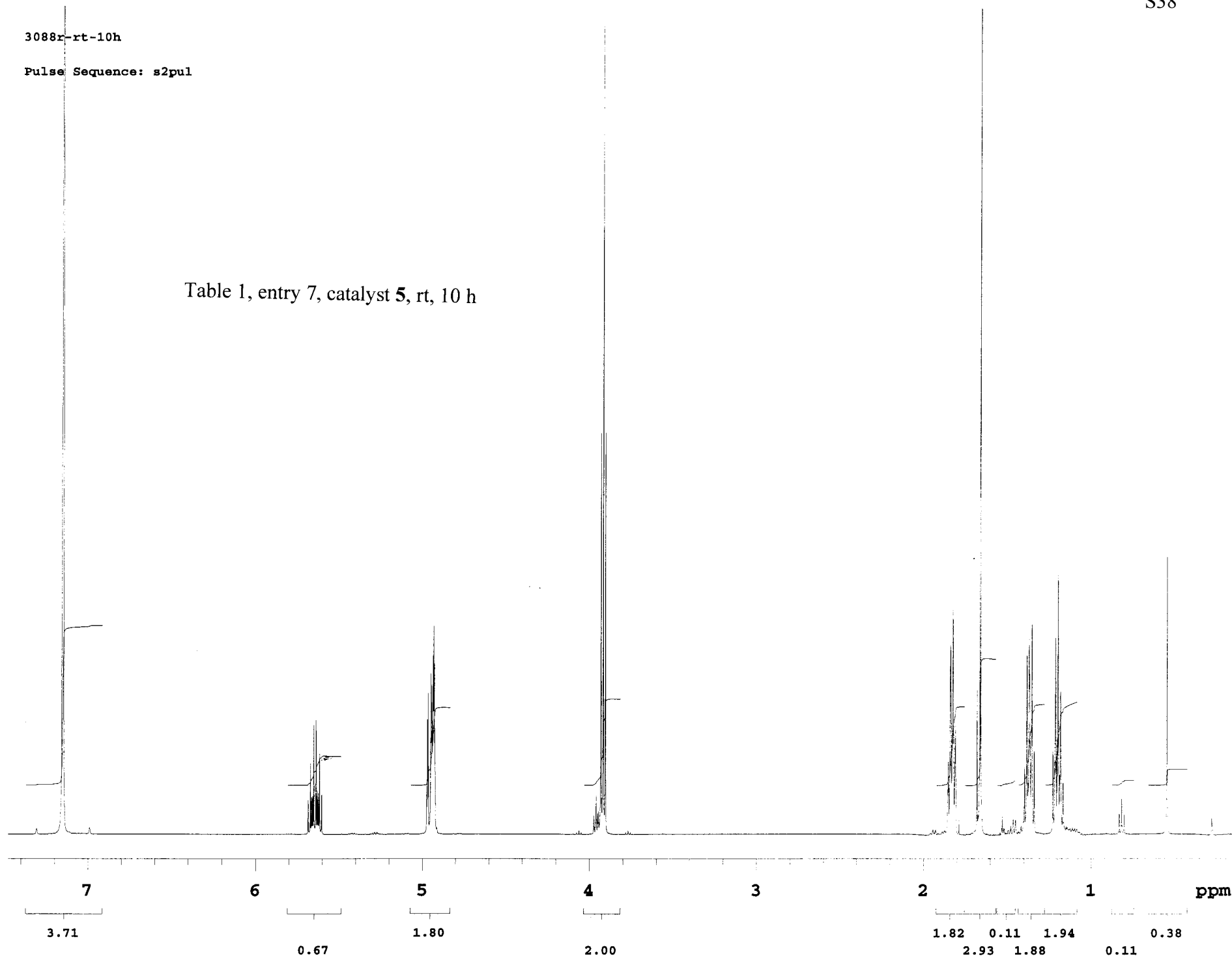
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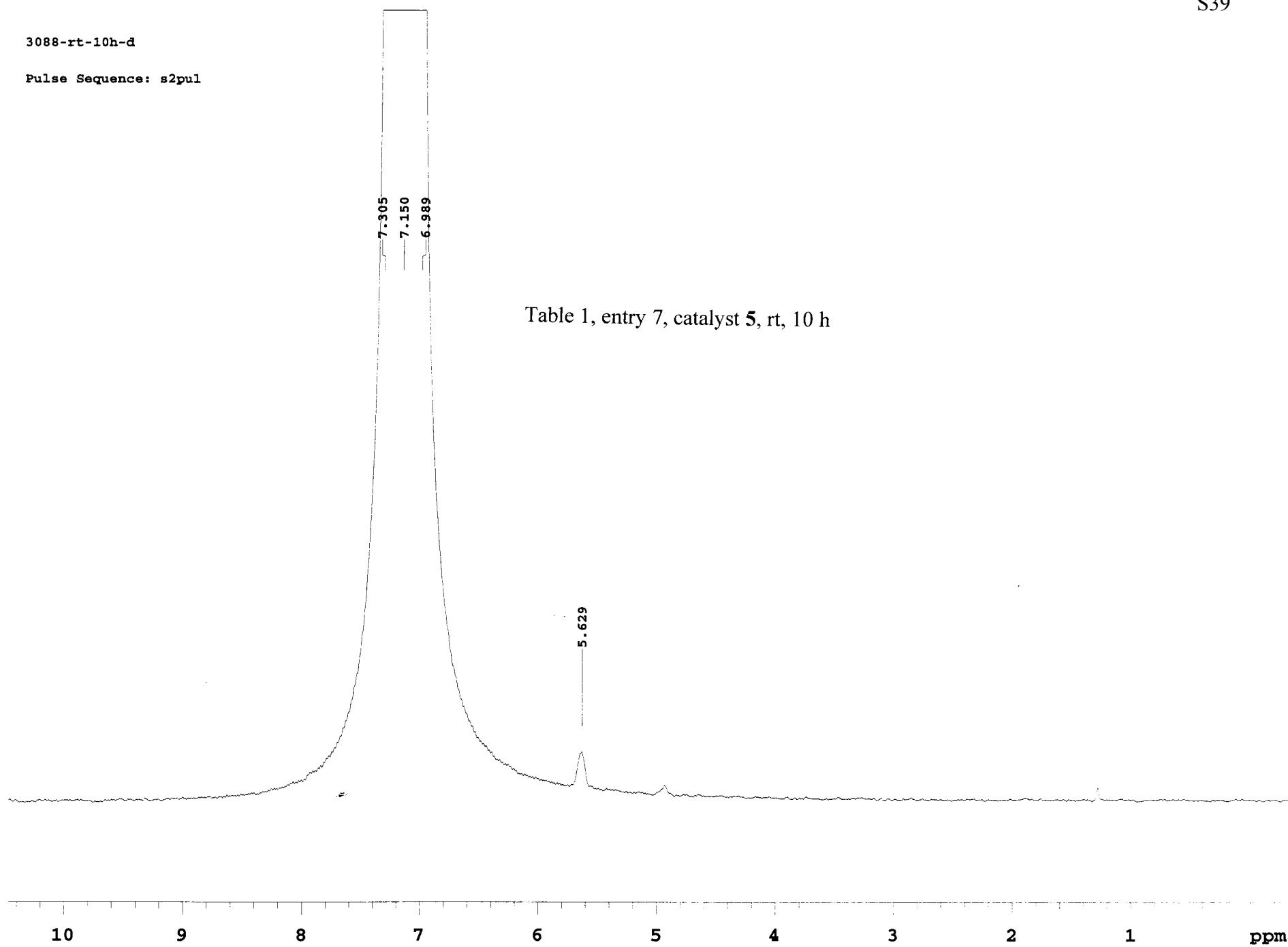
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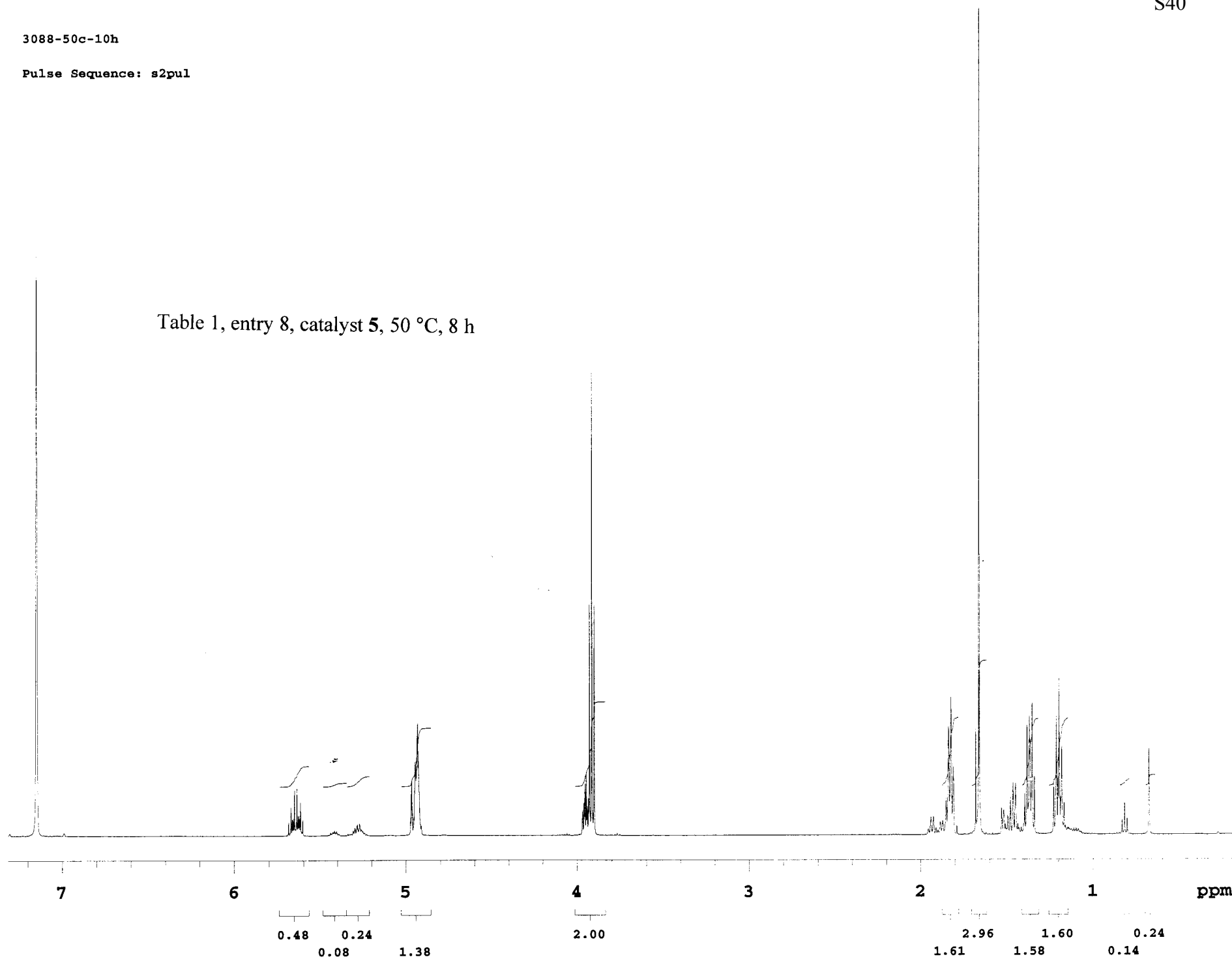
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Pulse Sequence: s2pul



3088-50c-10h

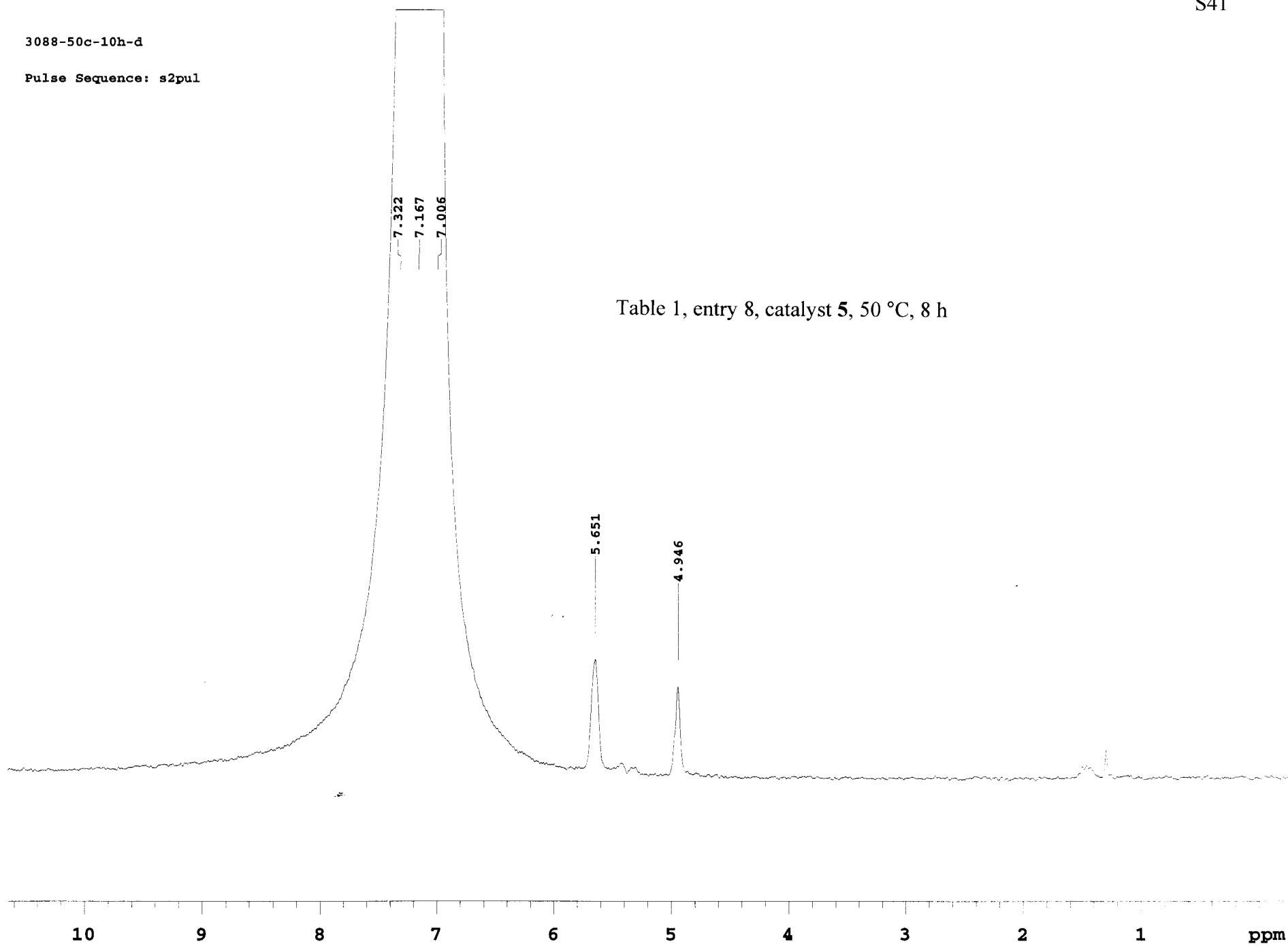
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Table 1, entry 8, catalyst **5**, 50 °C, 8 h

3088-50c-10h-d

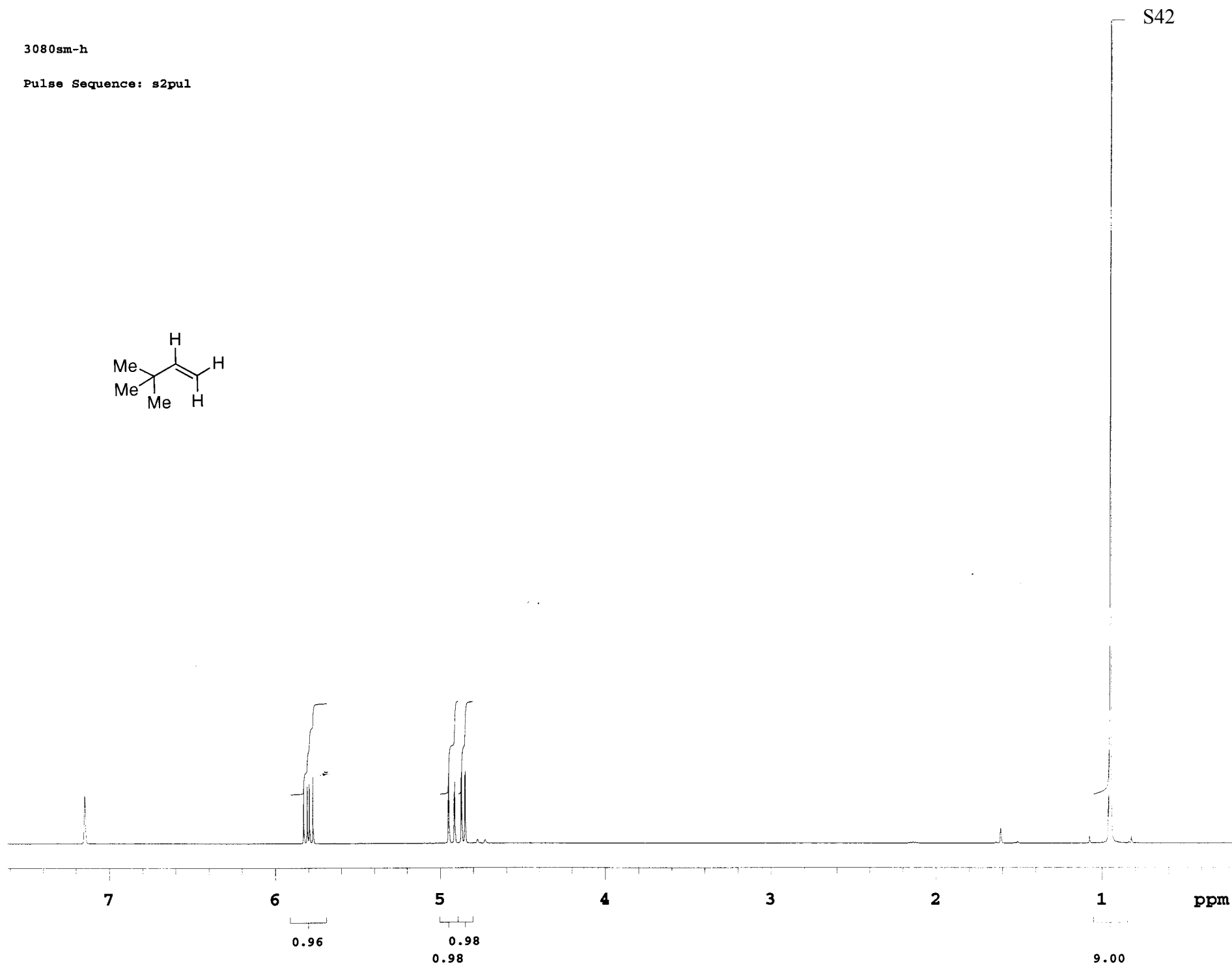
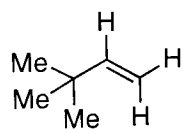
Pulse Sequence: s2pul

Table 1, entry 8, catalyst 5, 50 °C, 8 h



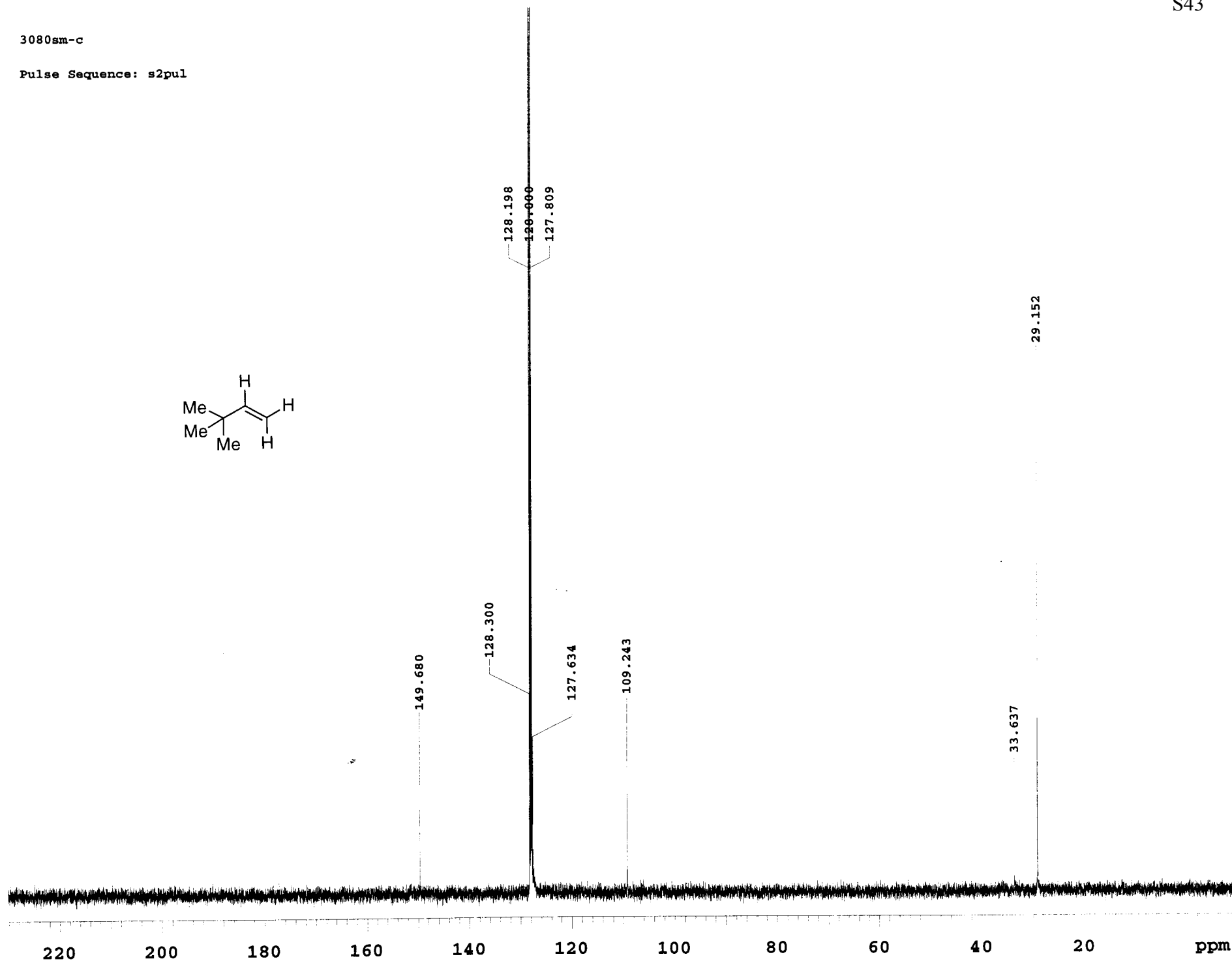
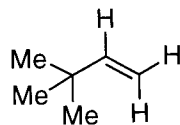
3080sm-h

Pulse Sequence: s2pul



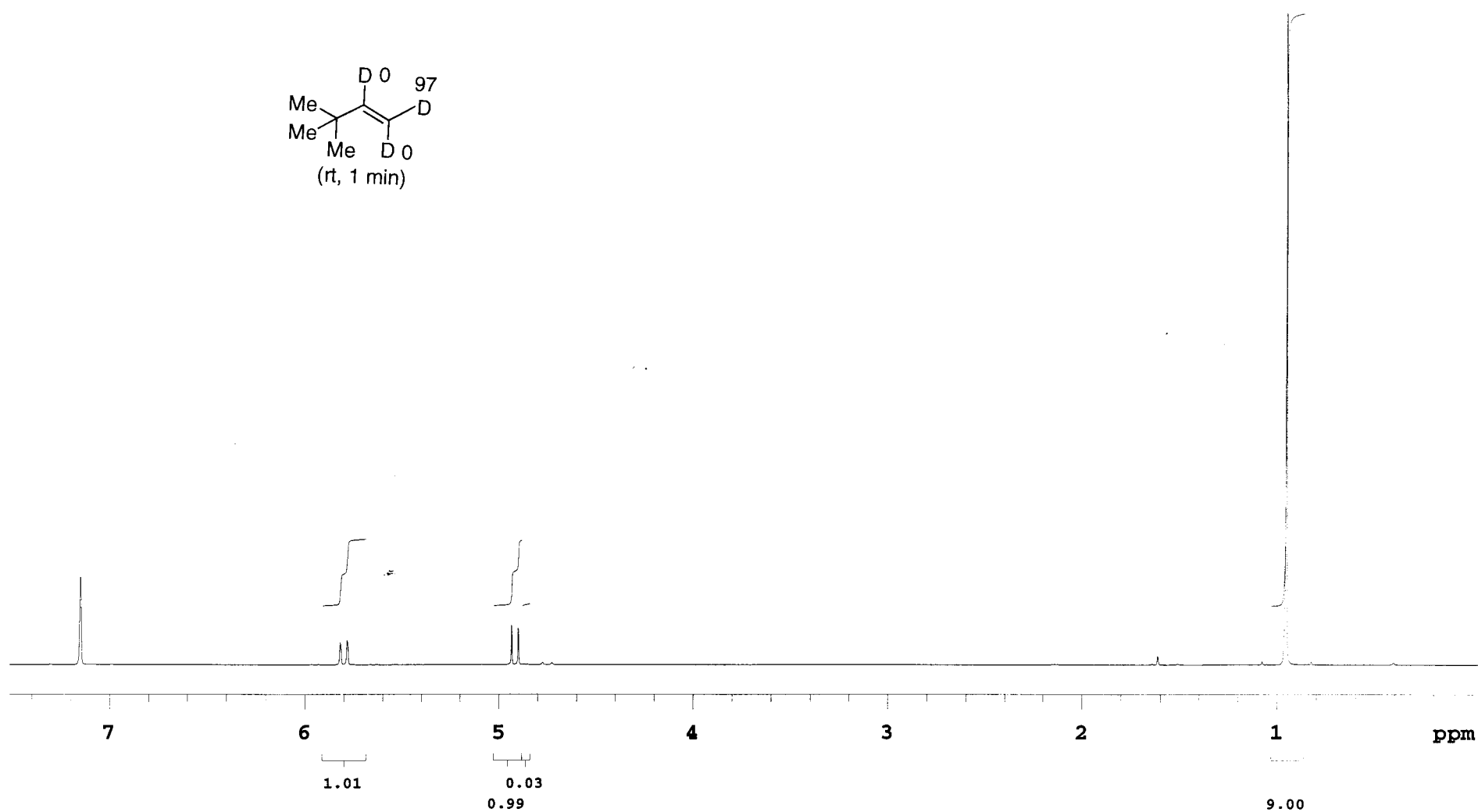
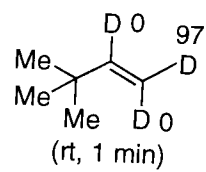
3080sm-c

Pulse Sequence: s2pul



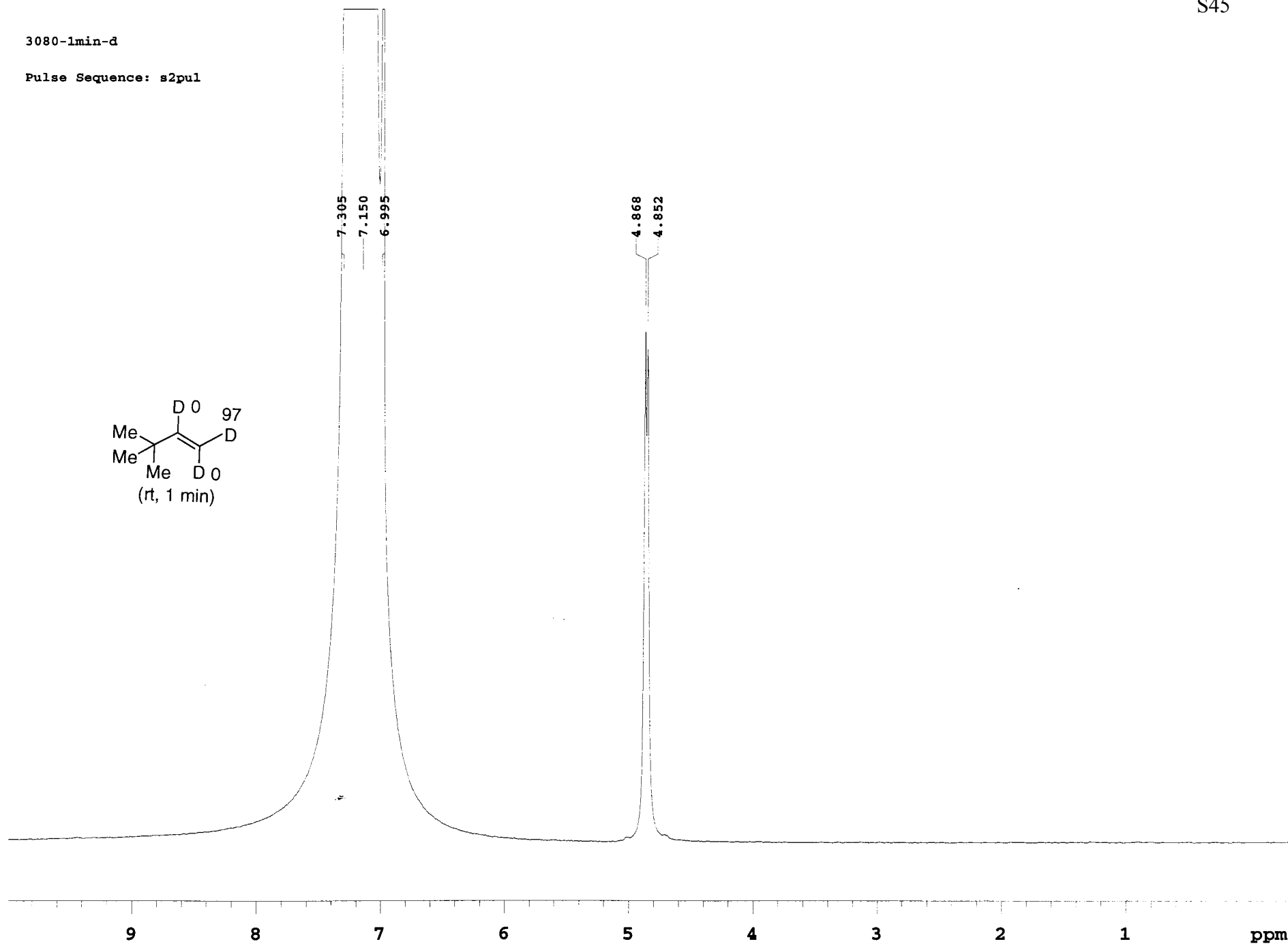
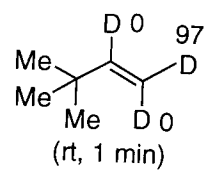
3080-1min

Pulse Sequence: s2pul



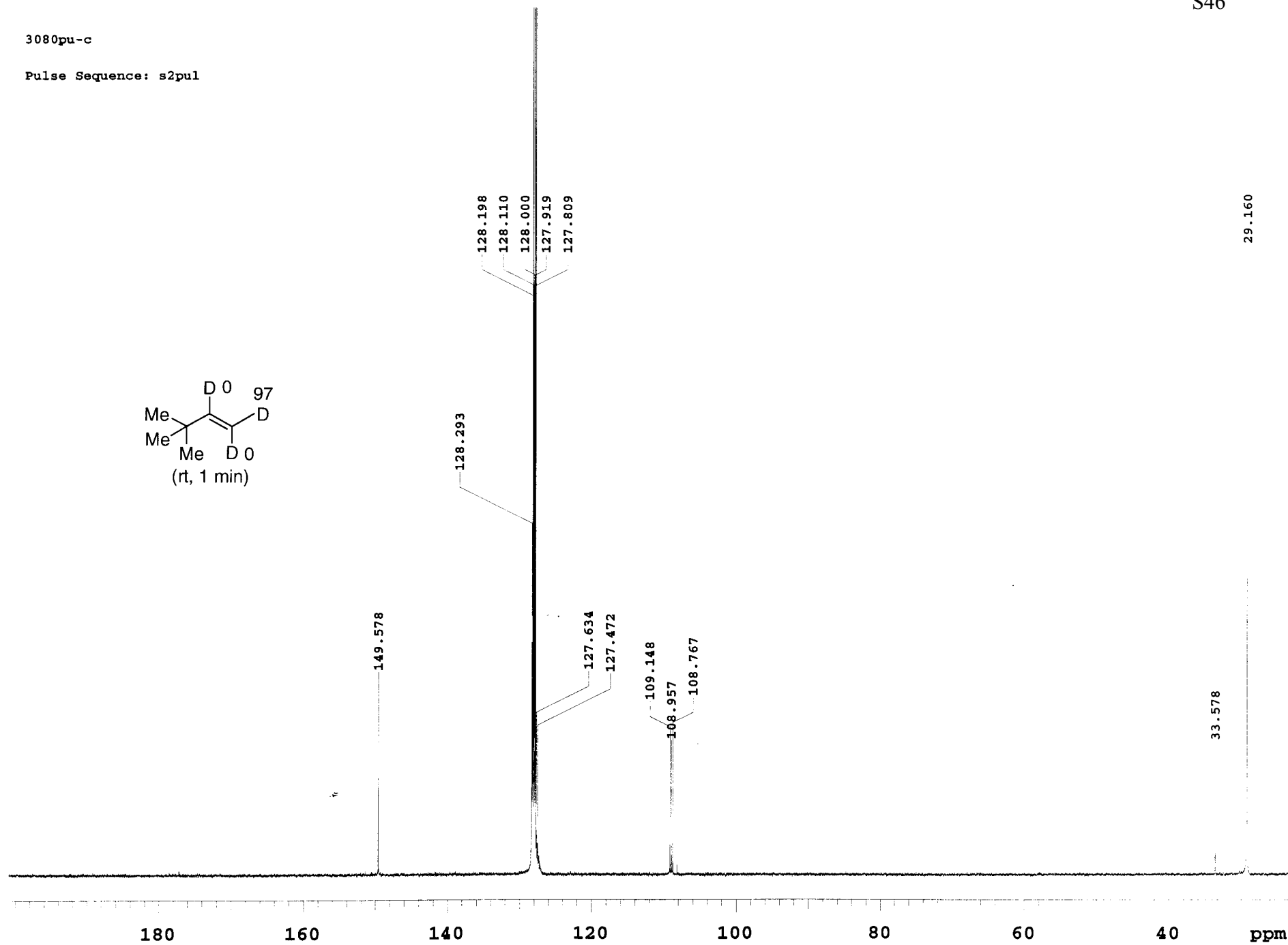
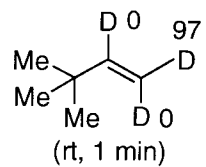
3080-1min-d

Pulse Sequence: s2pul



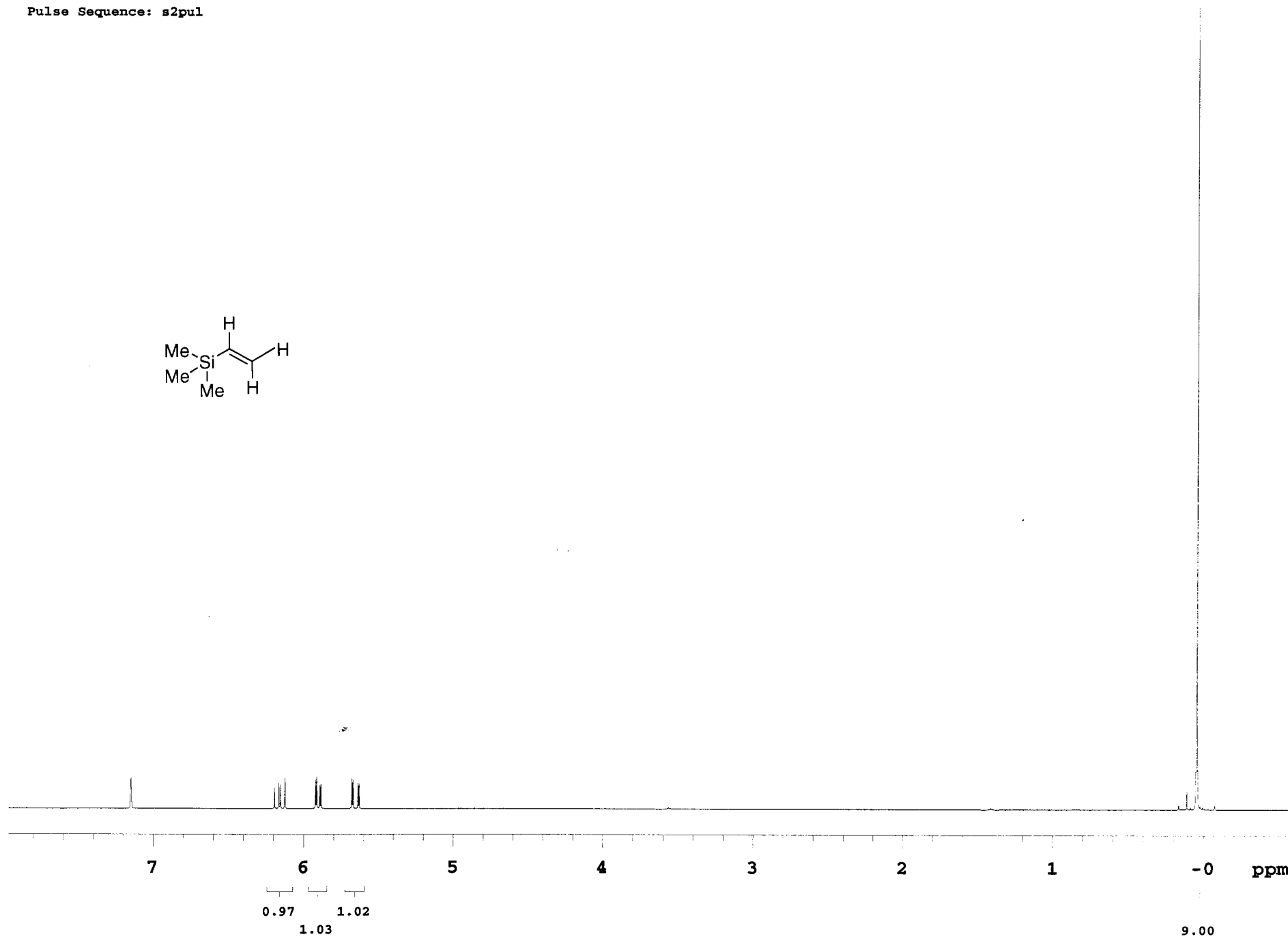
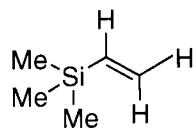
3080pu-c

Pulse Sequence: s2pul



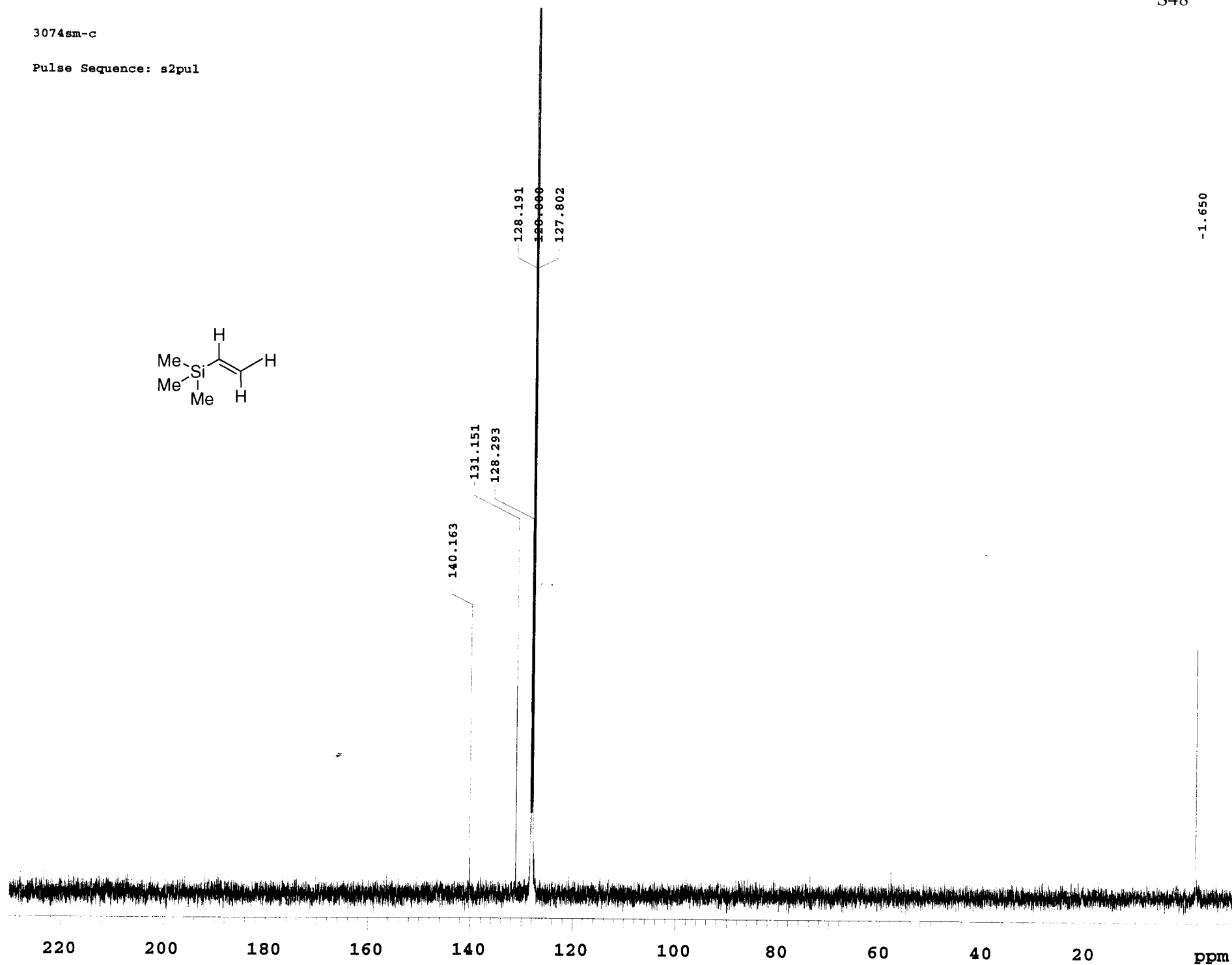
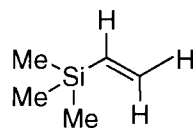
3074sm-h

Pulse Sequence: s2pul



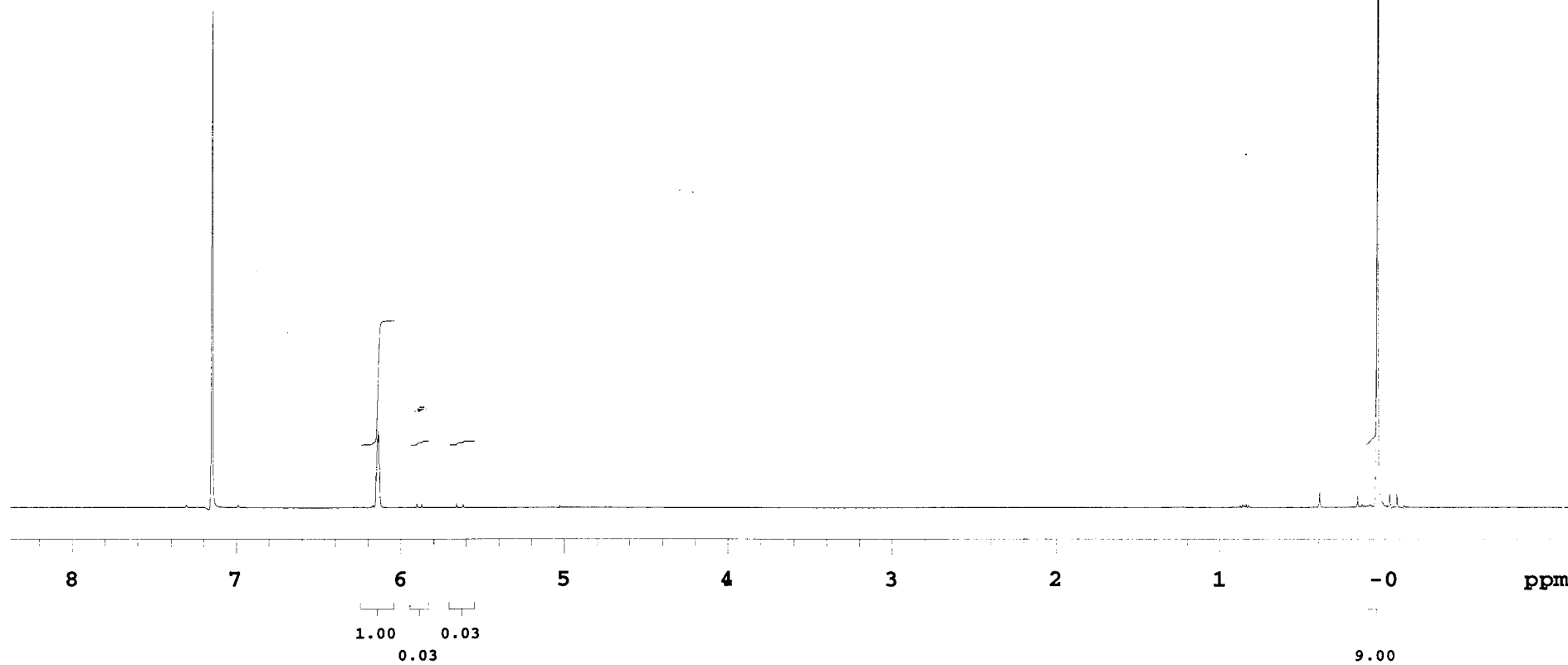
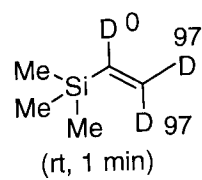
3074sm-c

Pulse Sequence: s2pul



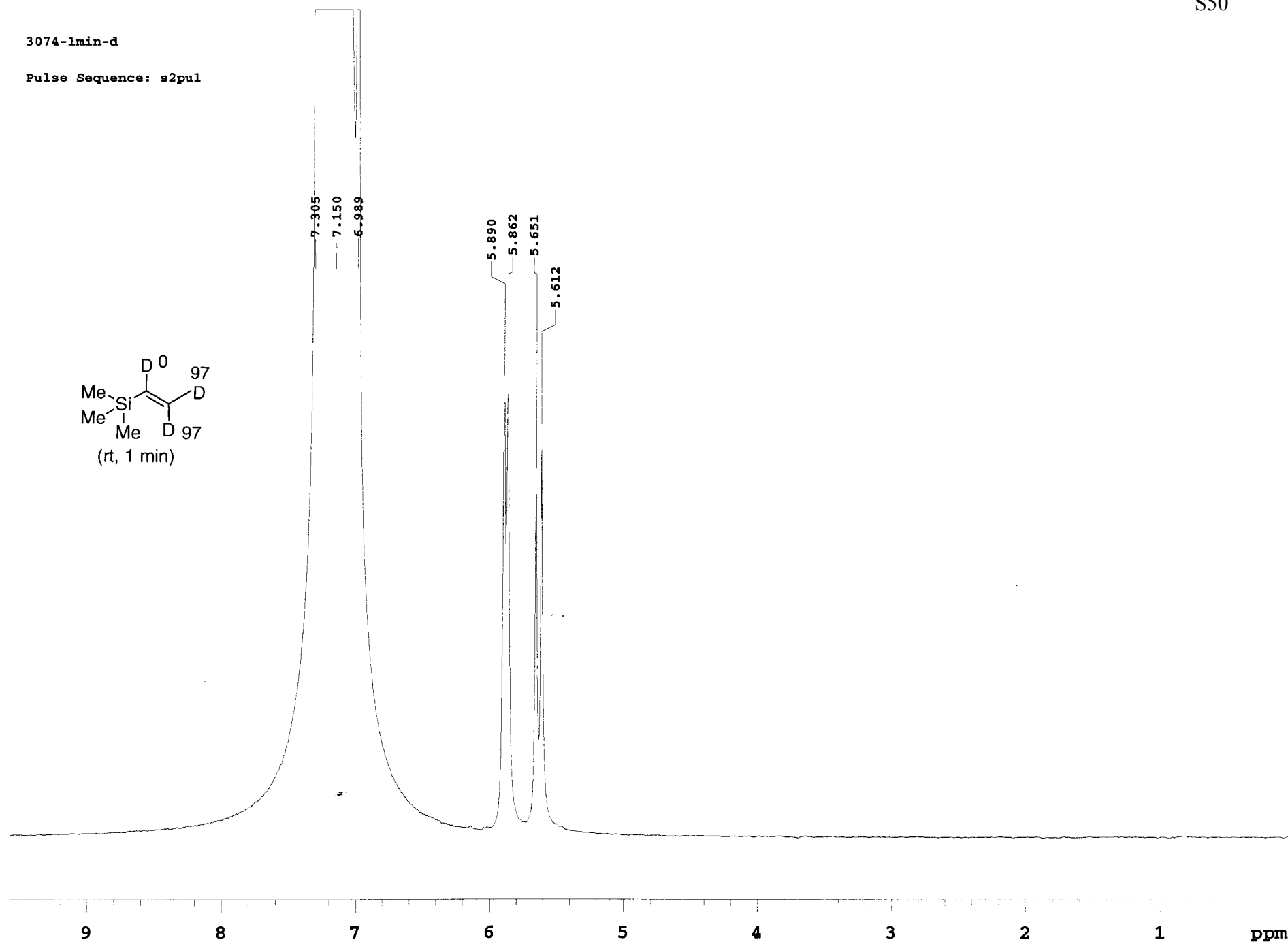
3074r-1min

Pulse Sequence: s2pul



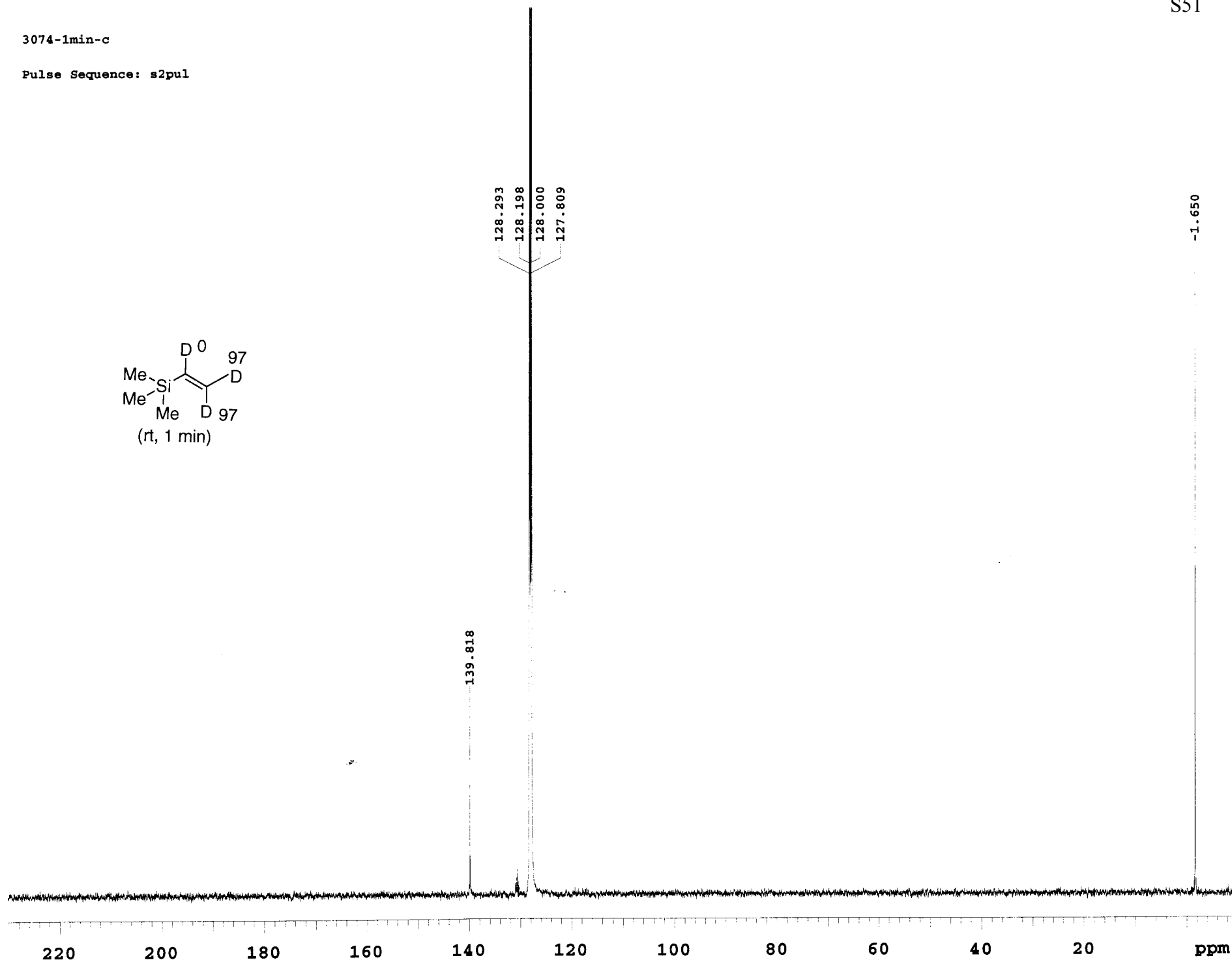
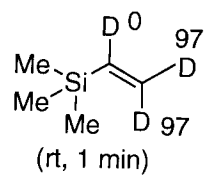
3074-1min-d

Pulse Sequence: s2pul



3074-1min-c

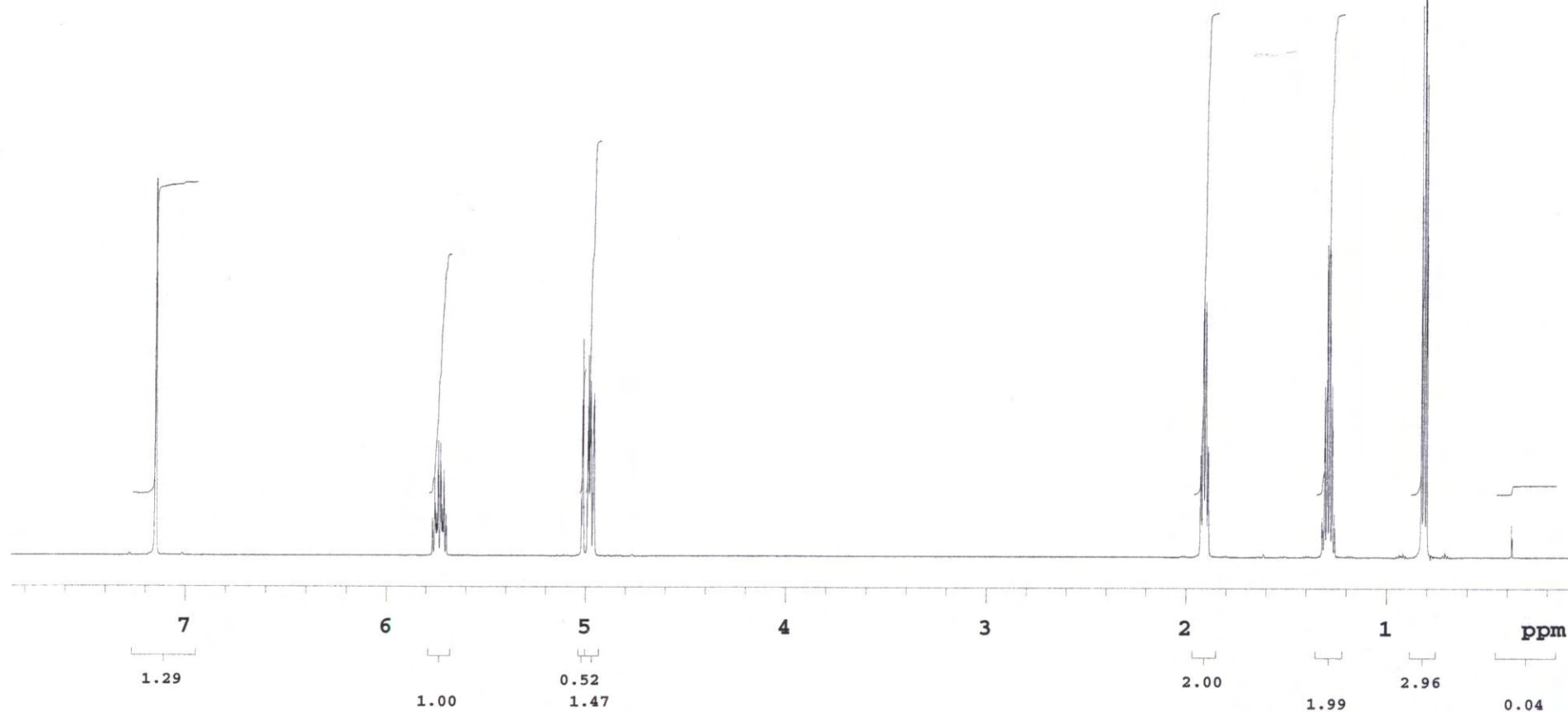
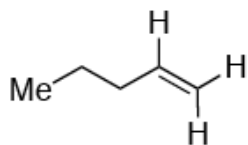
Pulse Sequence: s2pul



3096sm-h

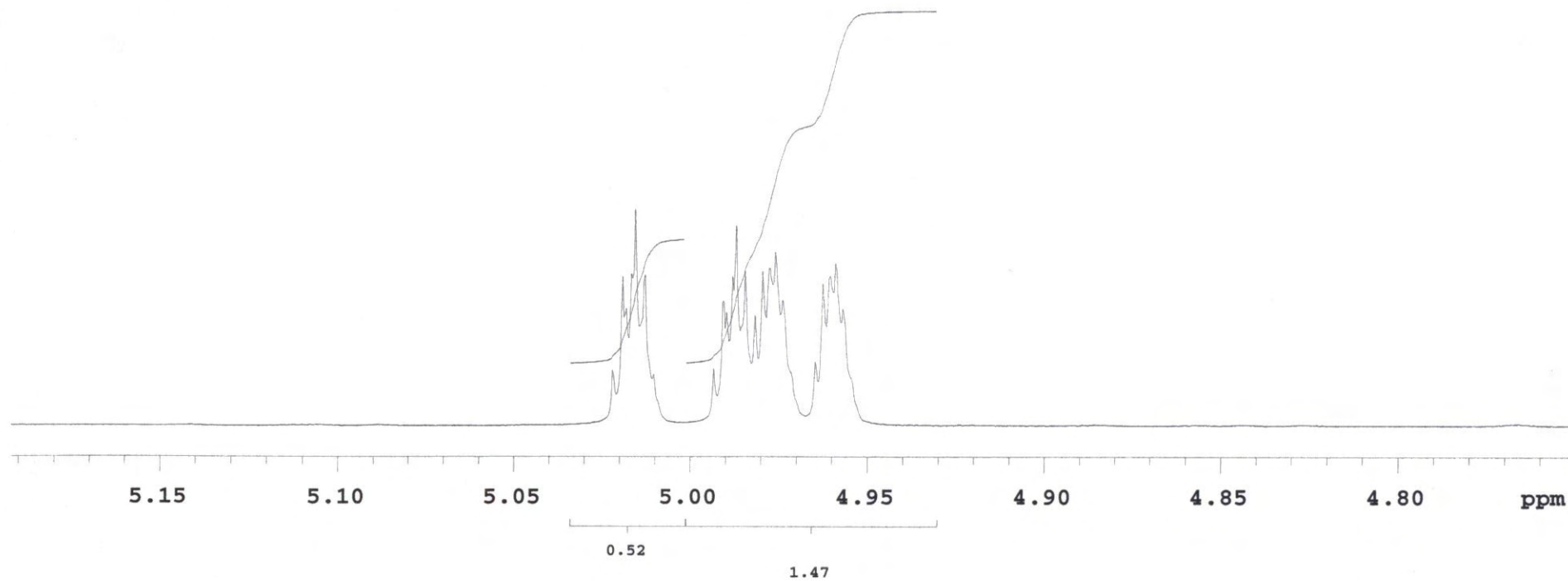
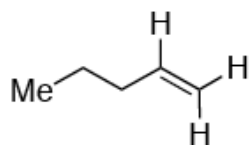
Pulse Sequence: s2pul

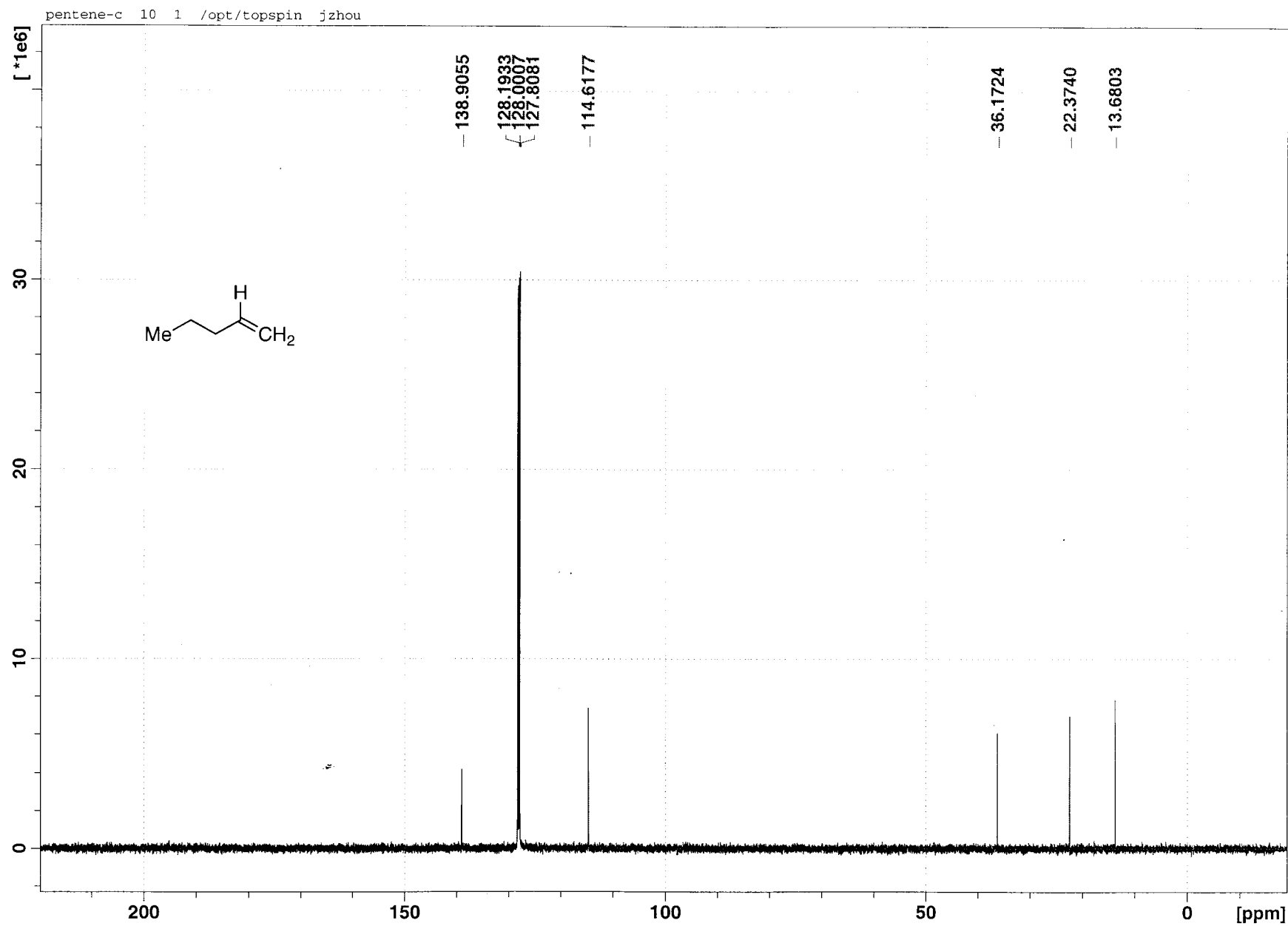
S52



3096sm-h

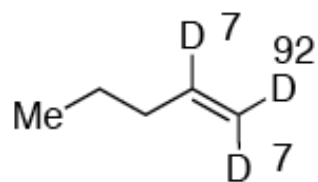
Pulse Sequence: s2pul



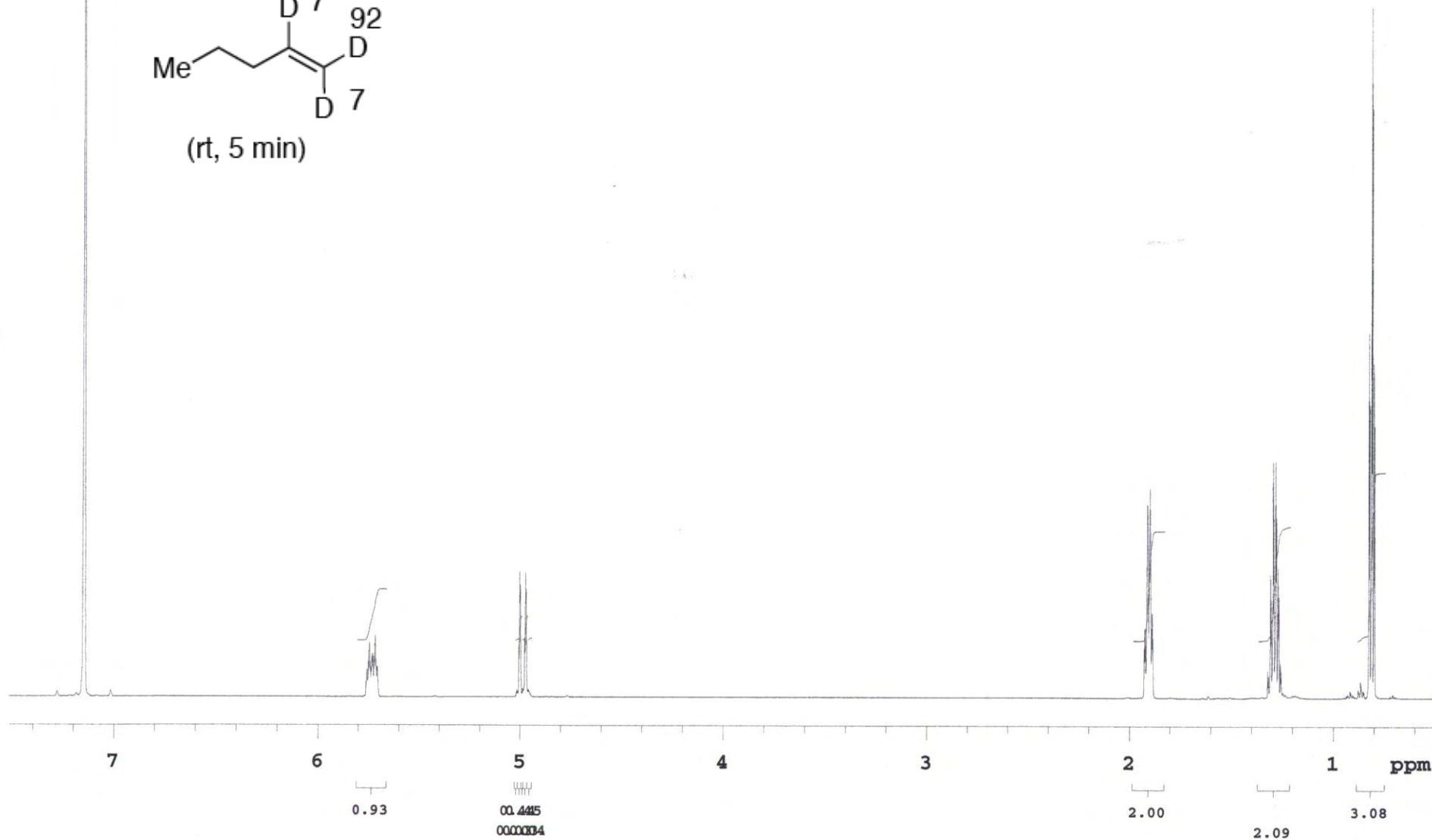


3096-5min

Pulse Sequence: s2pul

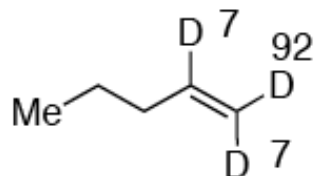


(rt, 5 min)

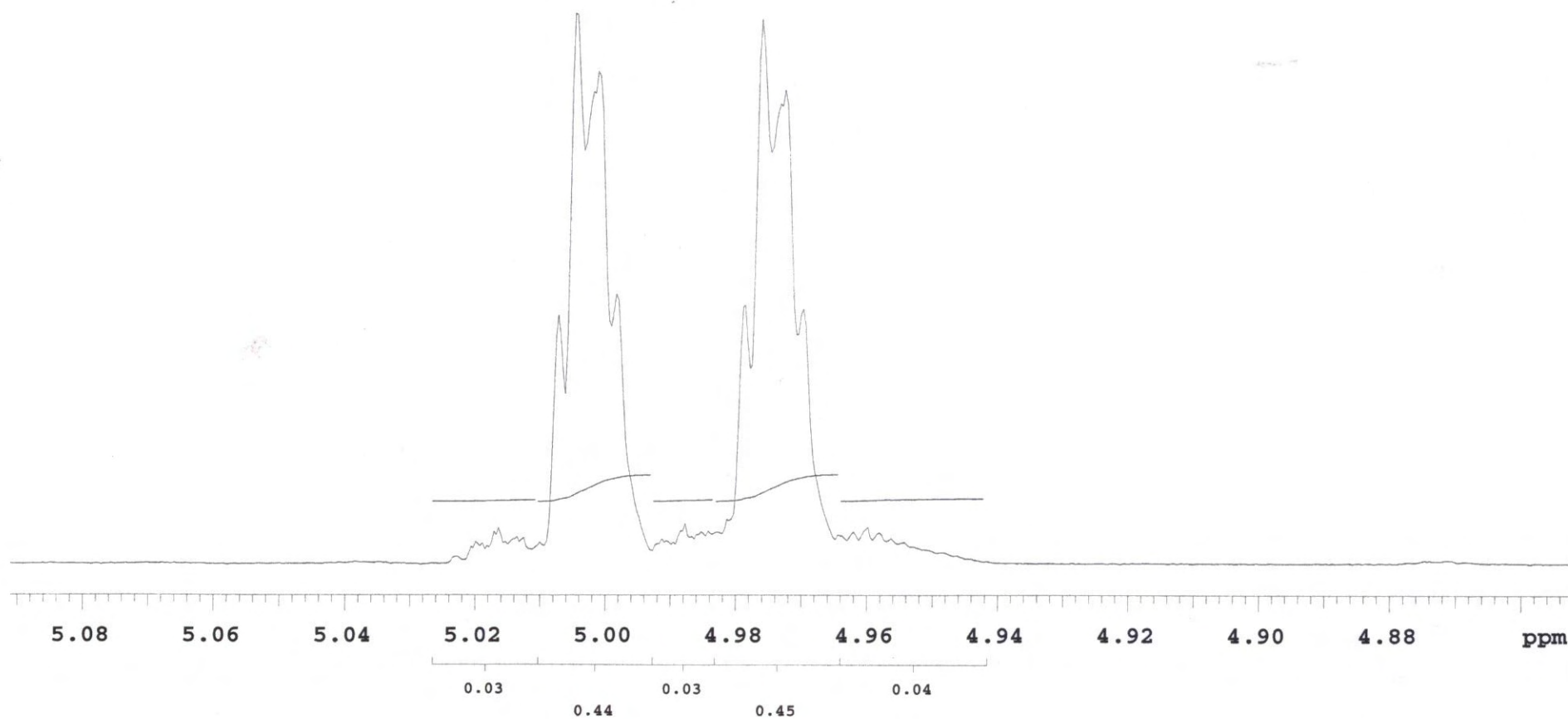


3096-5min

Pulse Sequence: s2pul



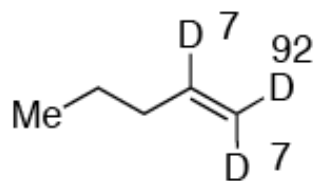
(rt, 5 min)



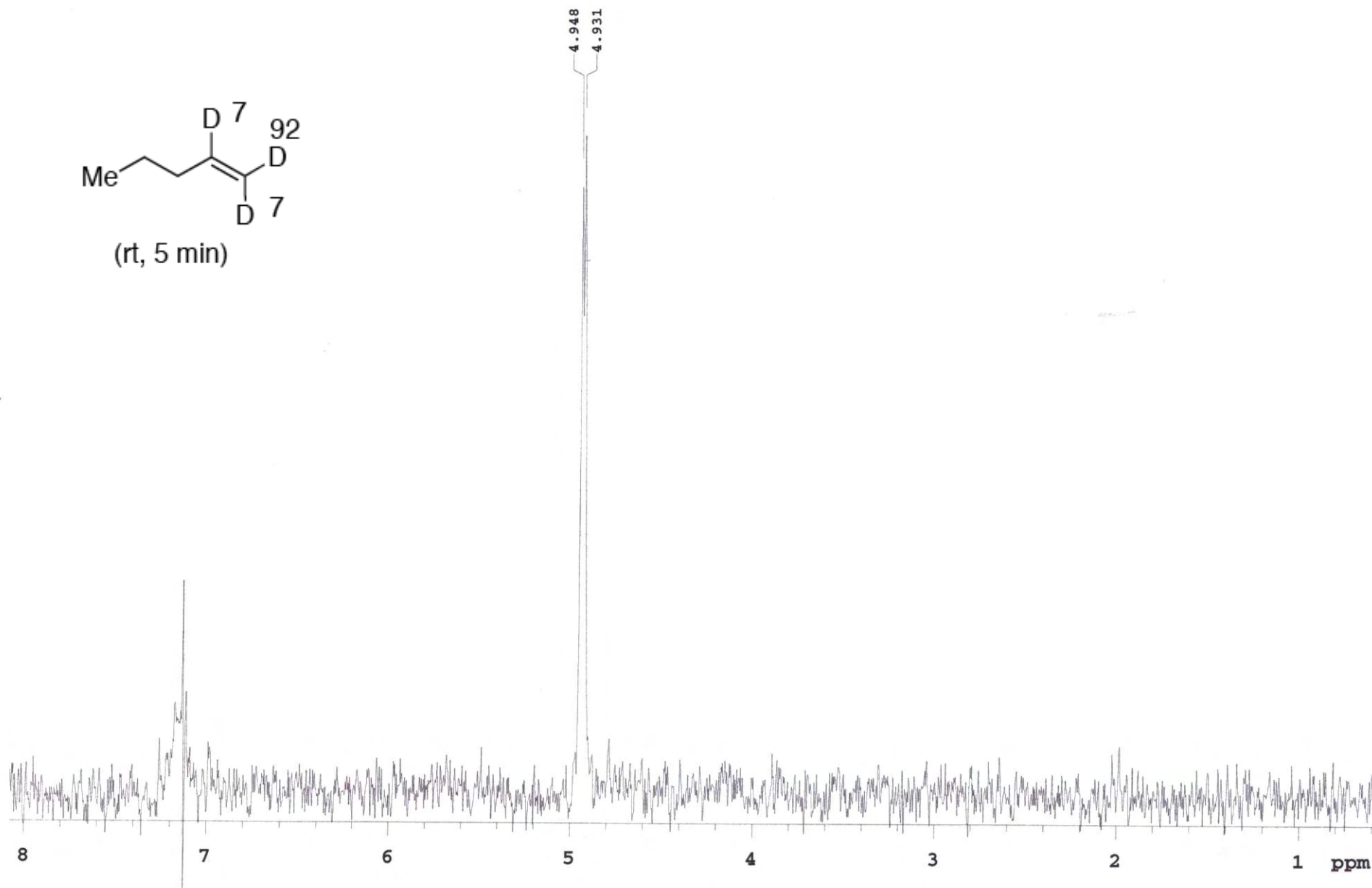
3096-5min

S57

Pulse Sequence: presat

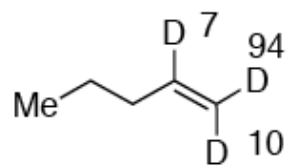
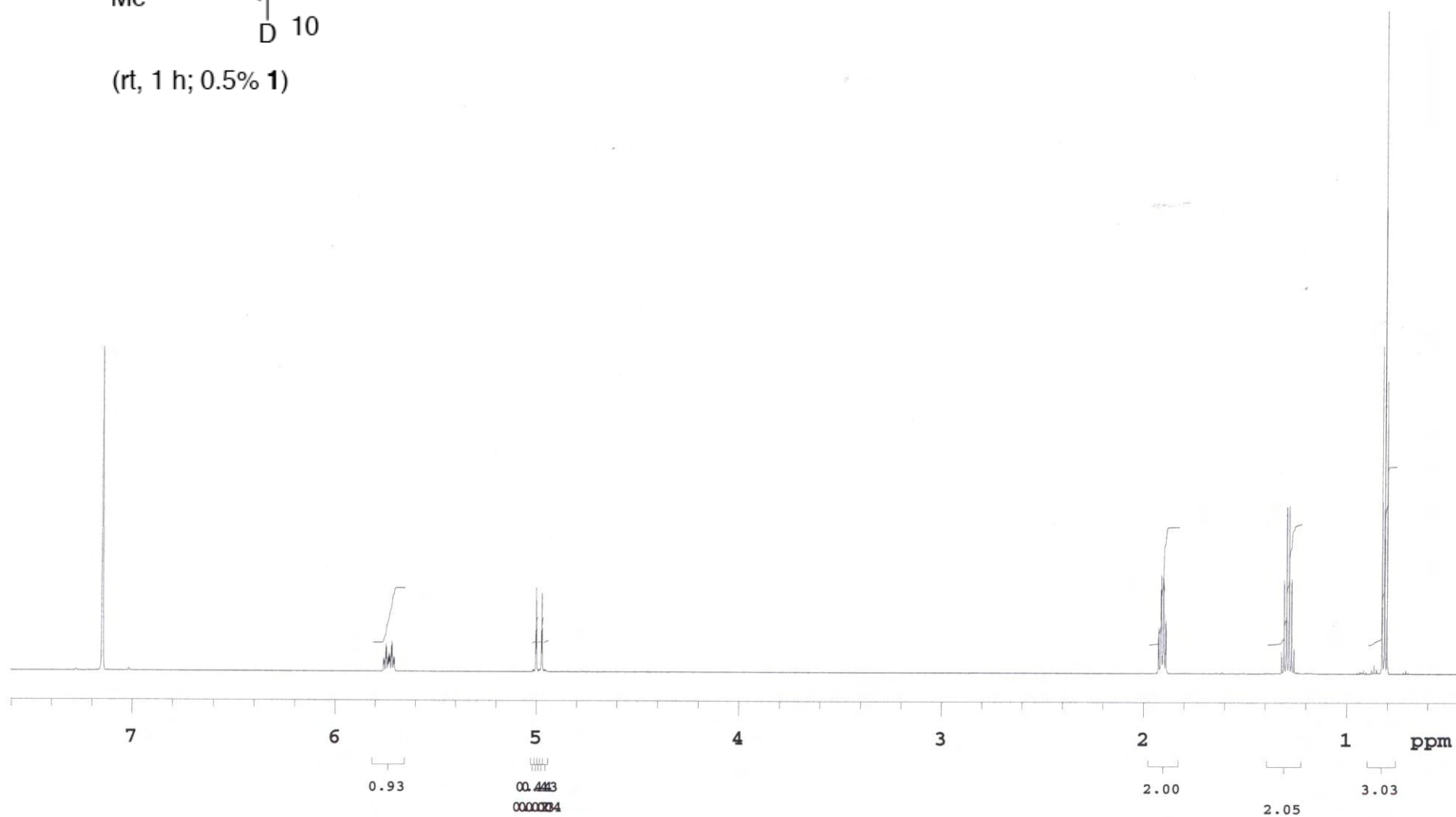


(rt, 5 min)



3097r-1h

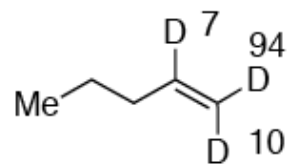
Pulse Sequence: s2pul

(rt, 1 h; 0.5% **1**)

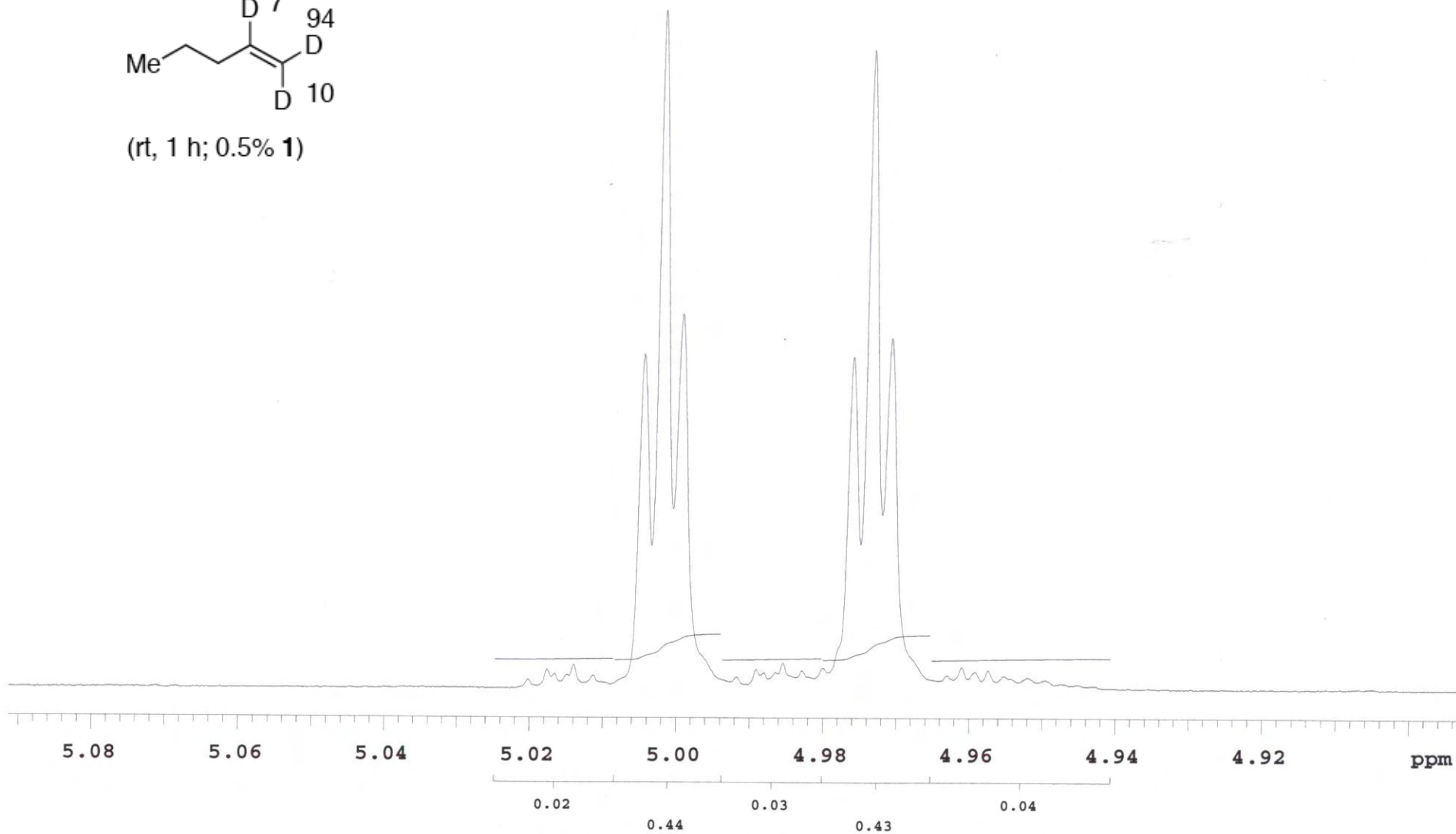
3097r-1h

S59

Pulse Sequence: s2pul

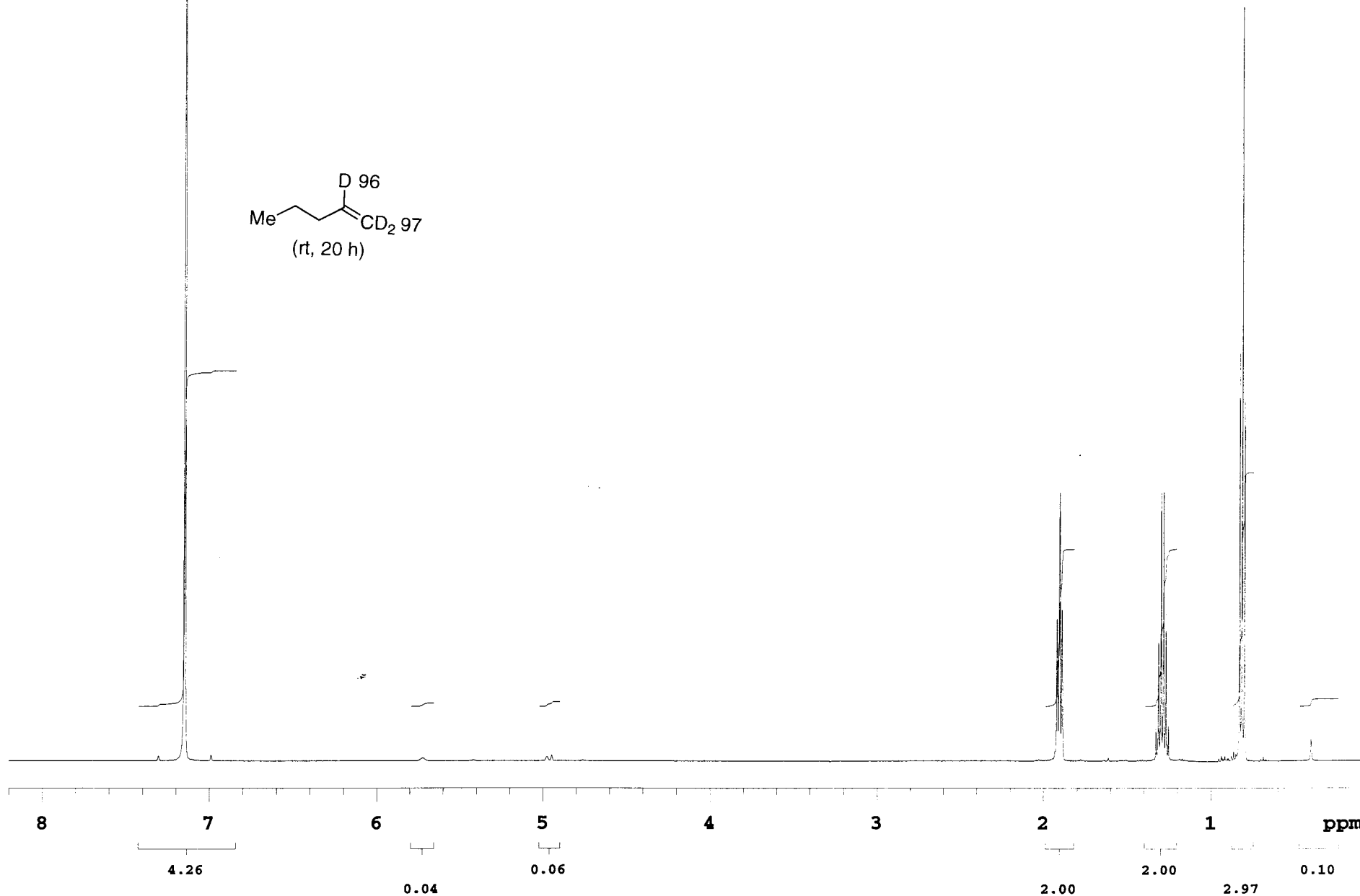
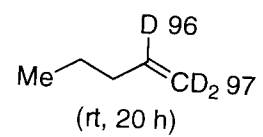


(rt, 1 h; 0.5% **1**)



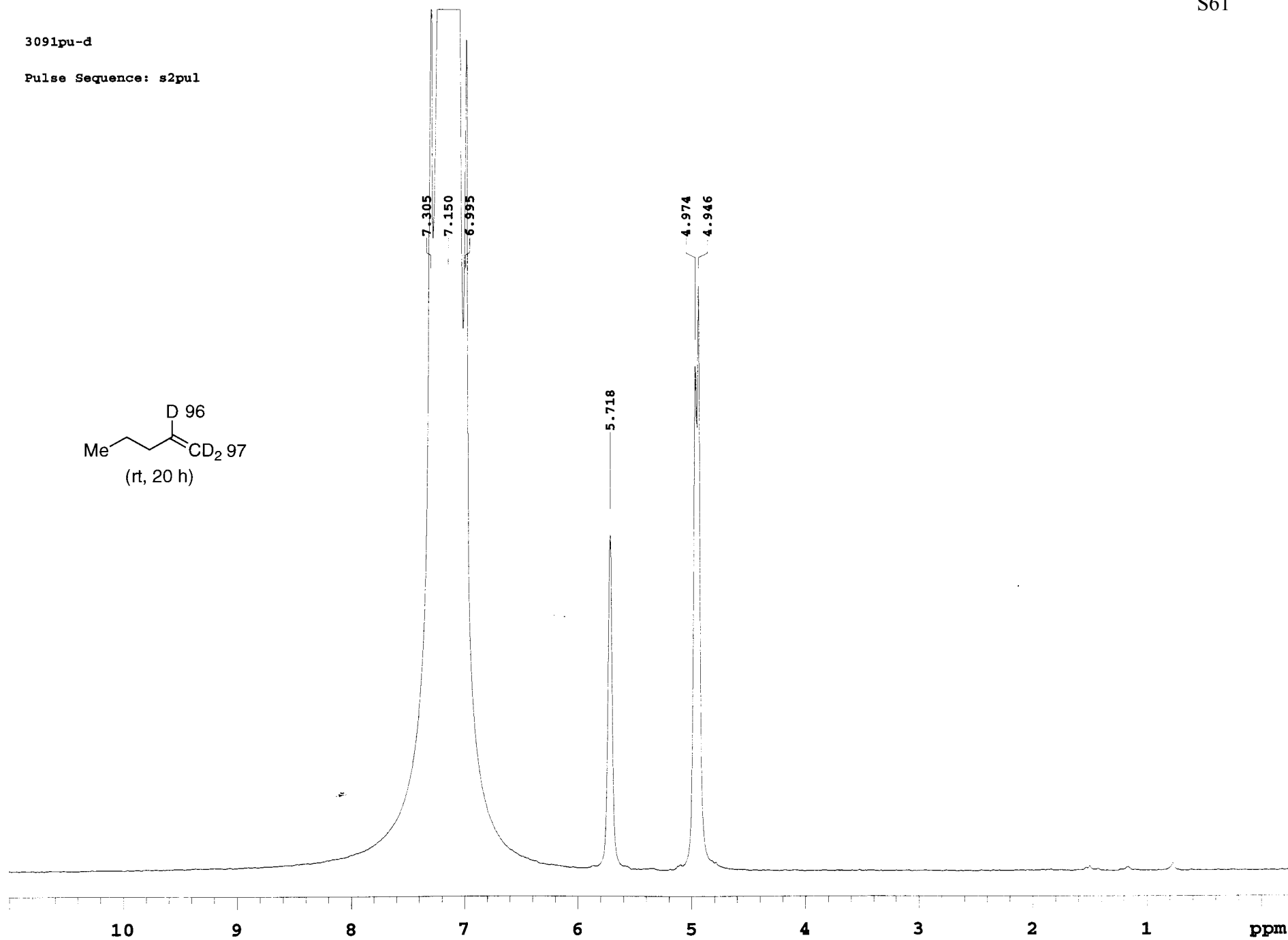
3091pu-h

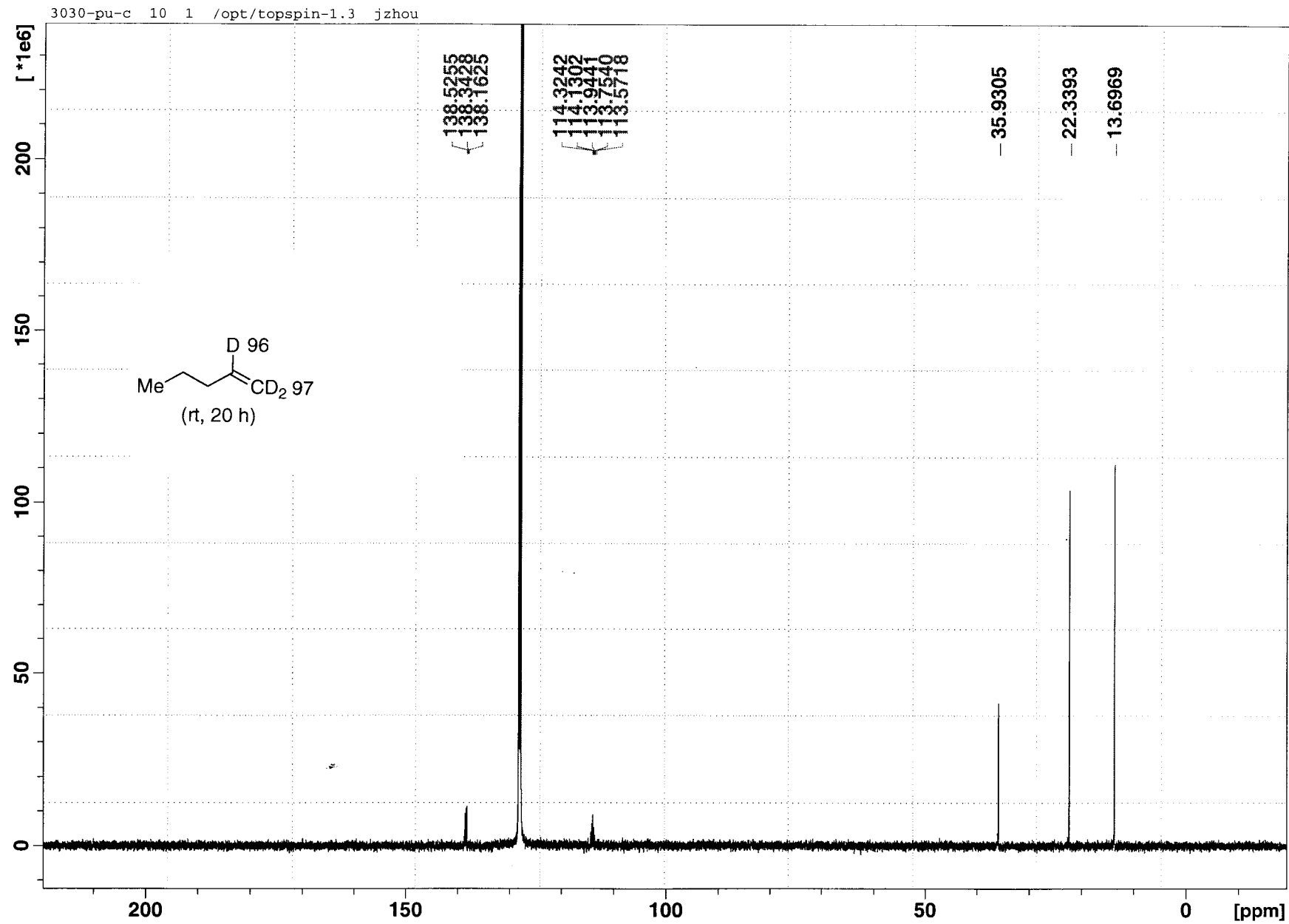
Pulse Sequence: s2pul



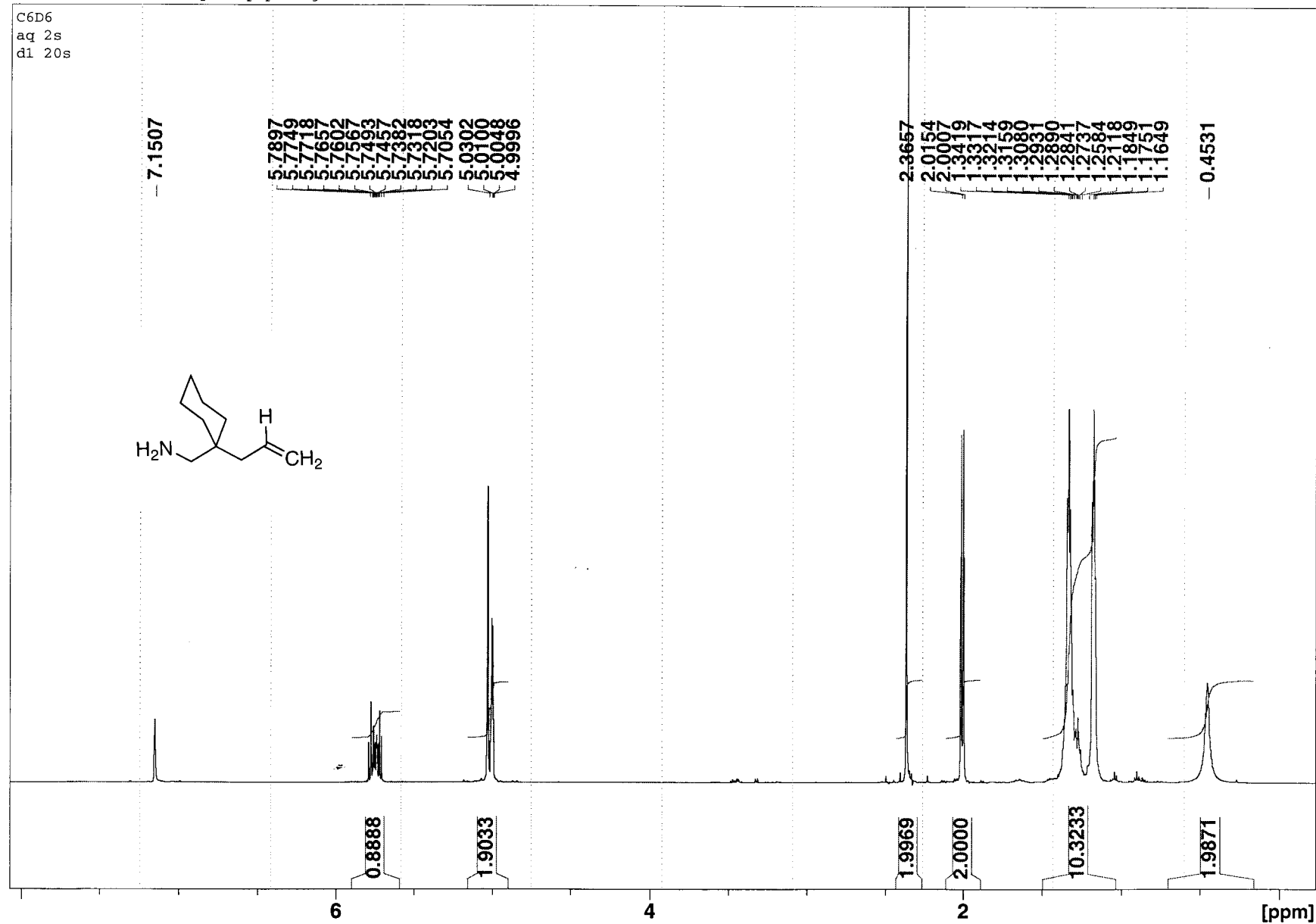
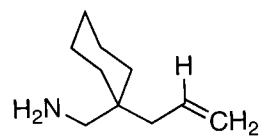
3091pu-d

Pulse Sequence: s2pul

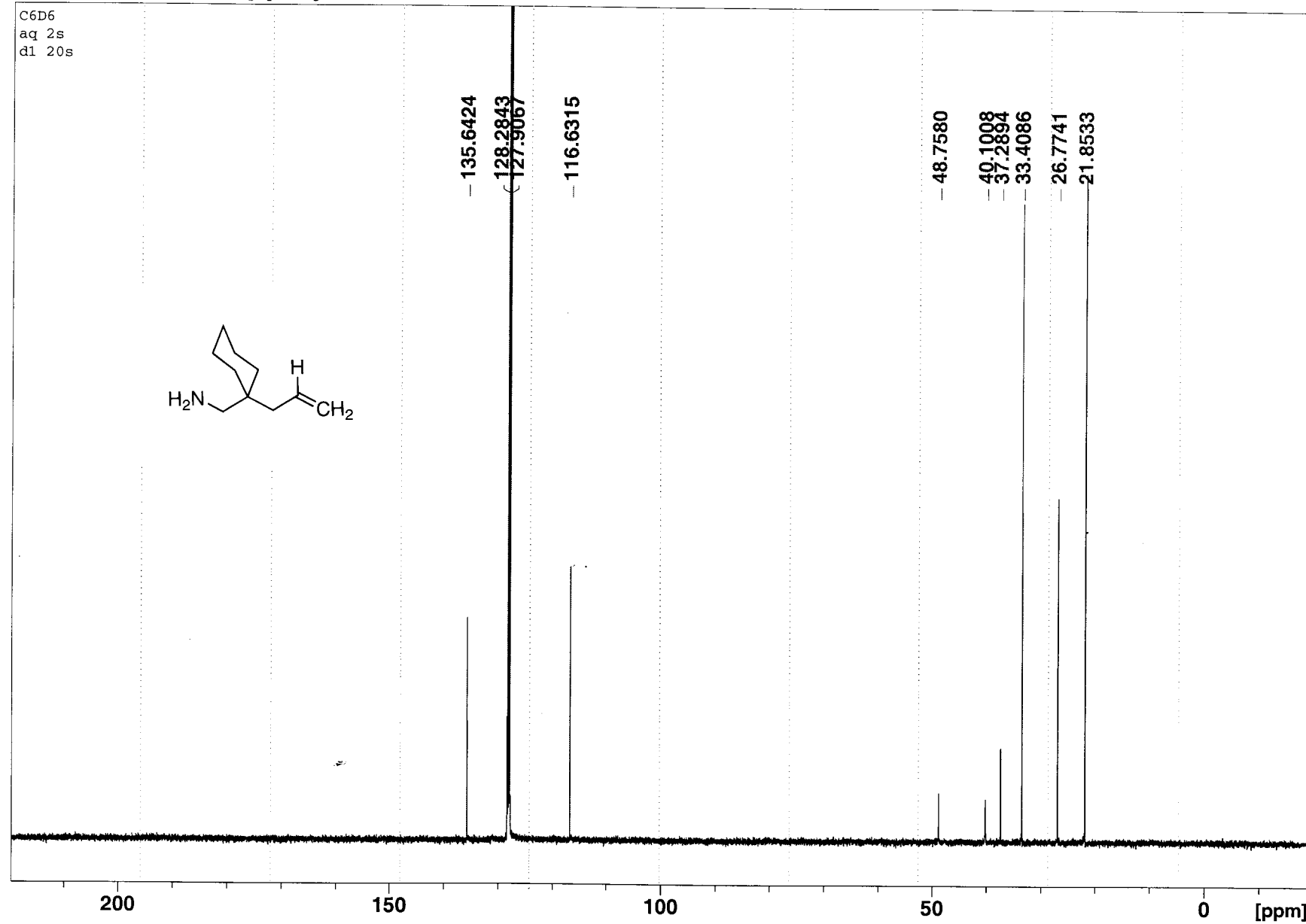
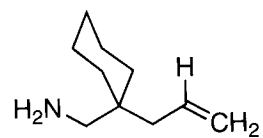


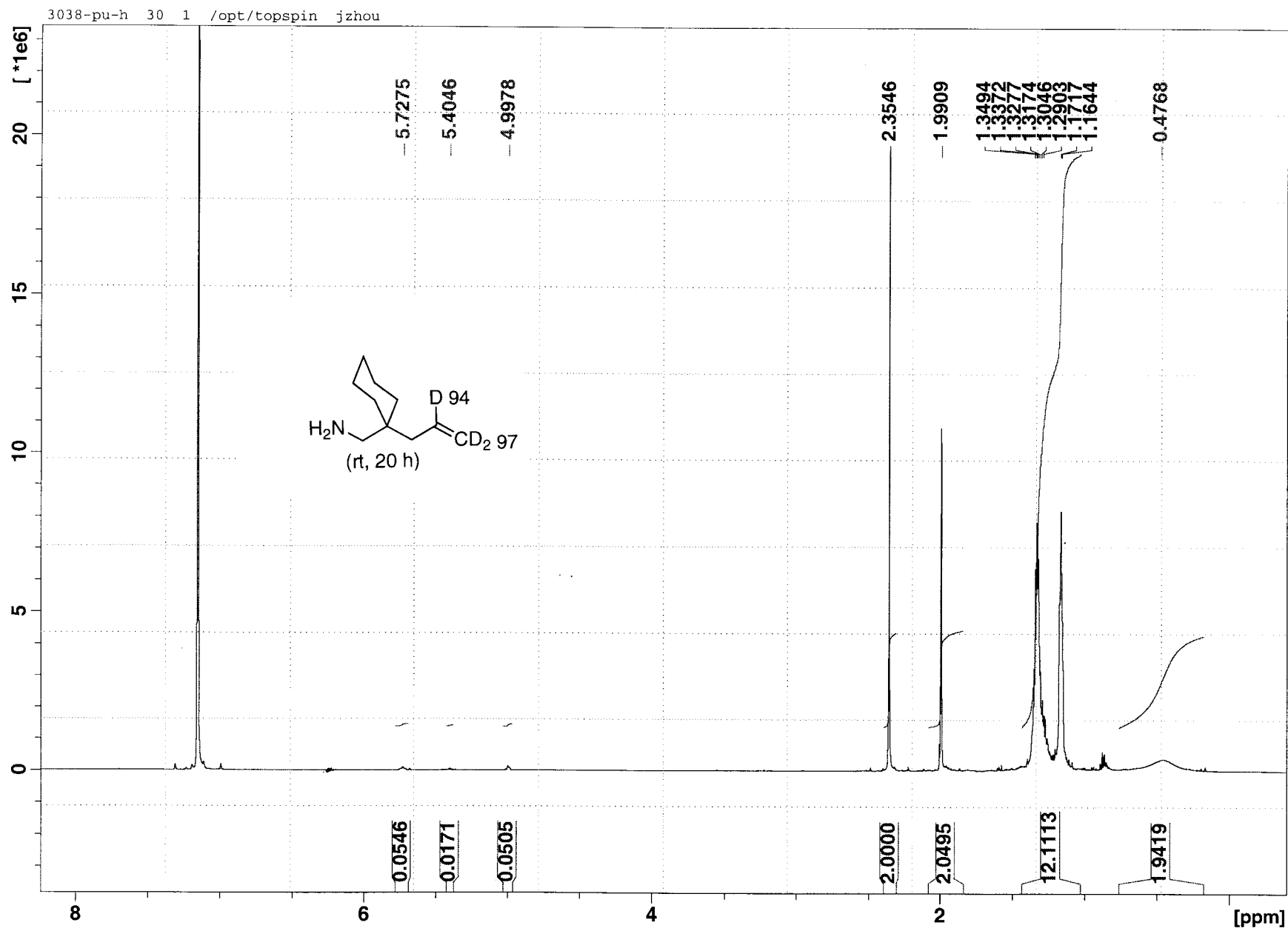


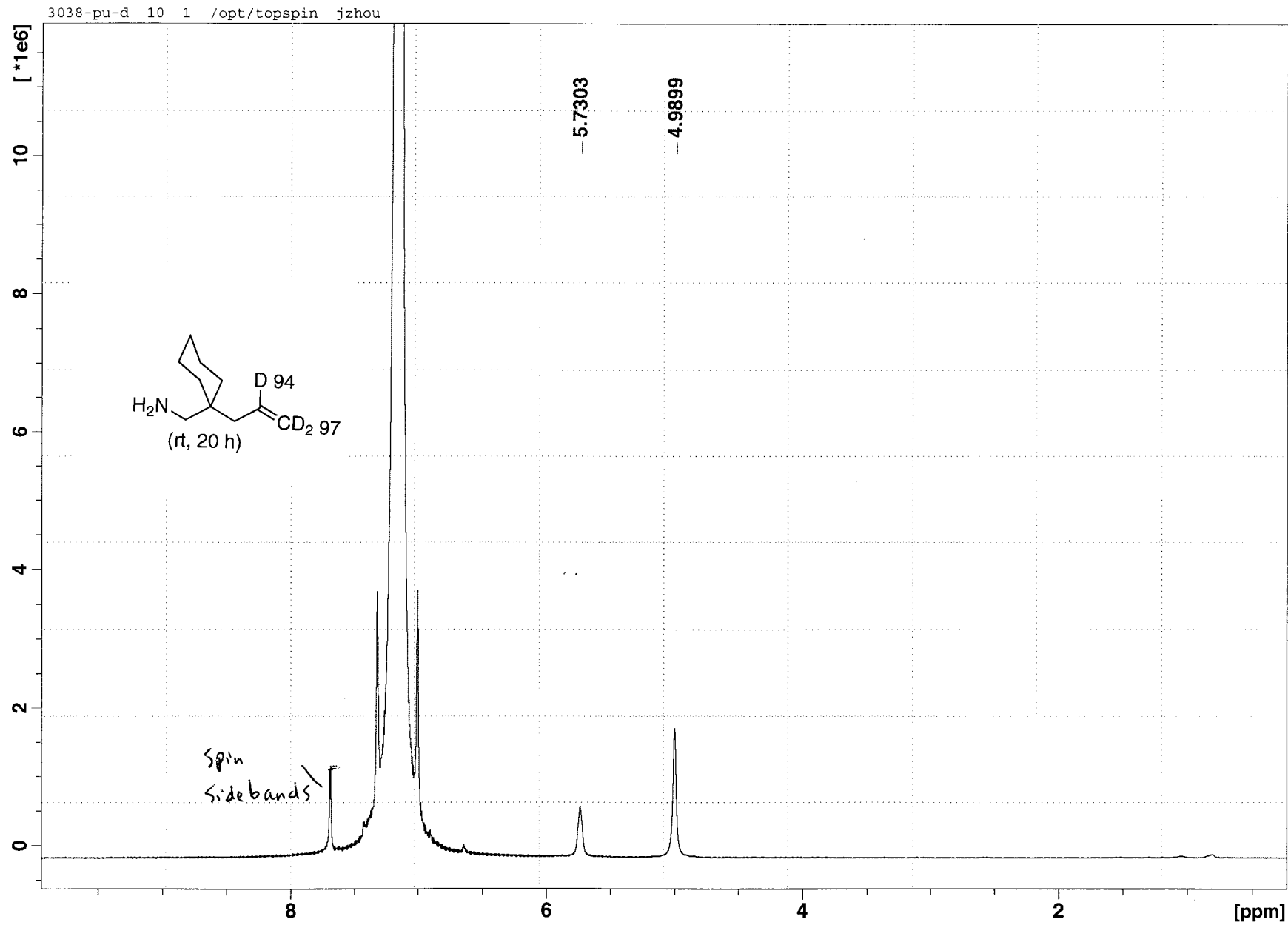
3038-sm-h 30 1 /opt/topspin jzhou

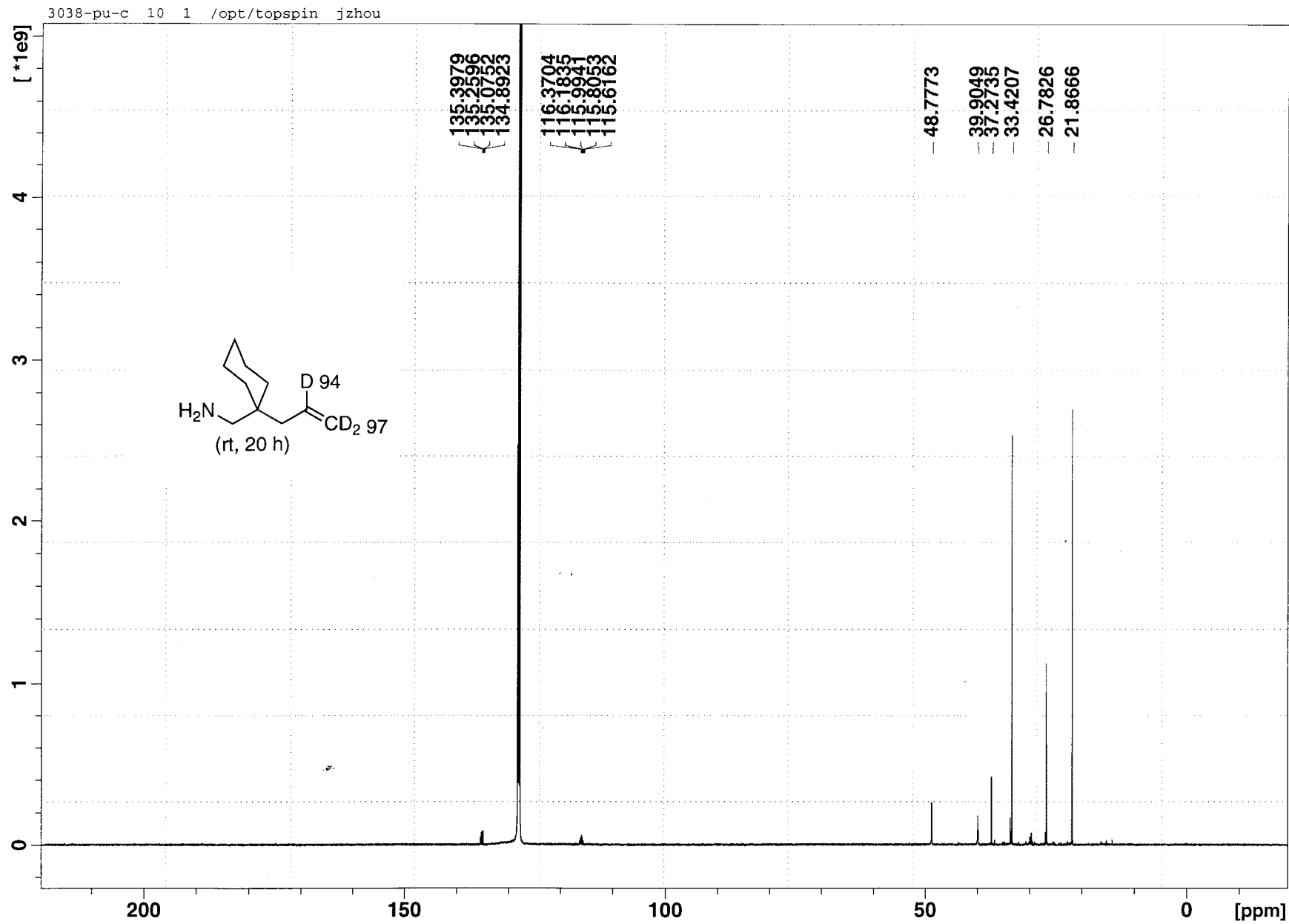
C6D6
aq 2s
d1 20s

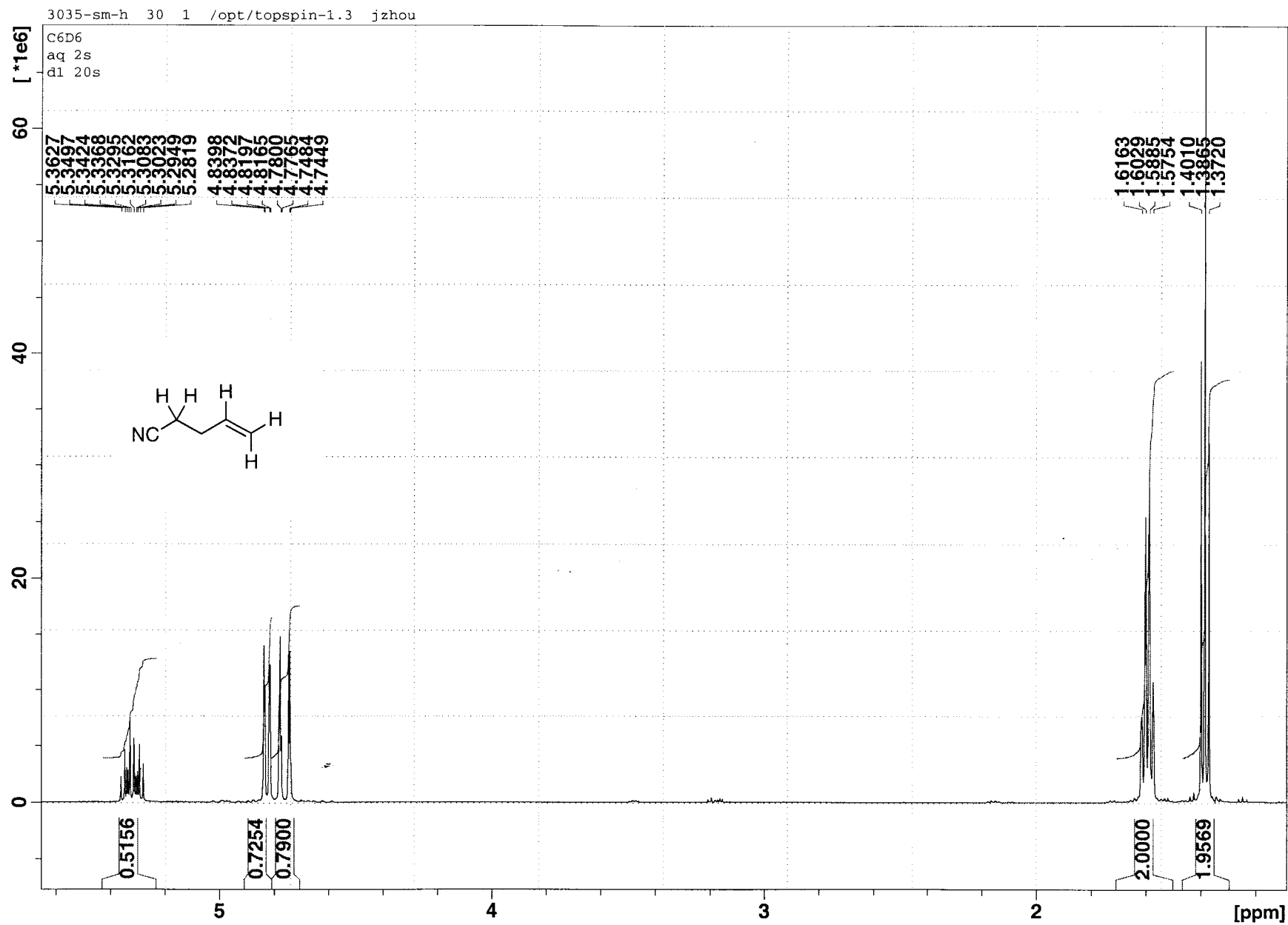
3038-sm-c 30 1 /opt/topspin jzhou

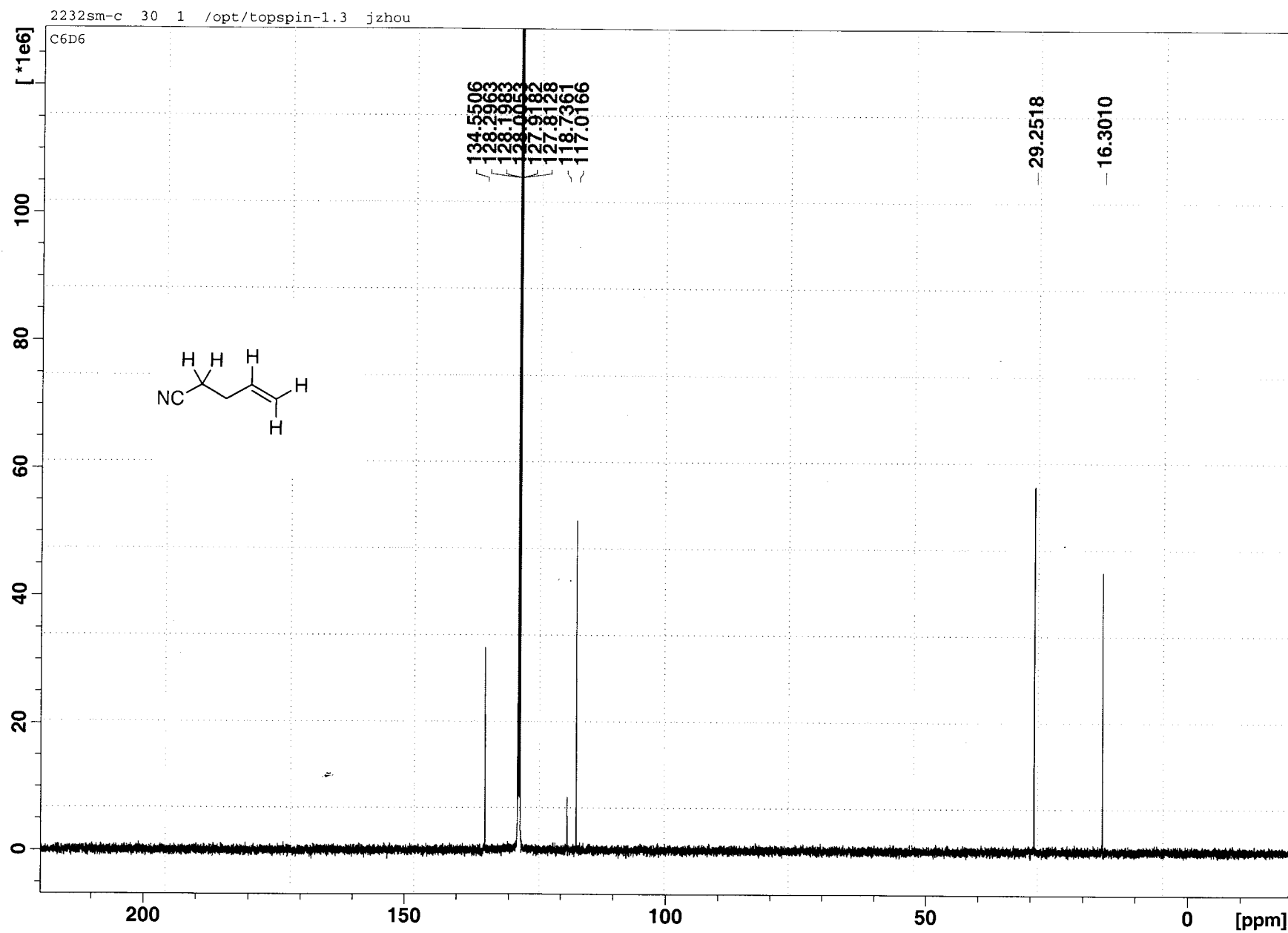
C6D6
aq 2s
d1 20s



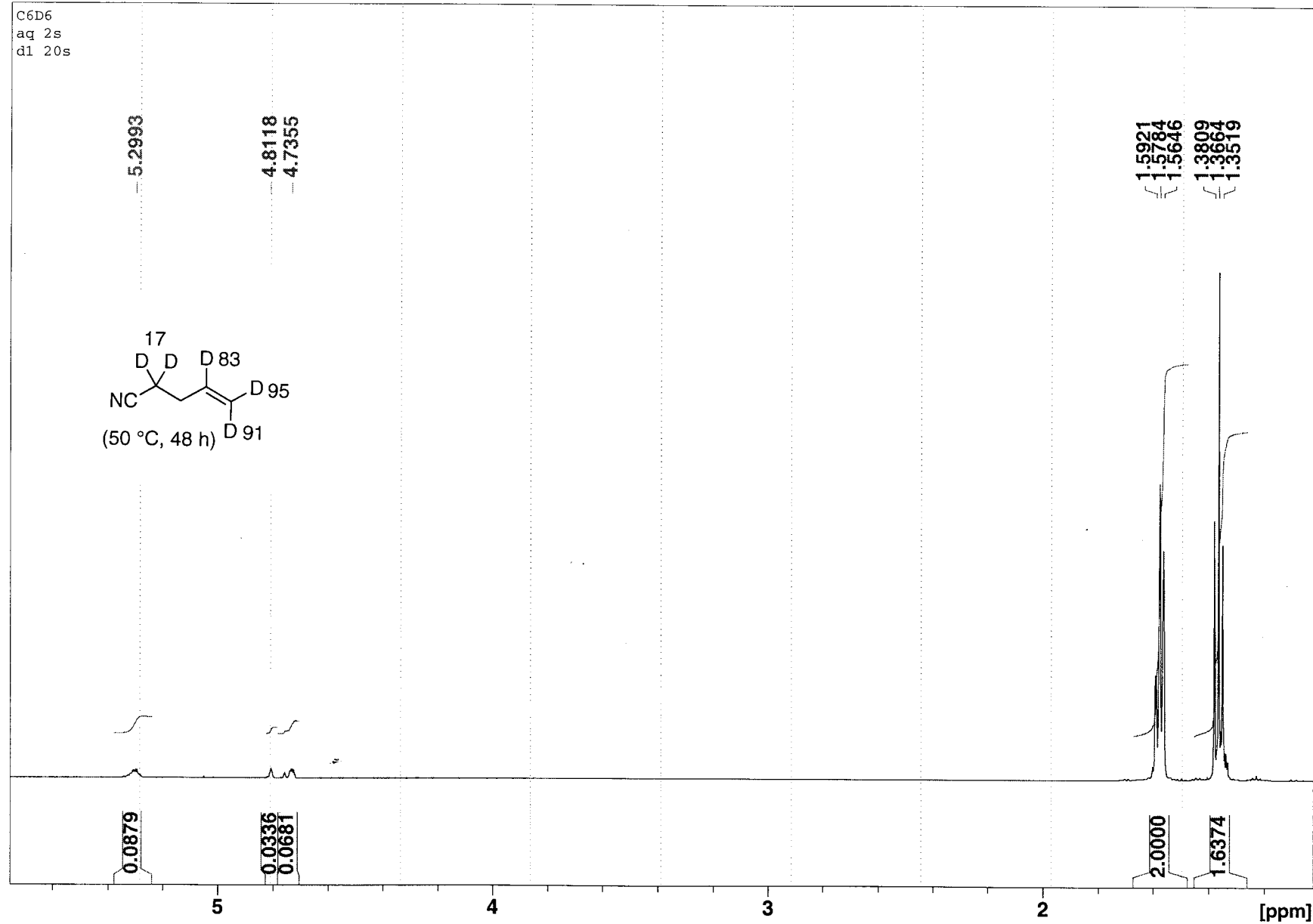
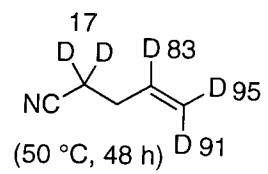


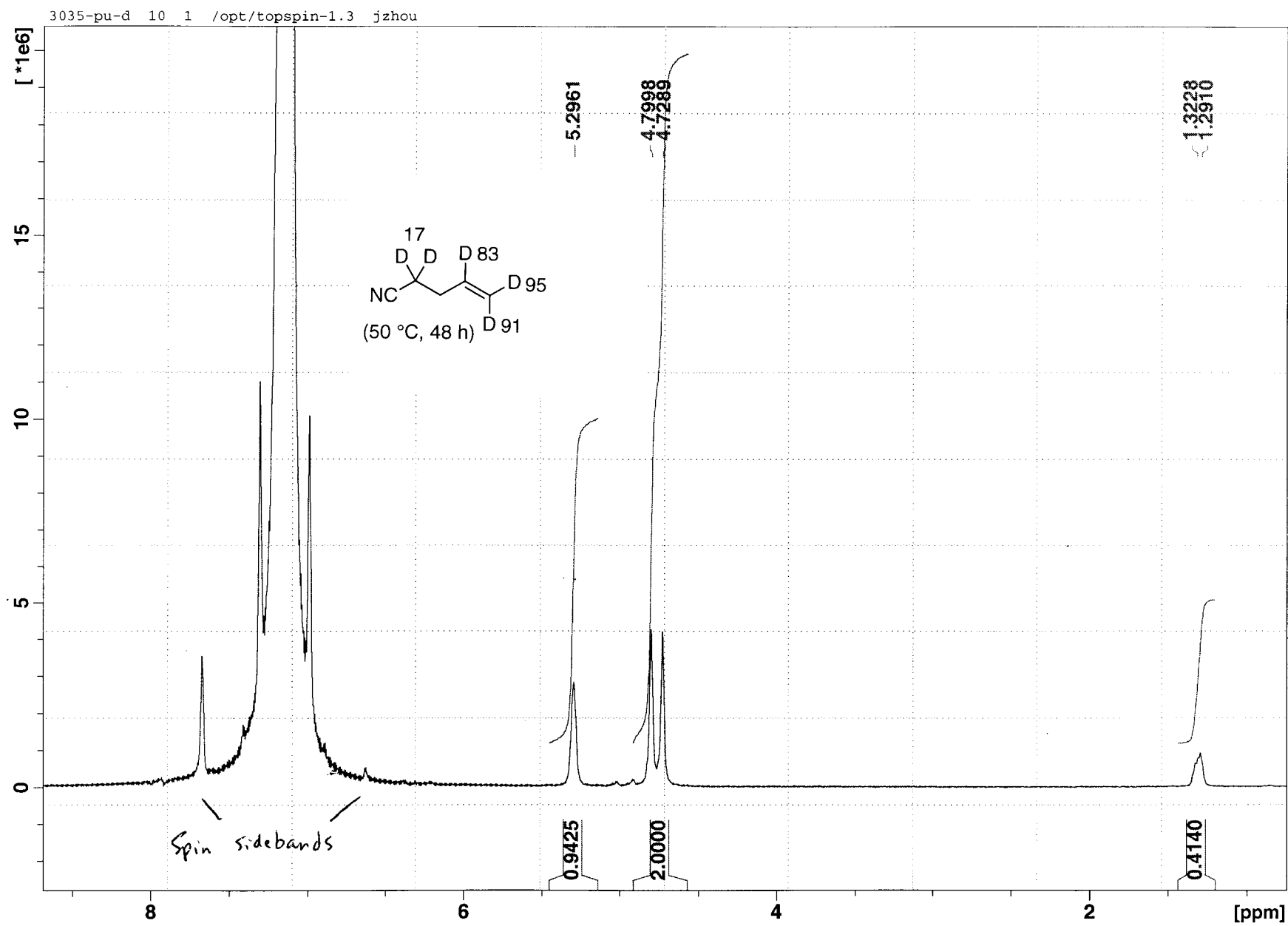




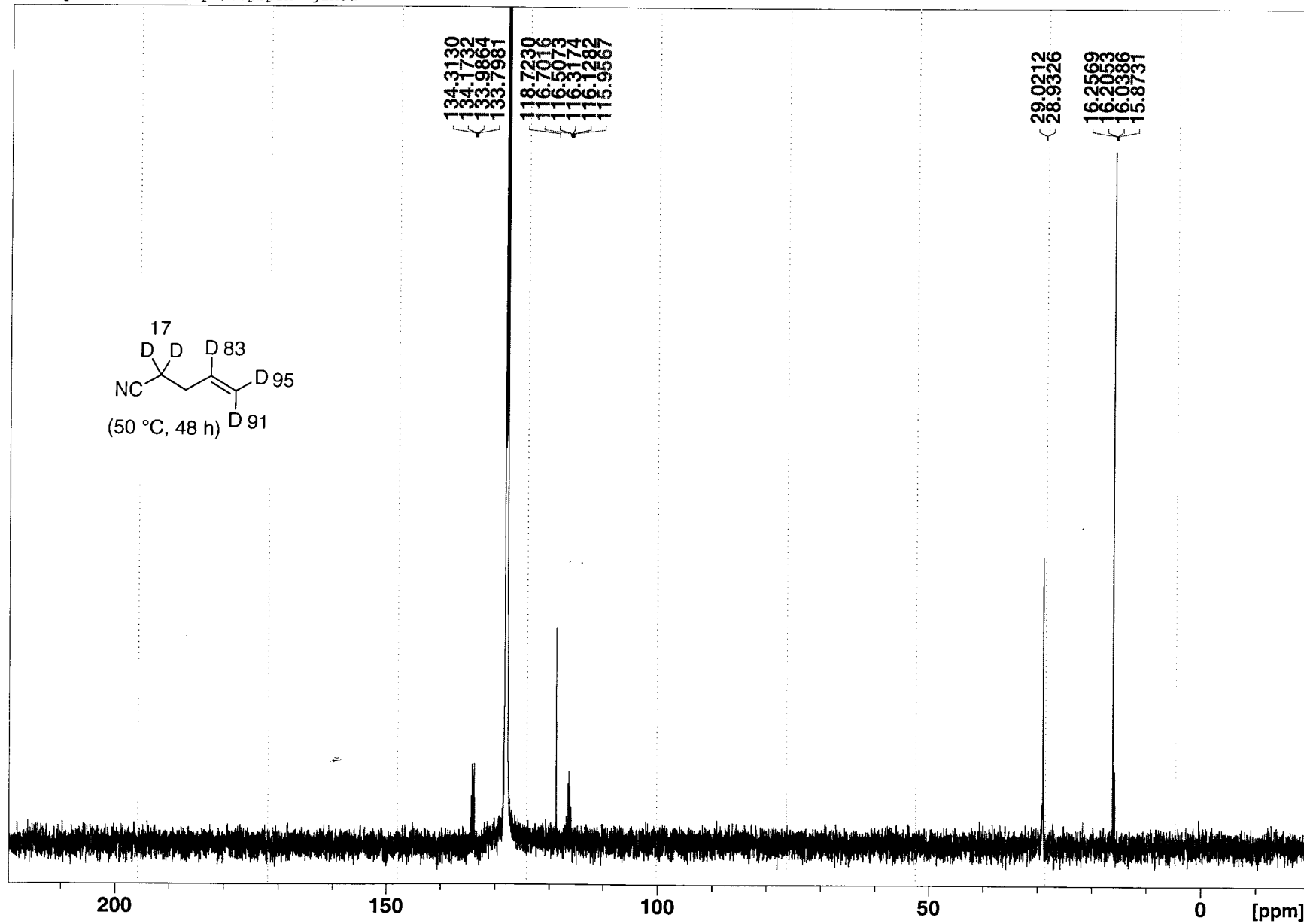


3035-pu-h 30 1 /opt/topspin jzhou

C6D6
aq 2s
d1 20s

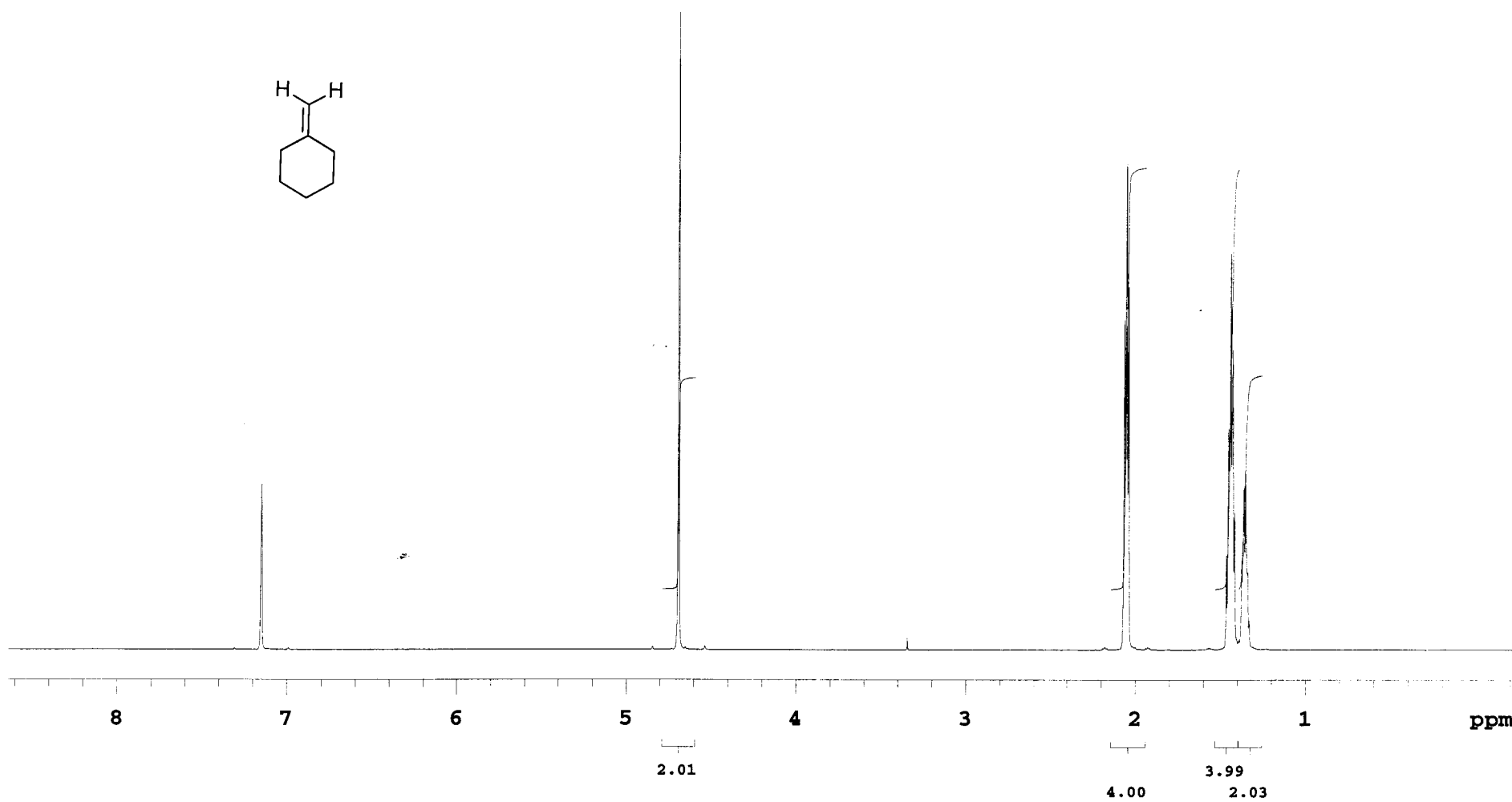
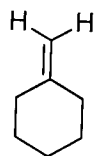


3035-pu-c 10 1 /opt/topspin jzhou



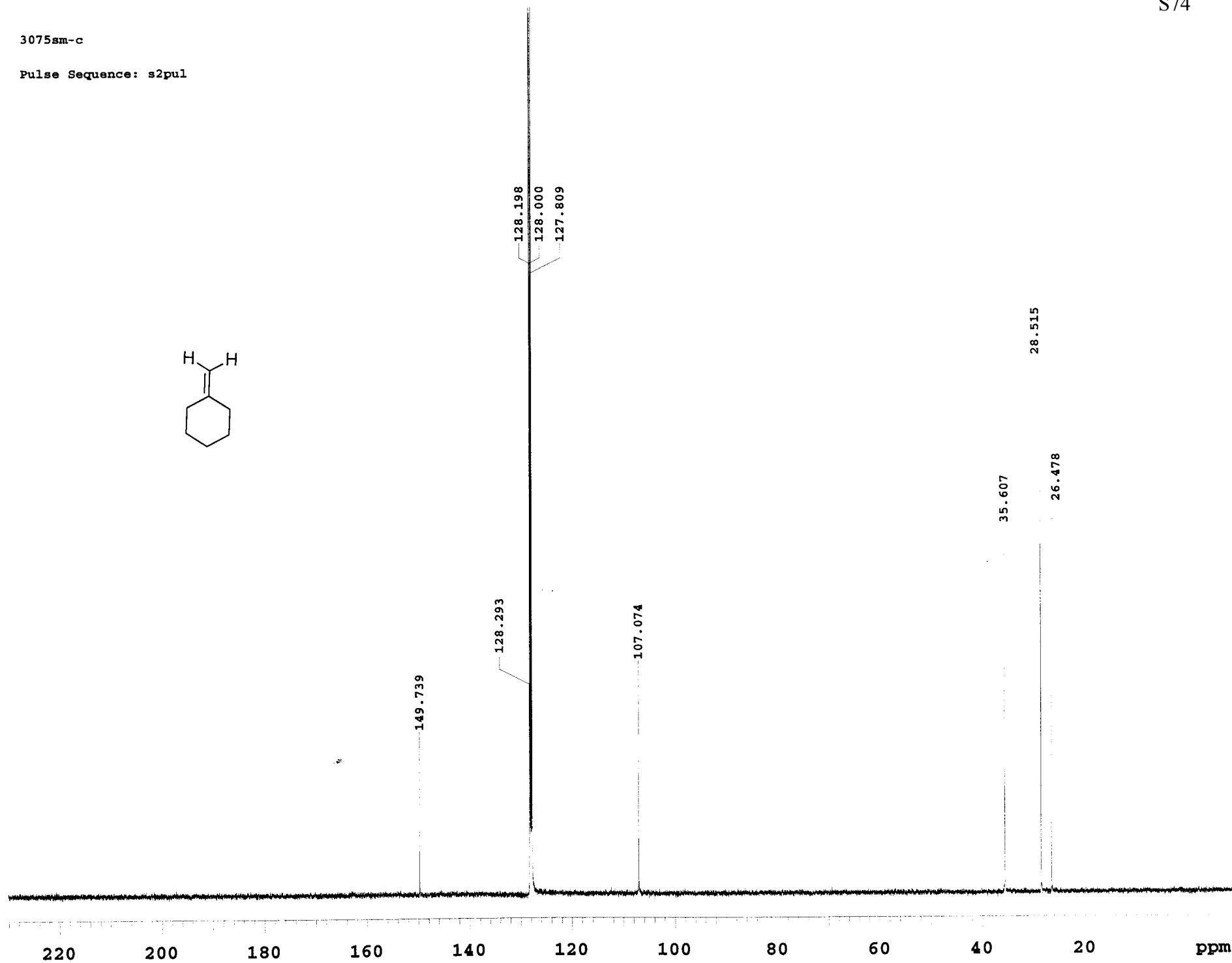
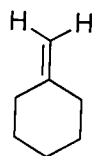
3075sm-h

Pulse Sequence: s2pul



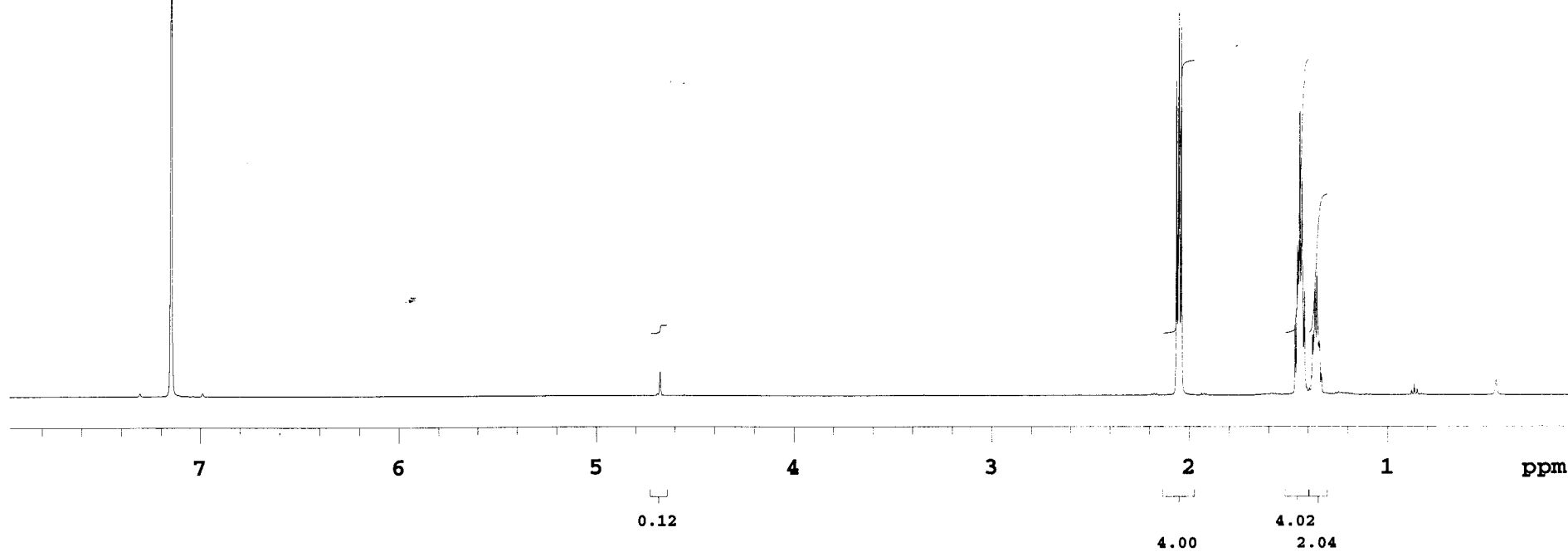
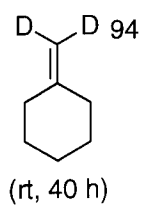
3075sm-c

Pulse Sequence: s2pul



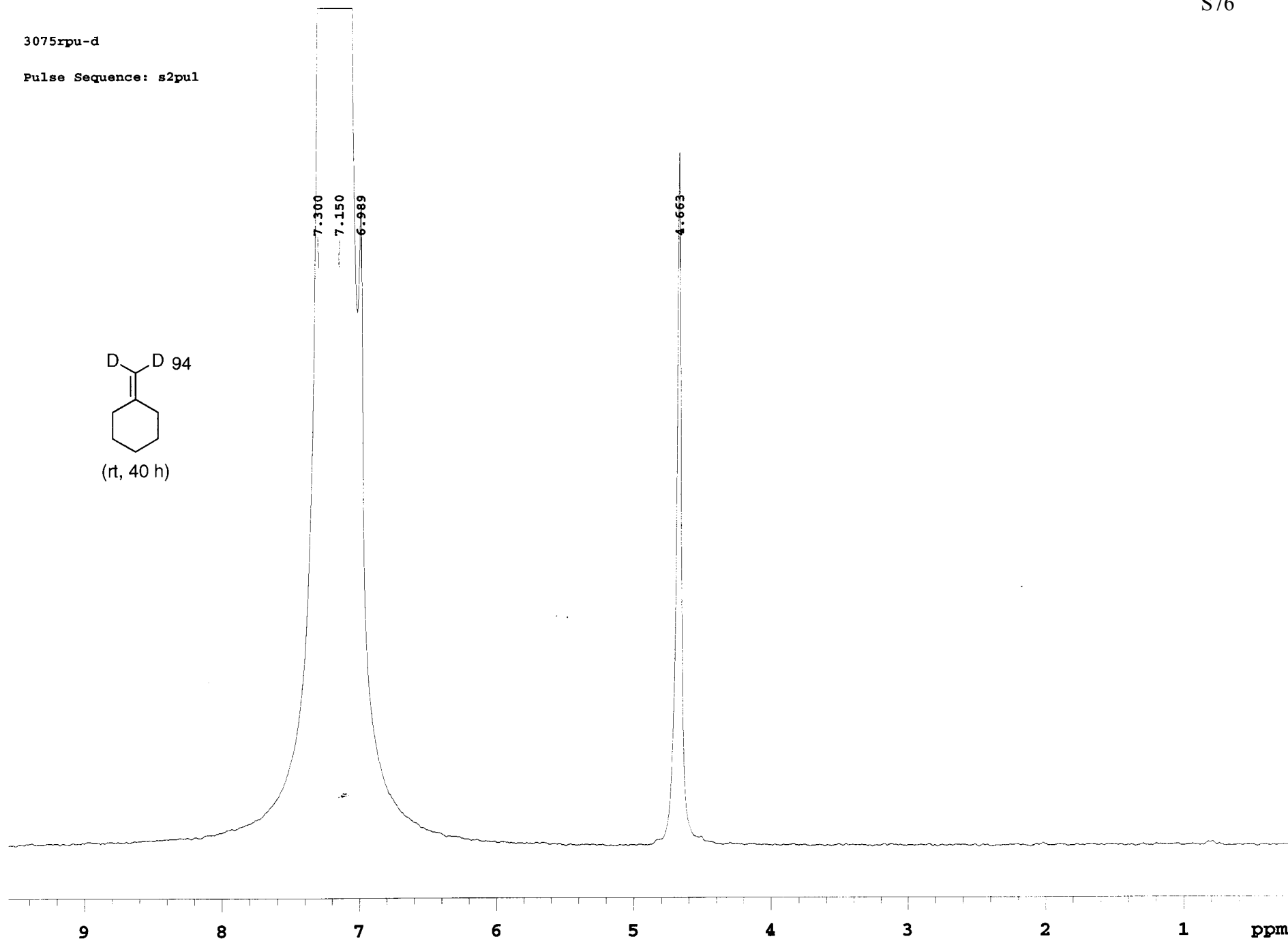
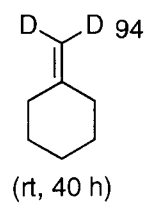
3075xpu-h

Pulse Sequence: s2pul



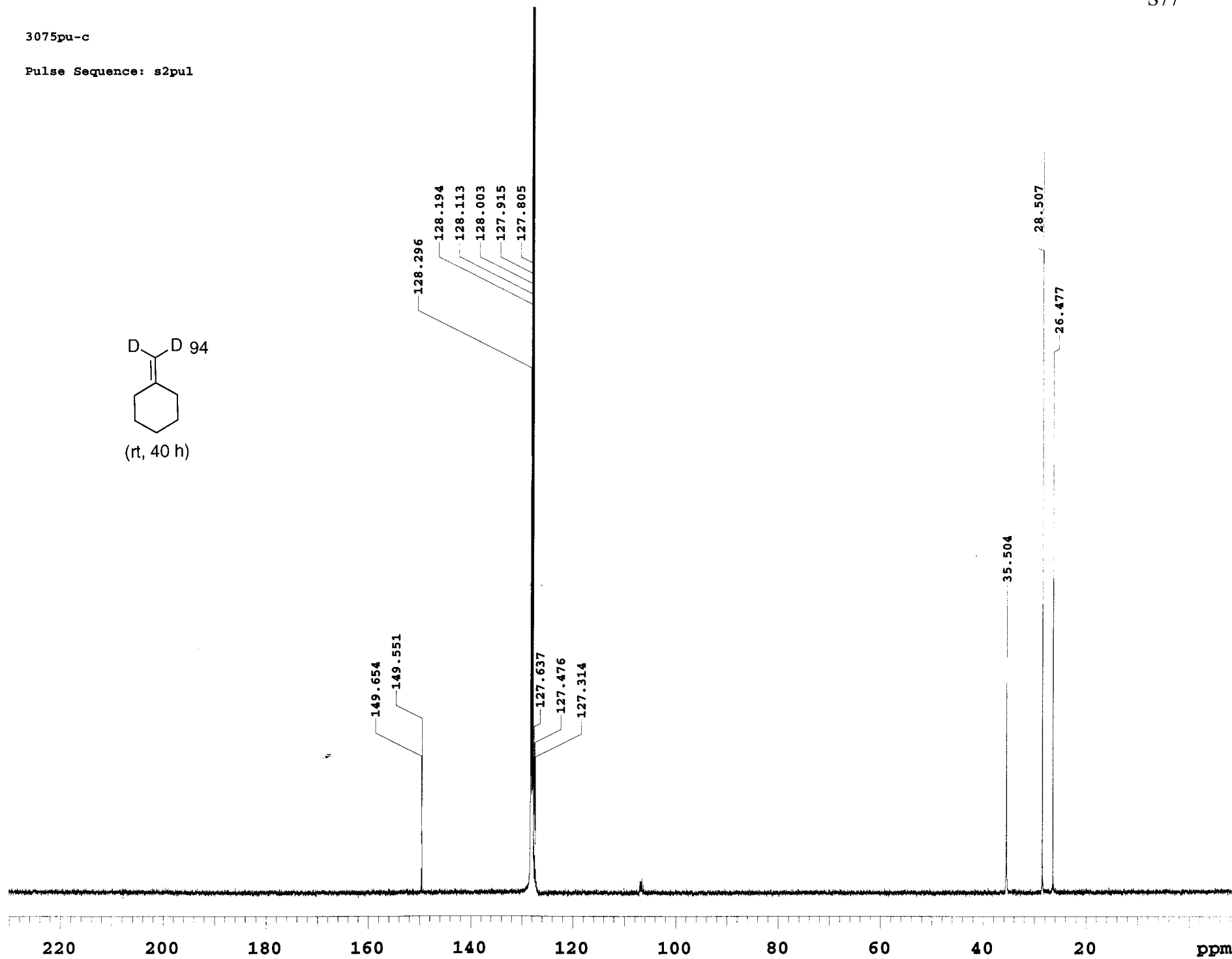
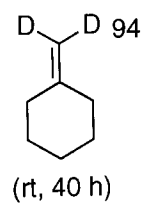
3075rpu-d

Pulse Sequence: s2pul

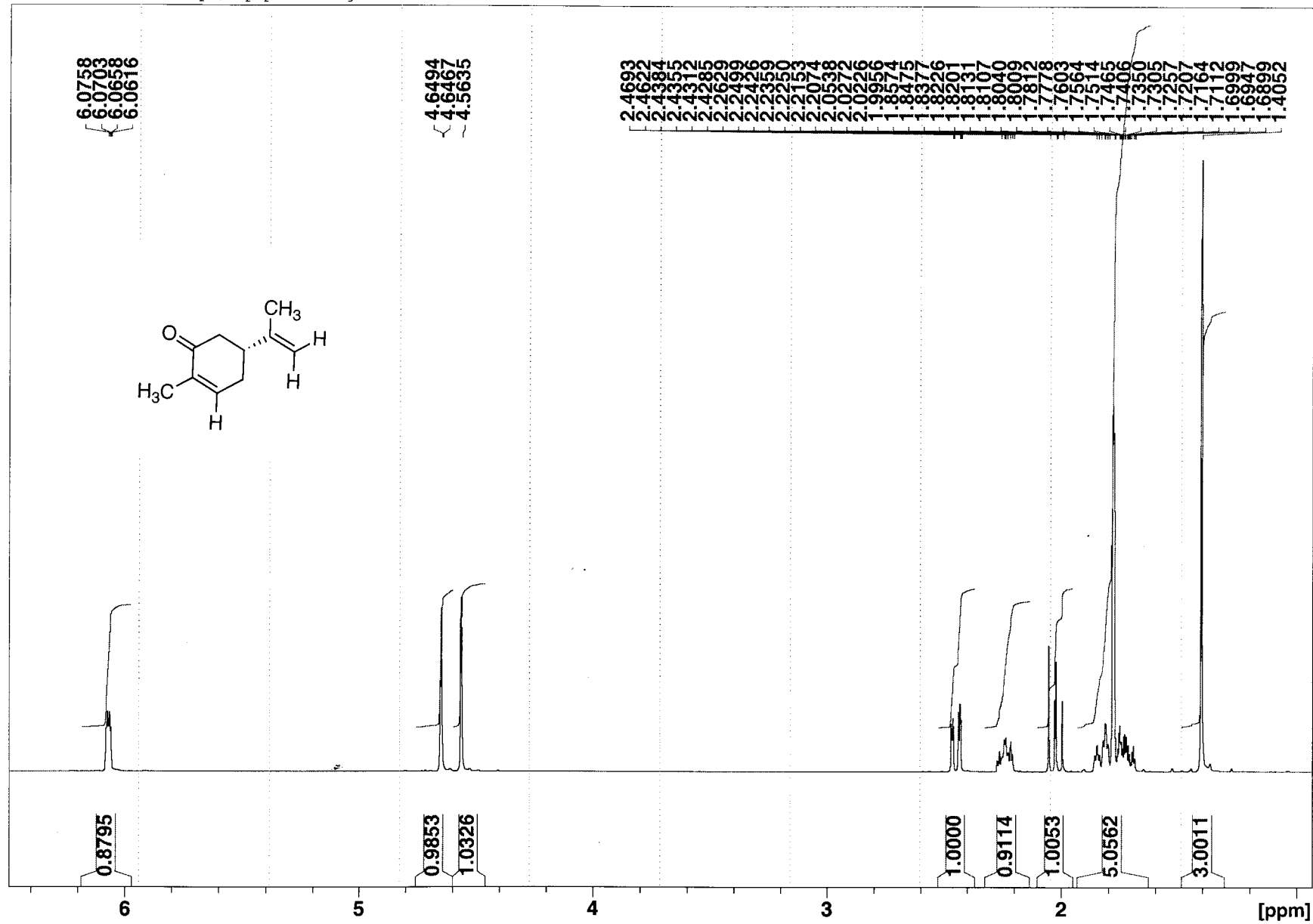


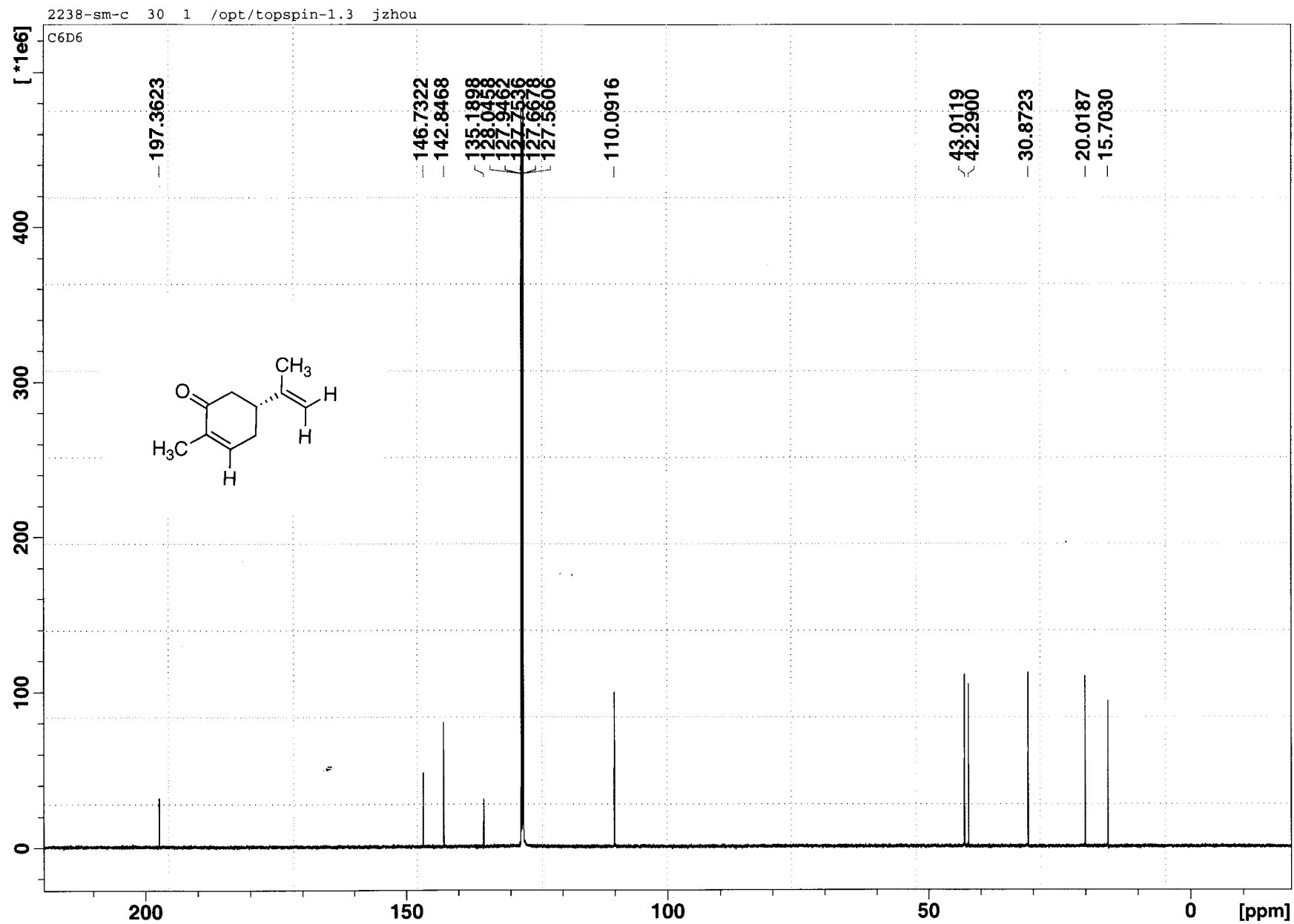
3075pu-c

Pulse Sequence: s2pul

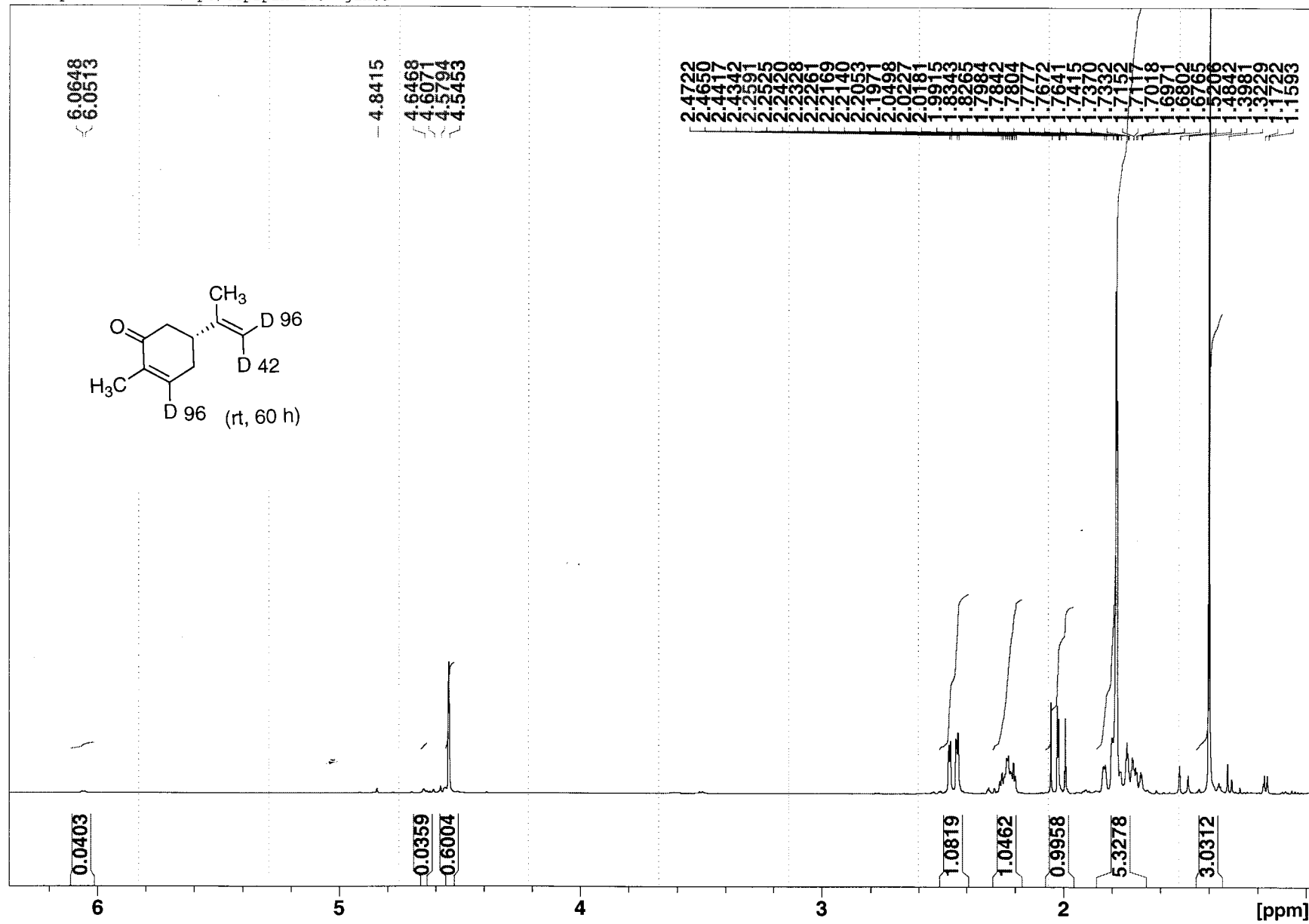


3032-sm-h 30 1 /opt/topspin-1.3 jzhou

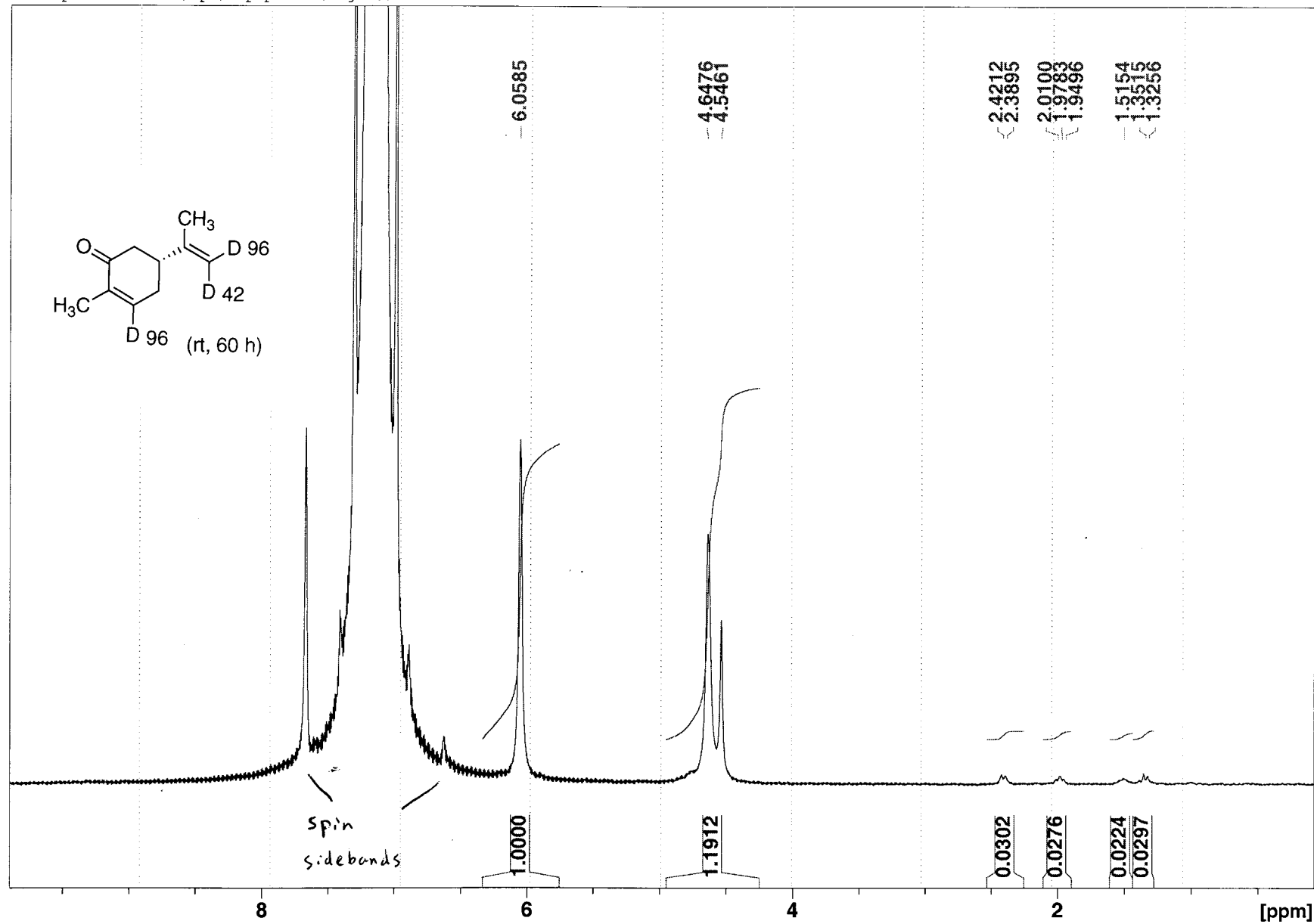


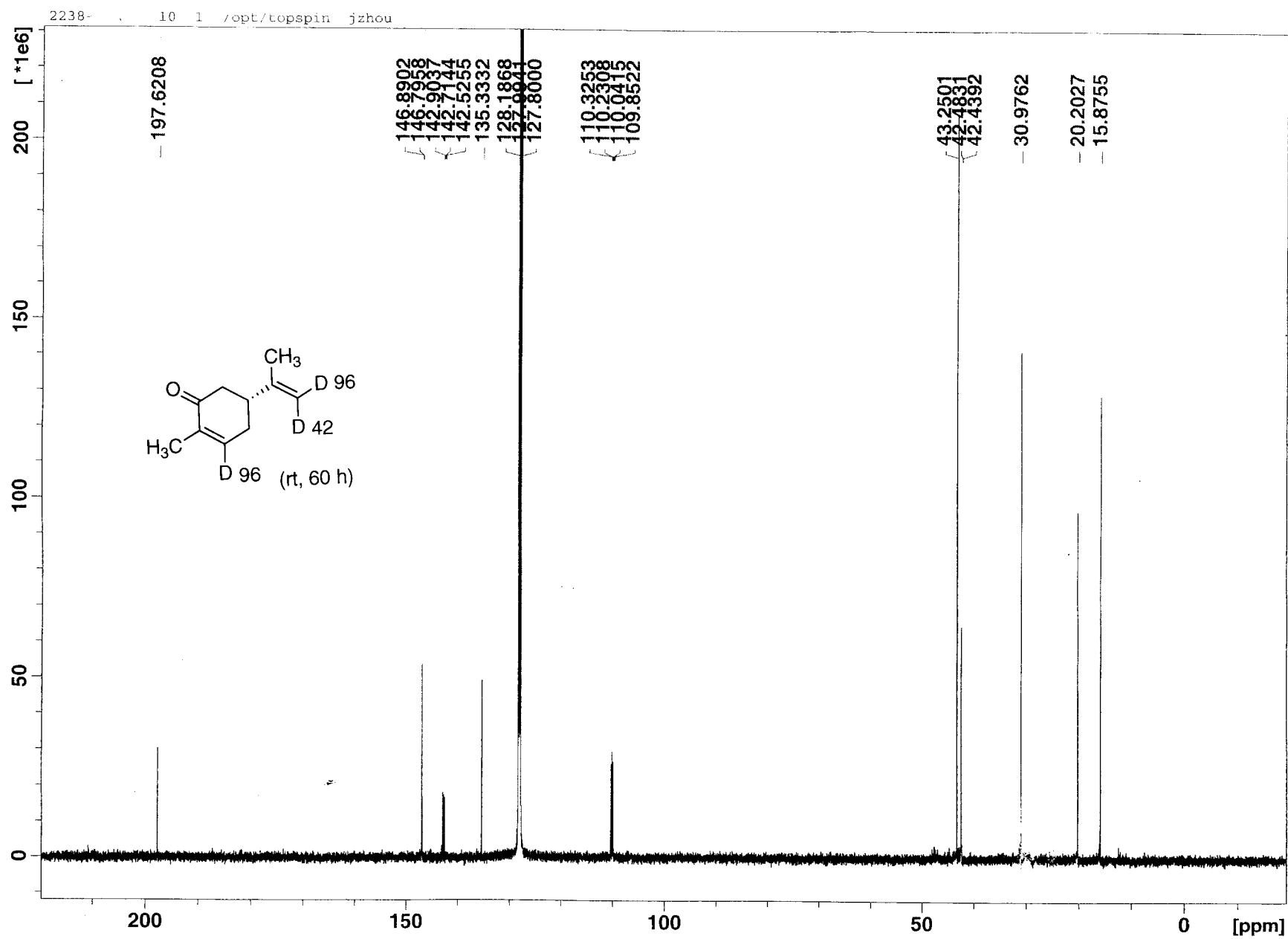


3032-pu-h 30 1 /opt/topspin-1.3 jzhou



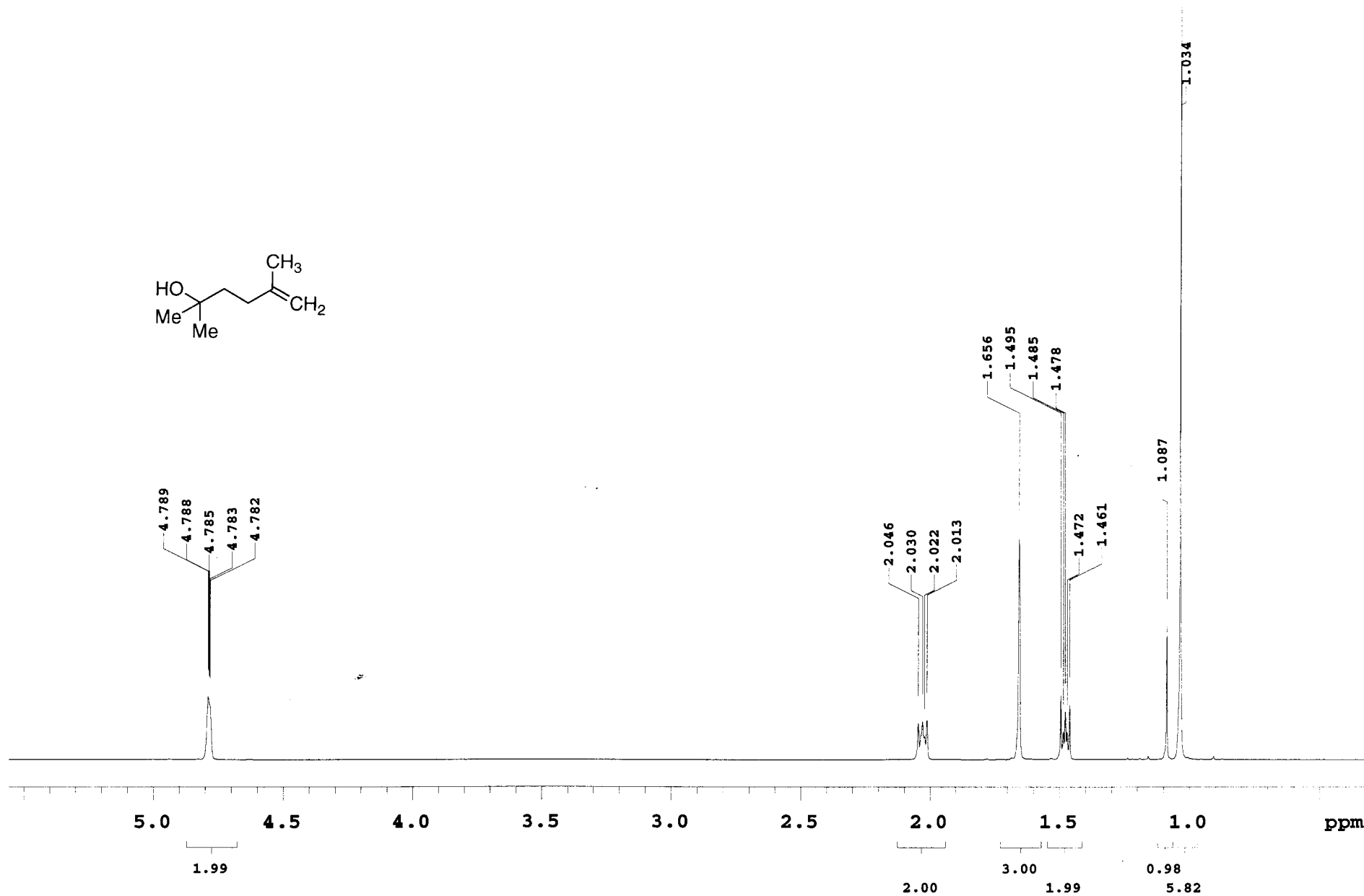
3032-pu-d 10 1 /opt/topspin-1.3 jzhou





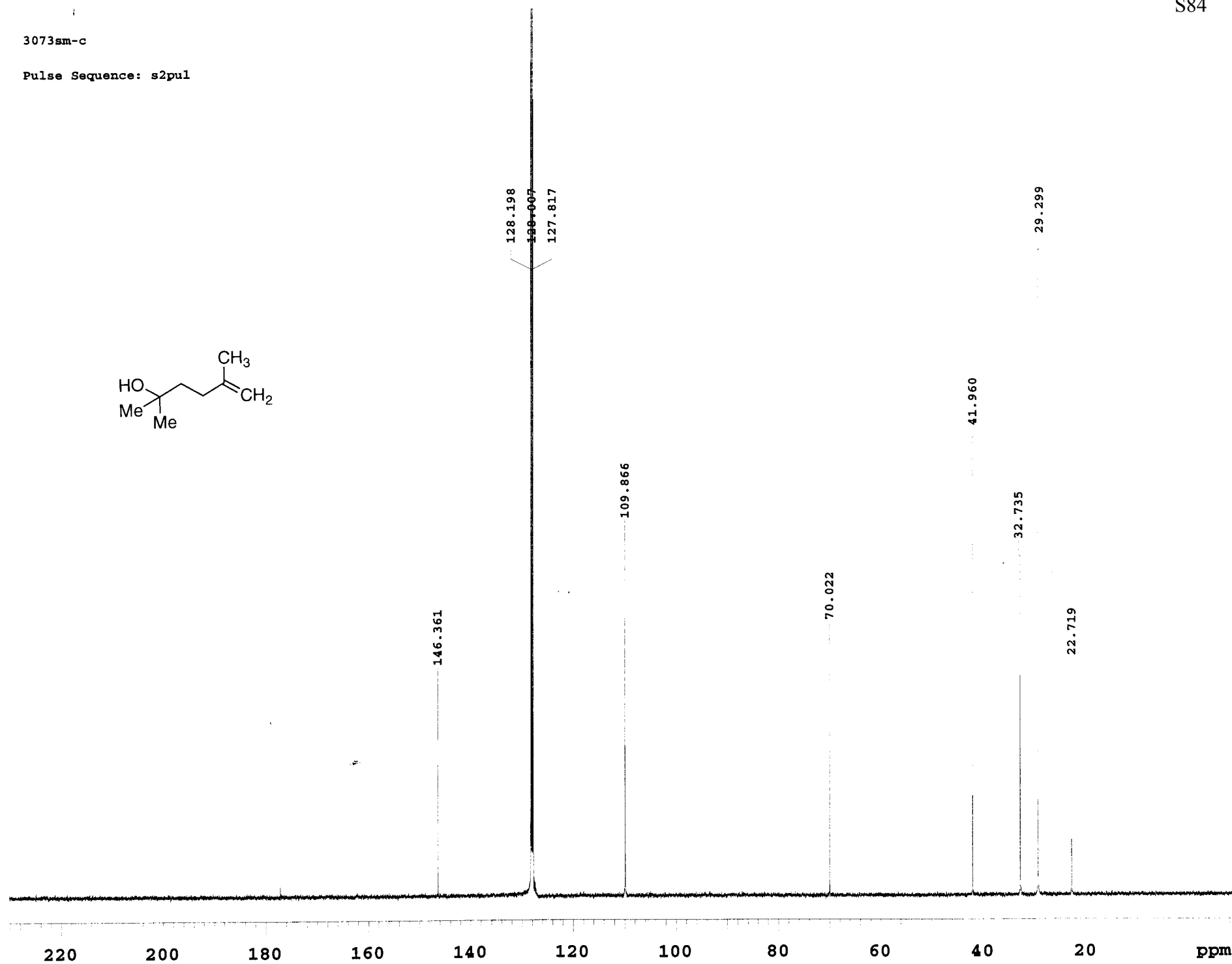
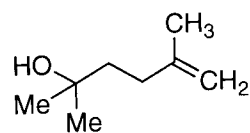
3073sm-h

Pulse Sequence: s2pul



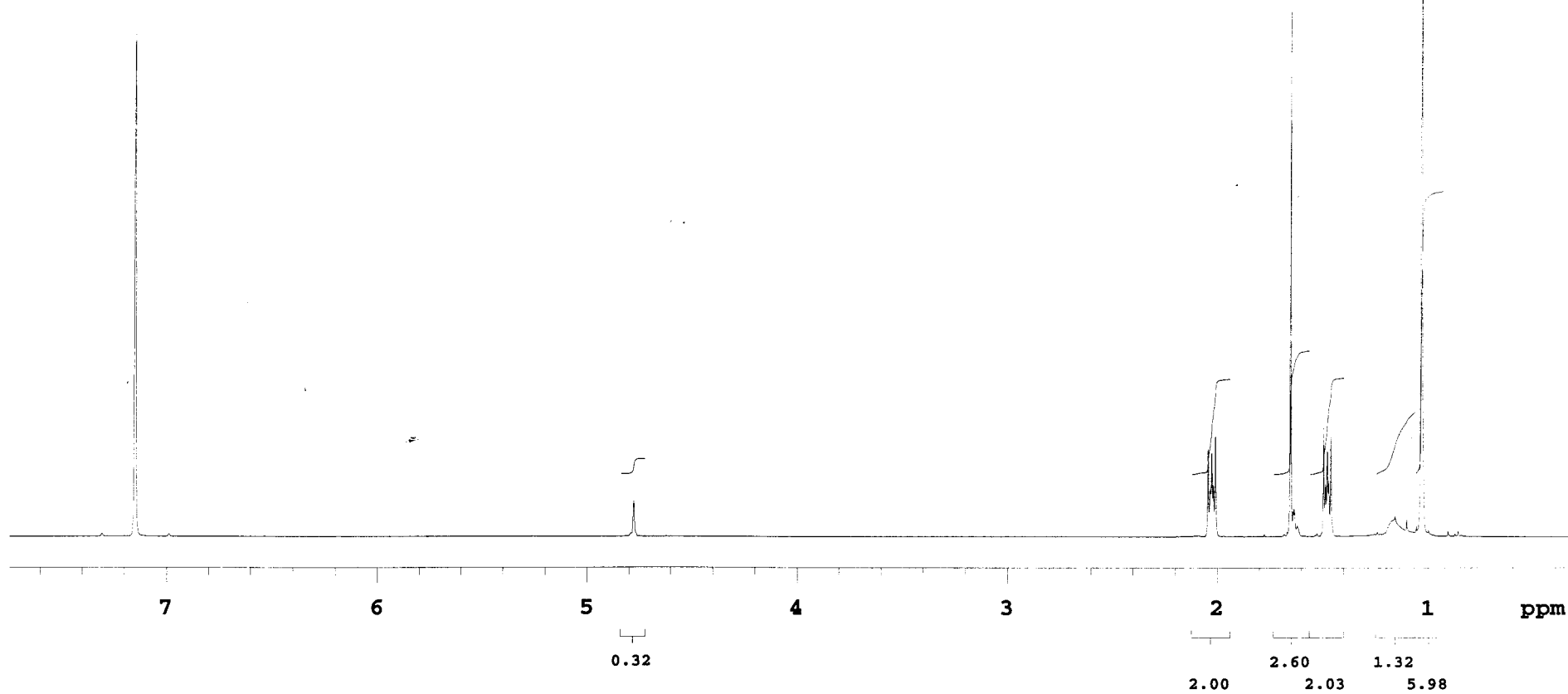
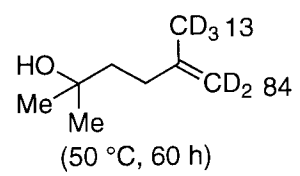
3073sm-c

Pulse Sequence: s2pul



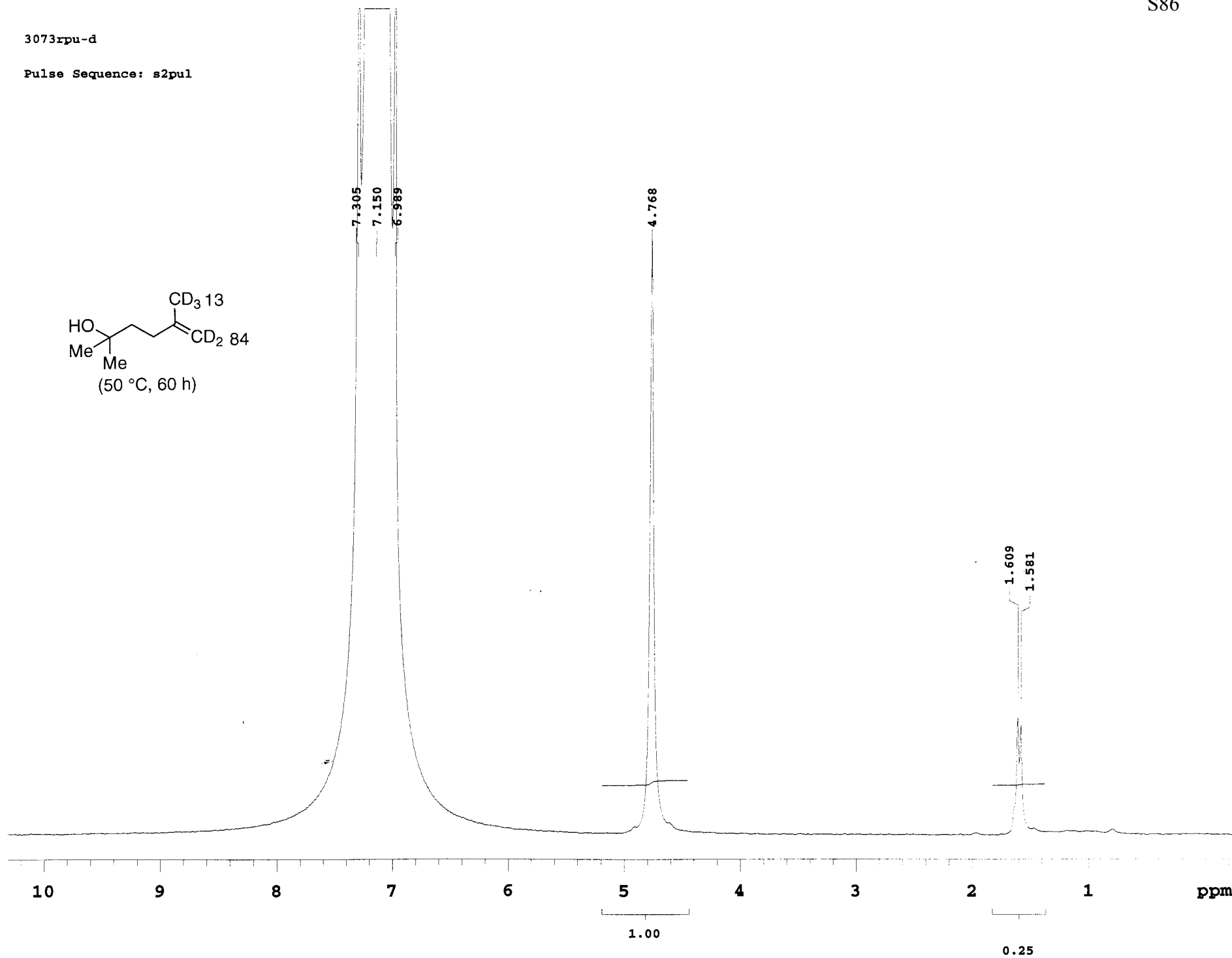
3073rpu-h

Pulse Sequence: s2pul



3073rpu-d

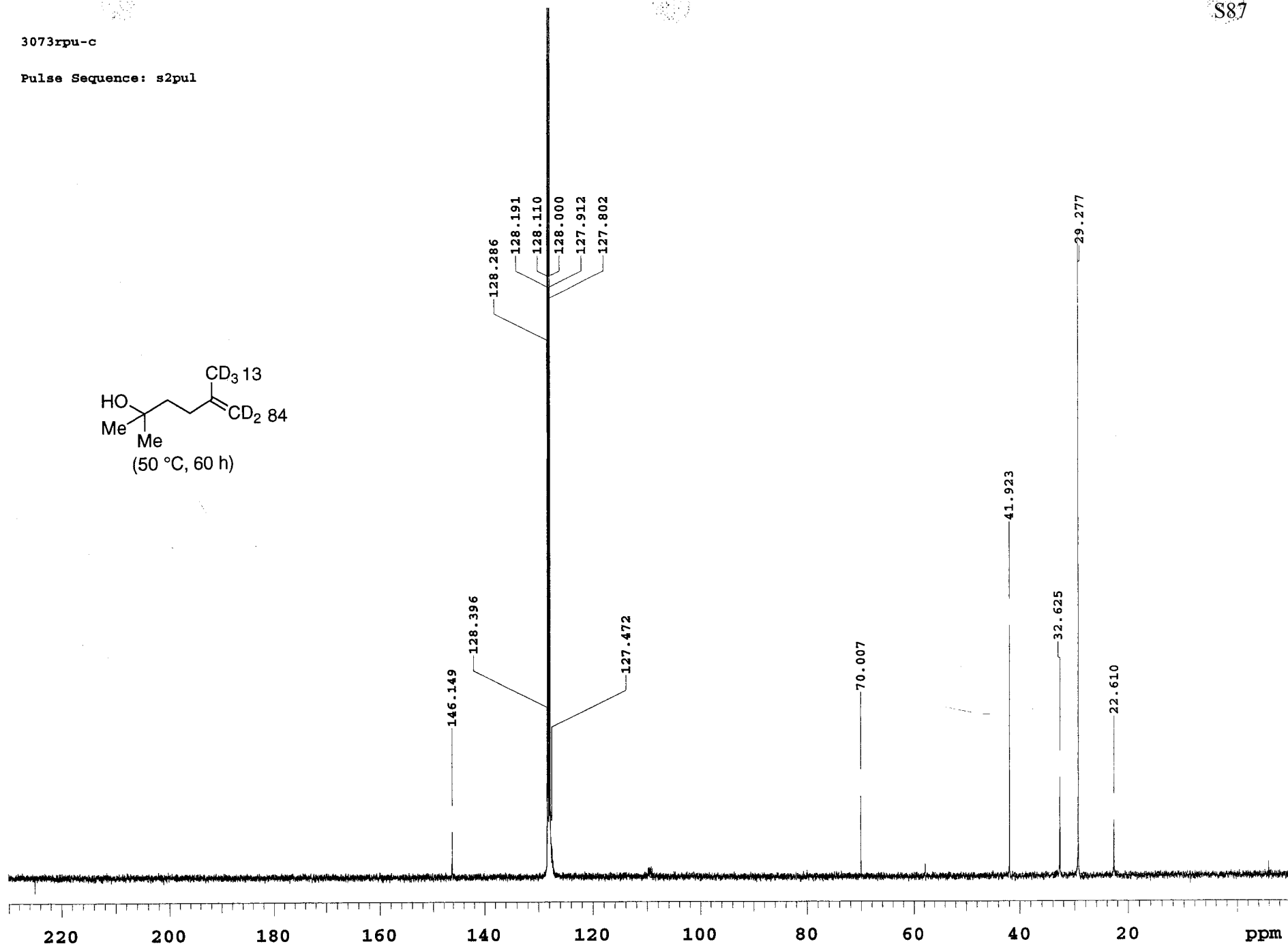
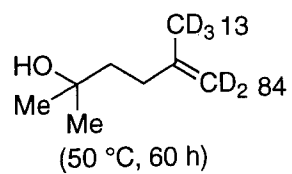
Pulse Sequence: s2pul



3073xpu-c

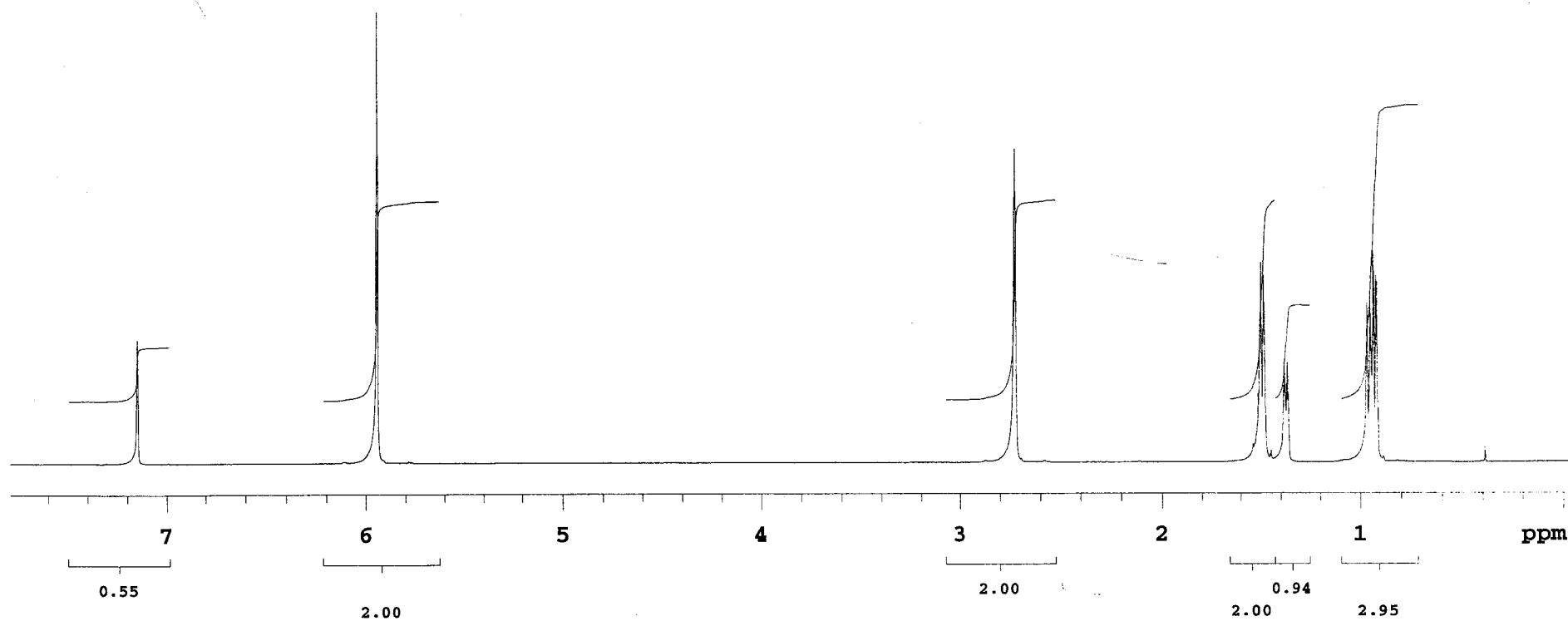
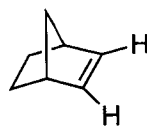
Pulse Sequence: s2pul

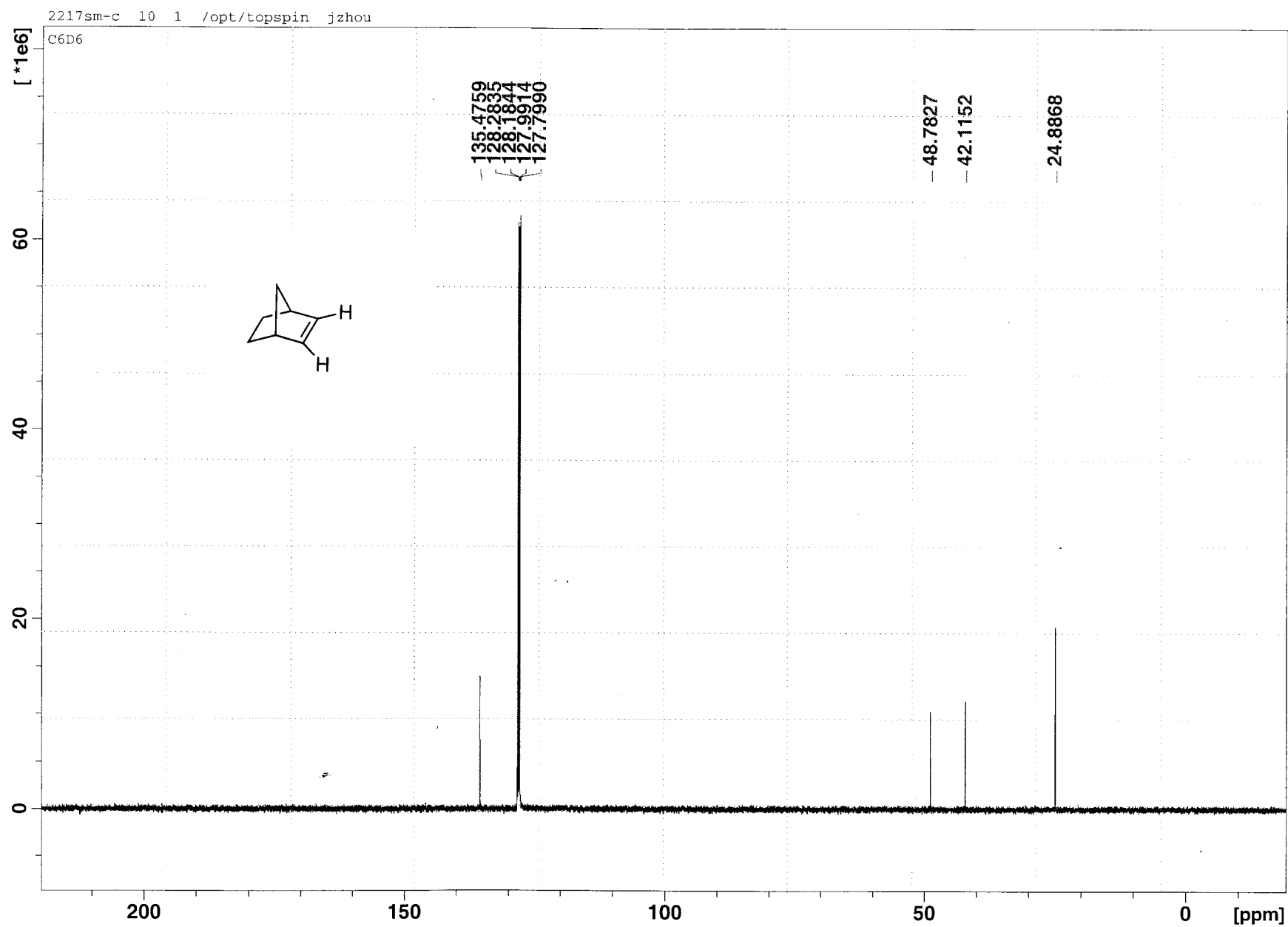
S87



2217sm-h

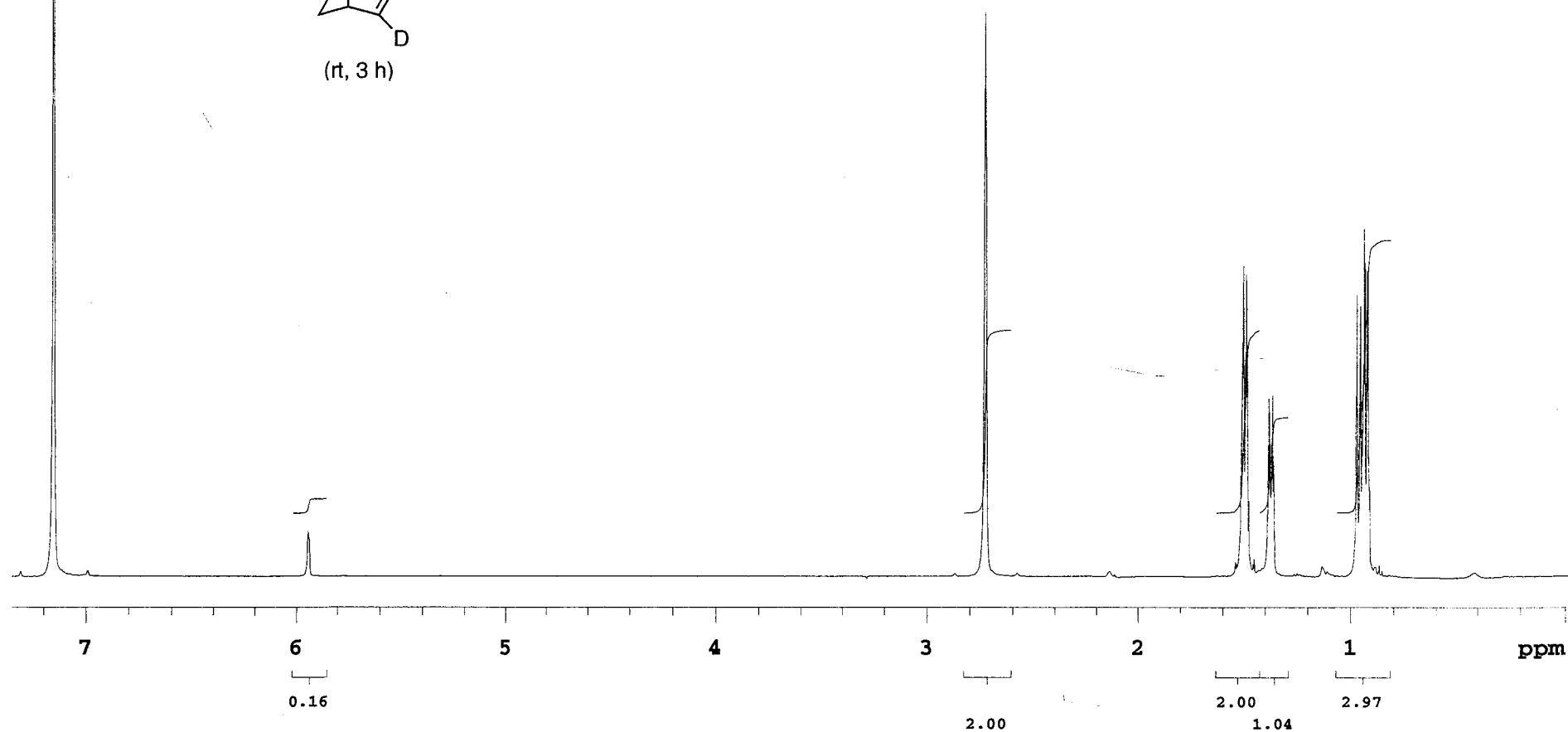
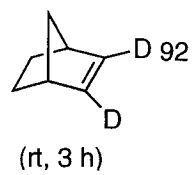
Pulse Sequence: s2pul





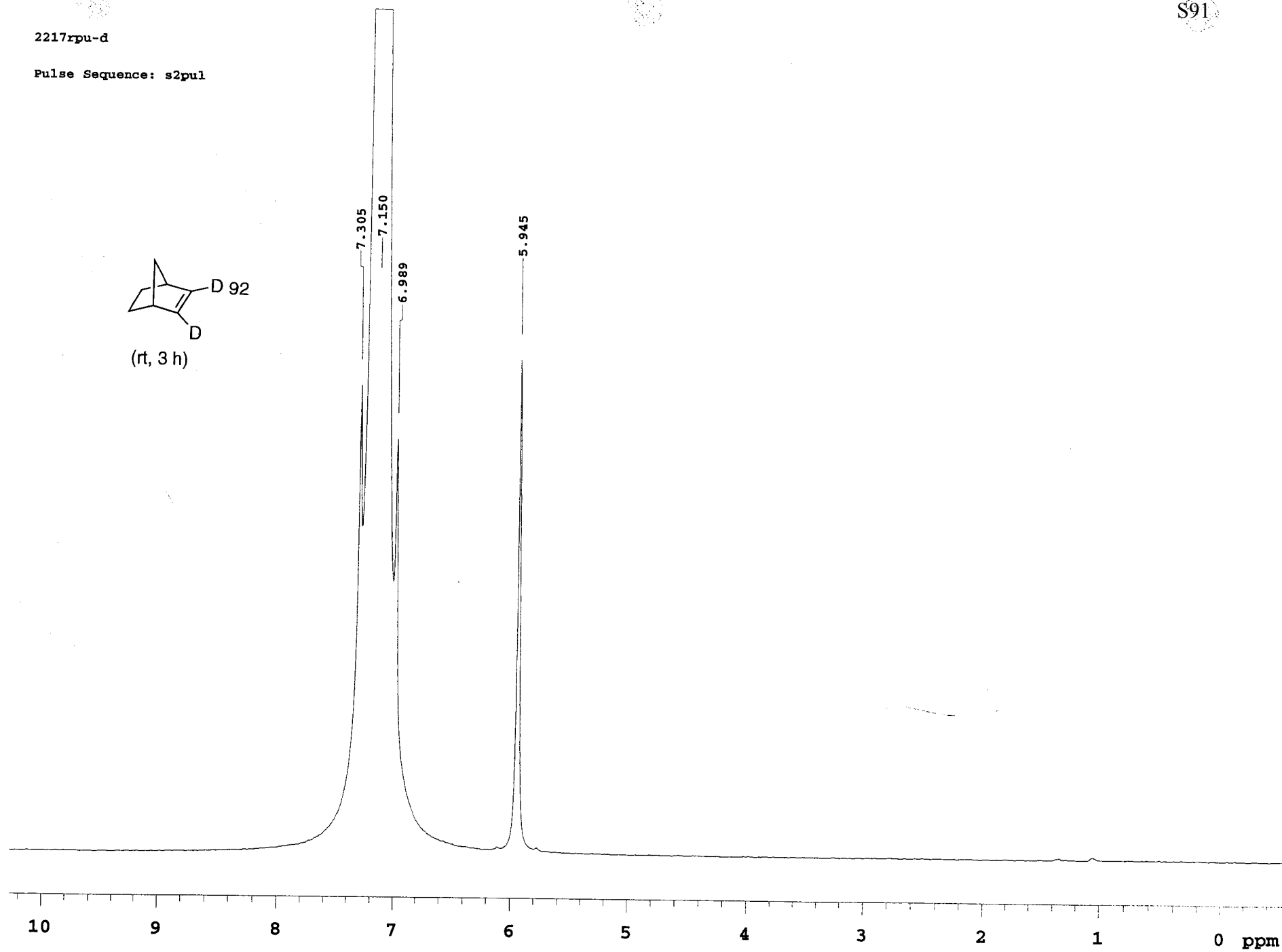
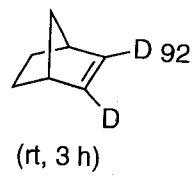
2217r-pu-h

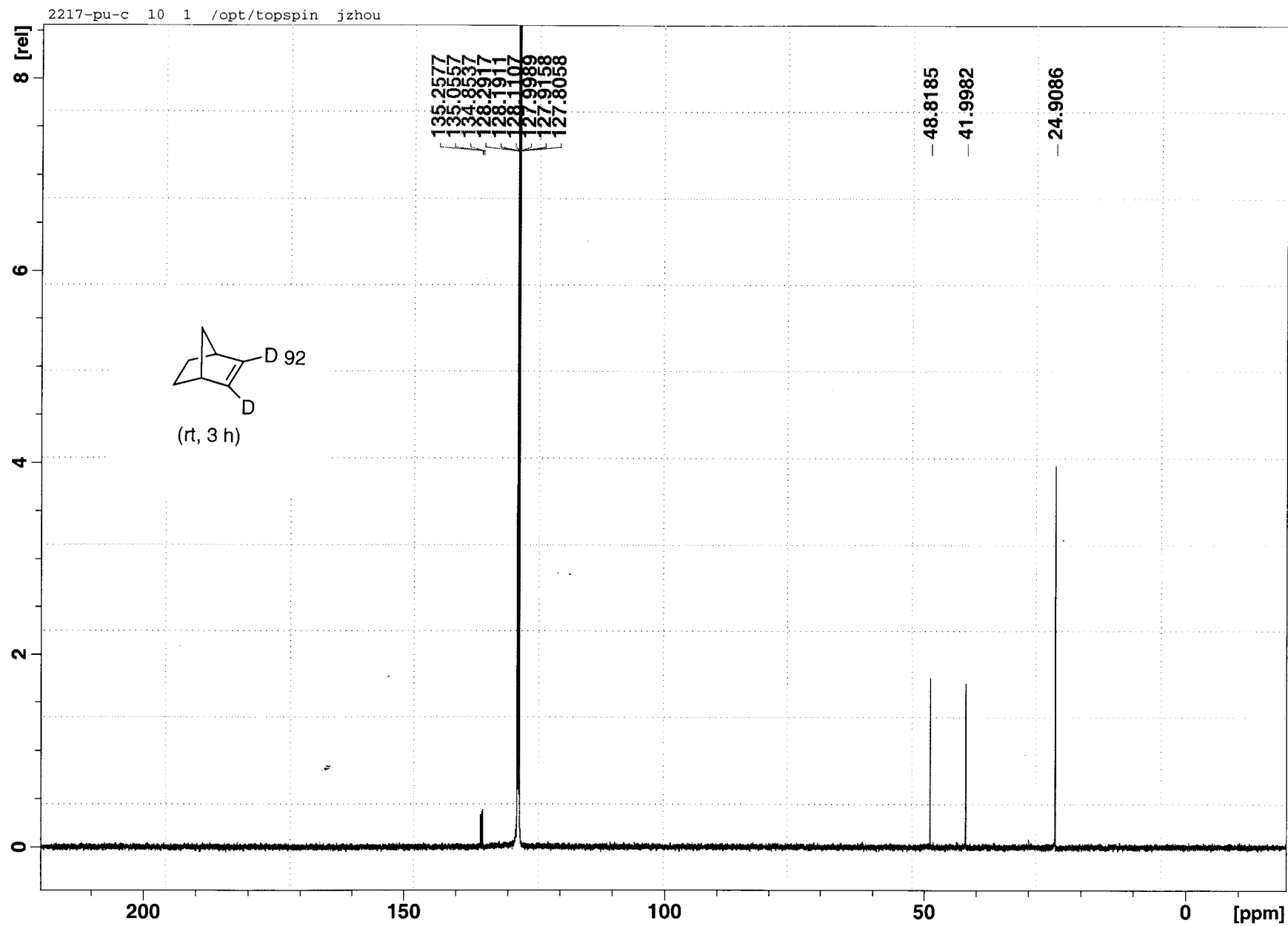
Pulse Sequence: s2pul



2217xpu-d

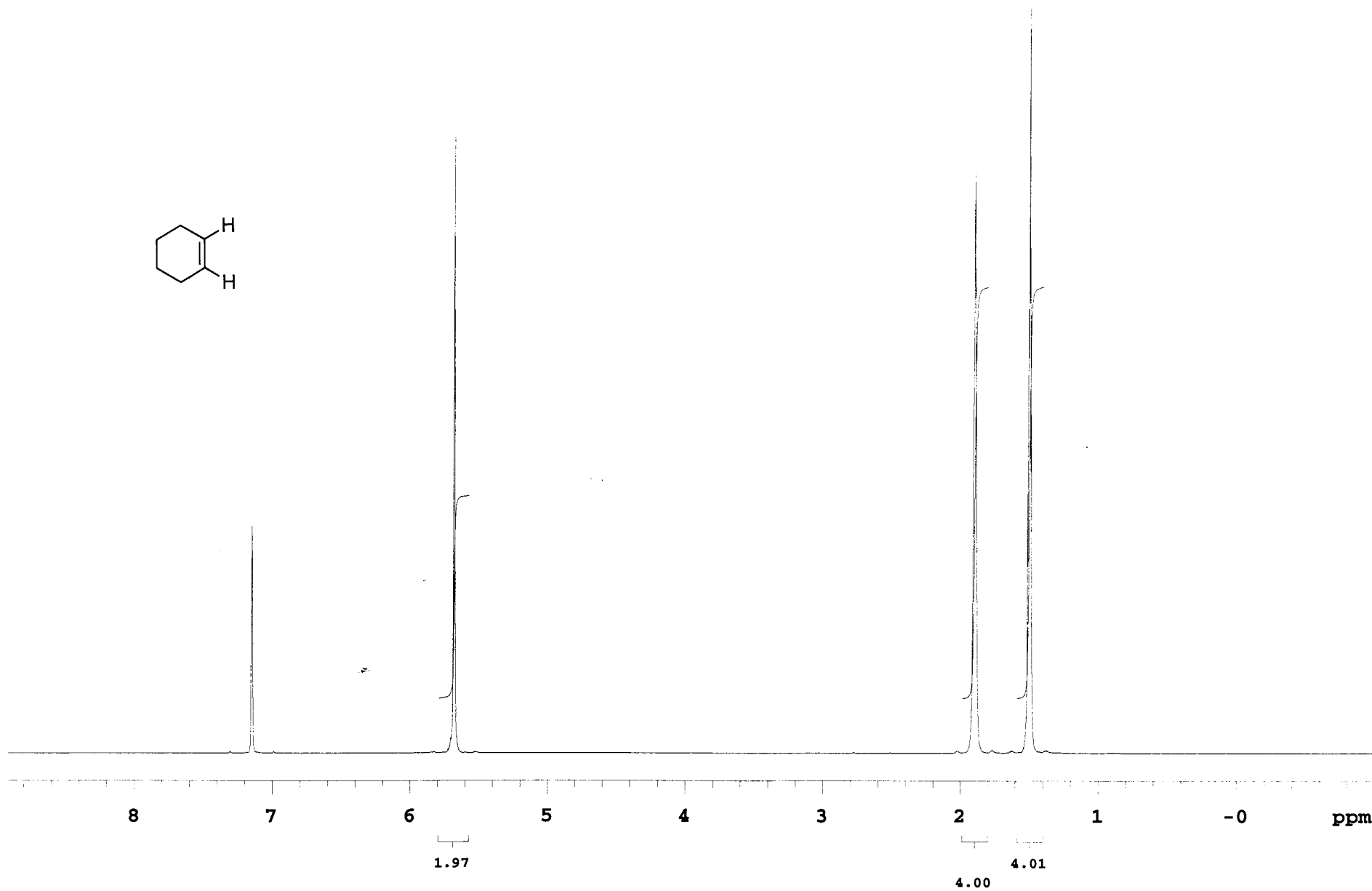
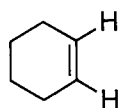
Pulse Sequence: s2pul





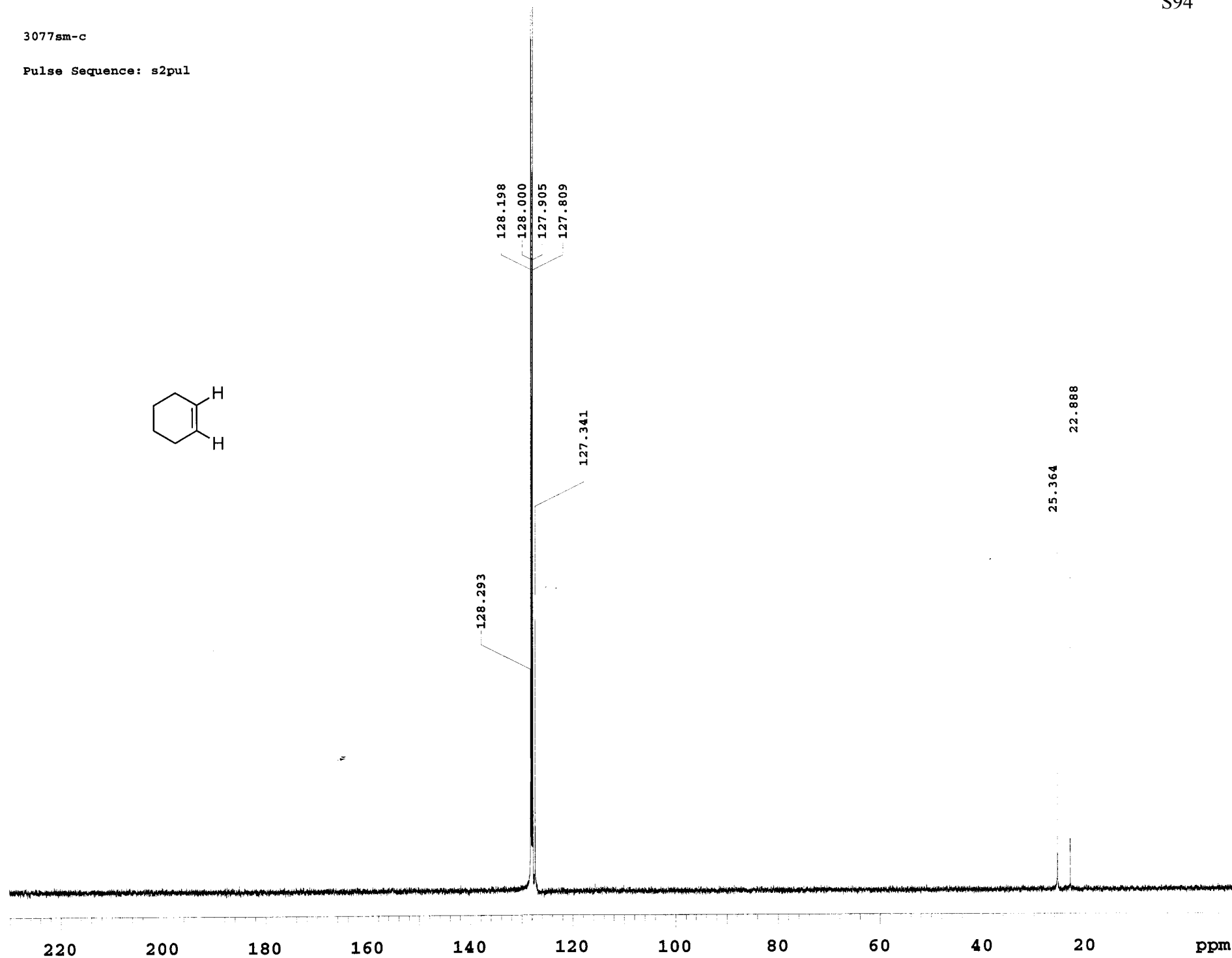
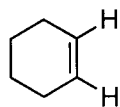
3077sm-h

Pulse Sequence: s2pul



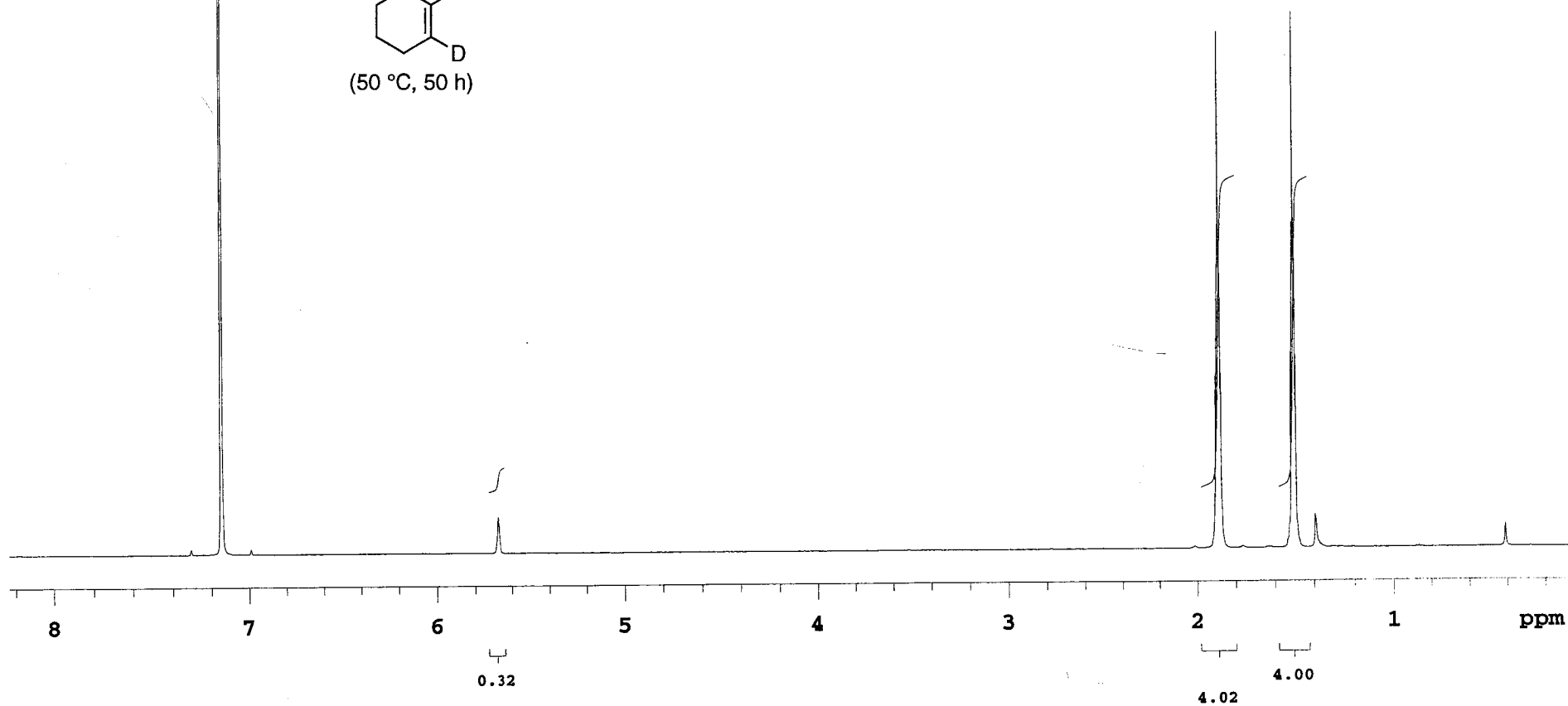
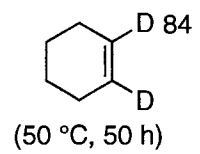
3077sm-c

Pulse Sequence: s2pul



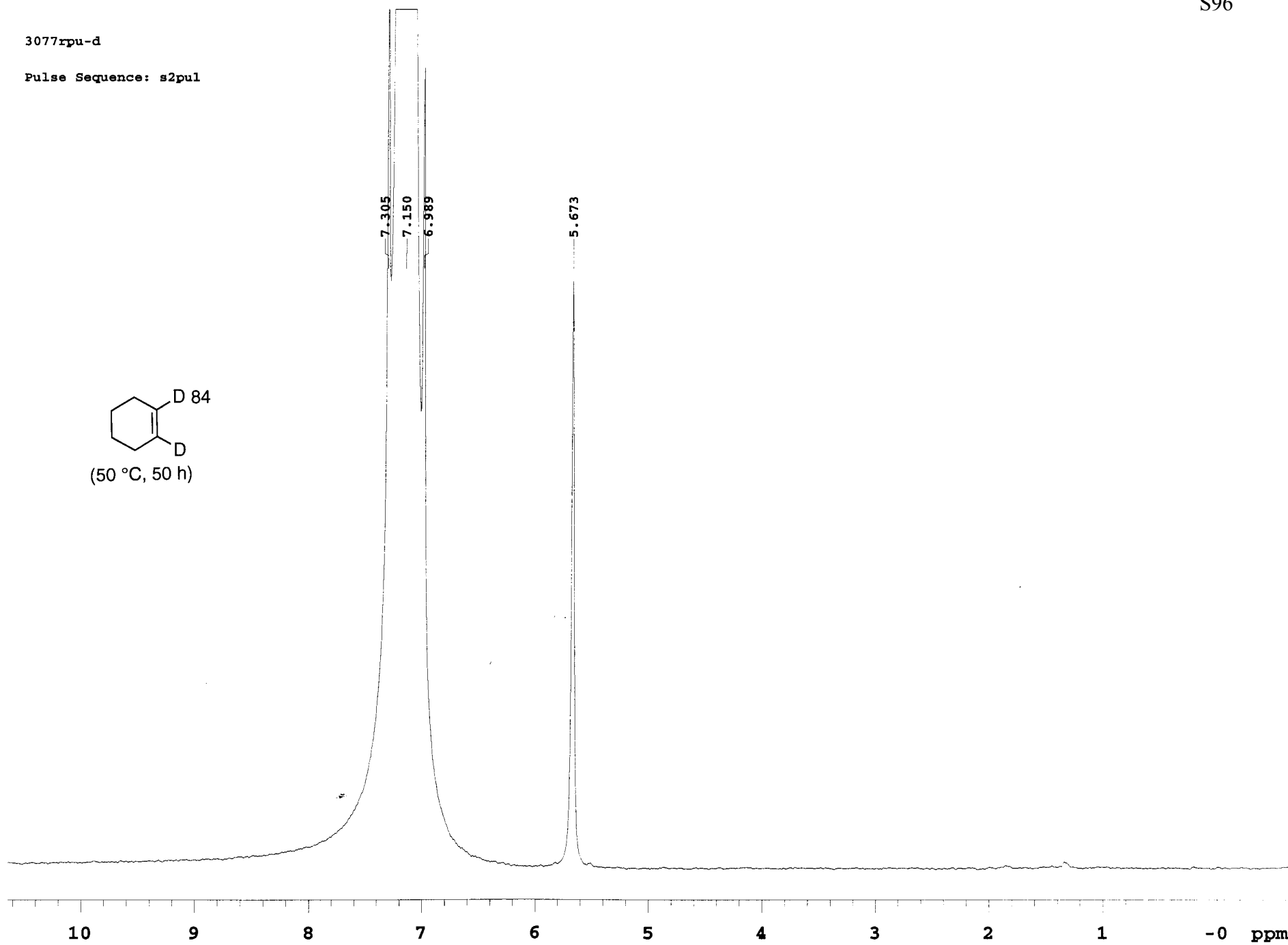
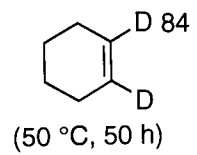
3077t-h

Pulse Sequence: s2pul



3077rpu-d

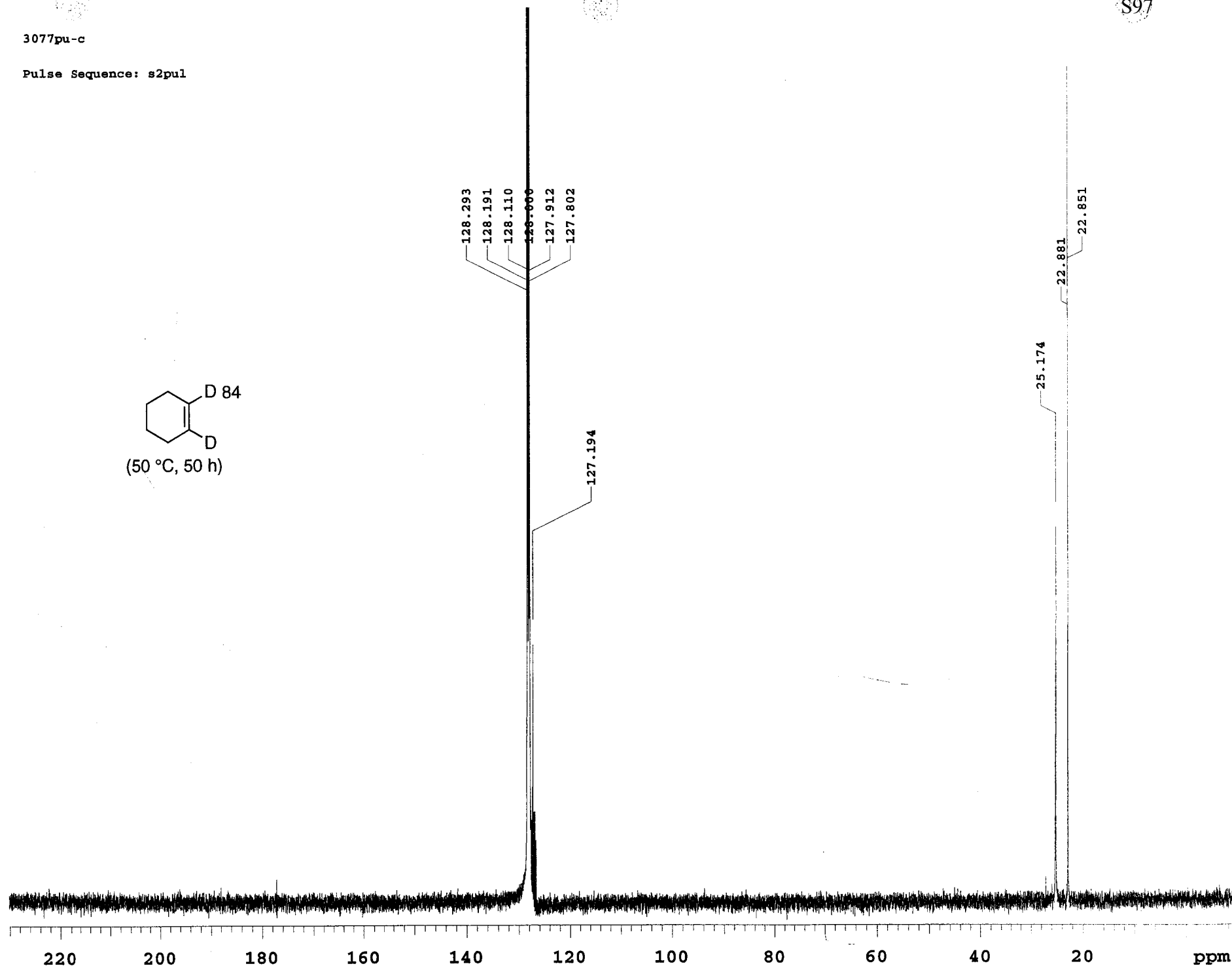
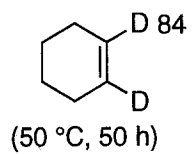
Pulse Sequence: s2pul



3077pu-c

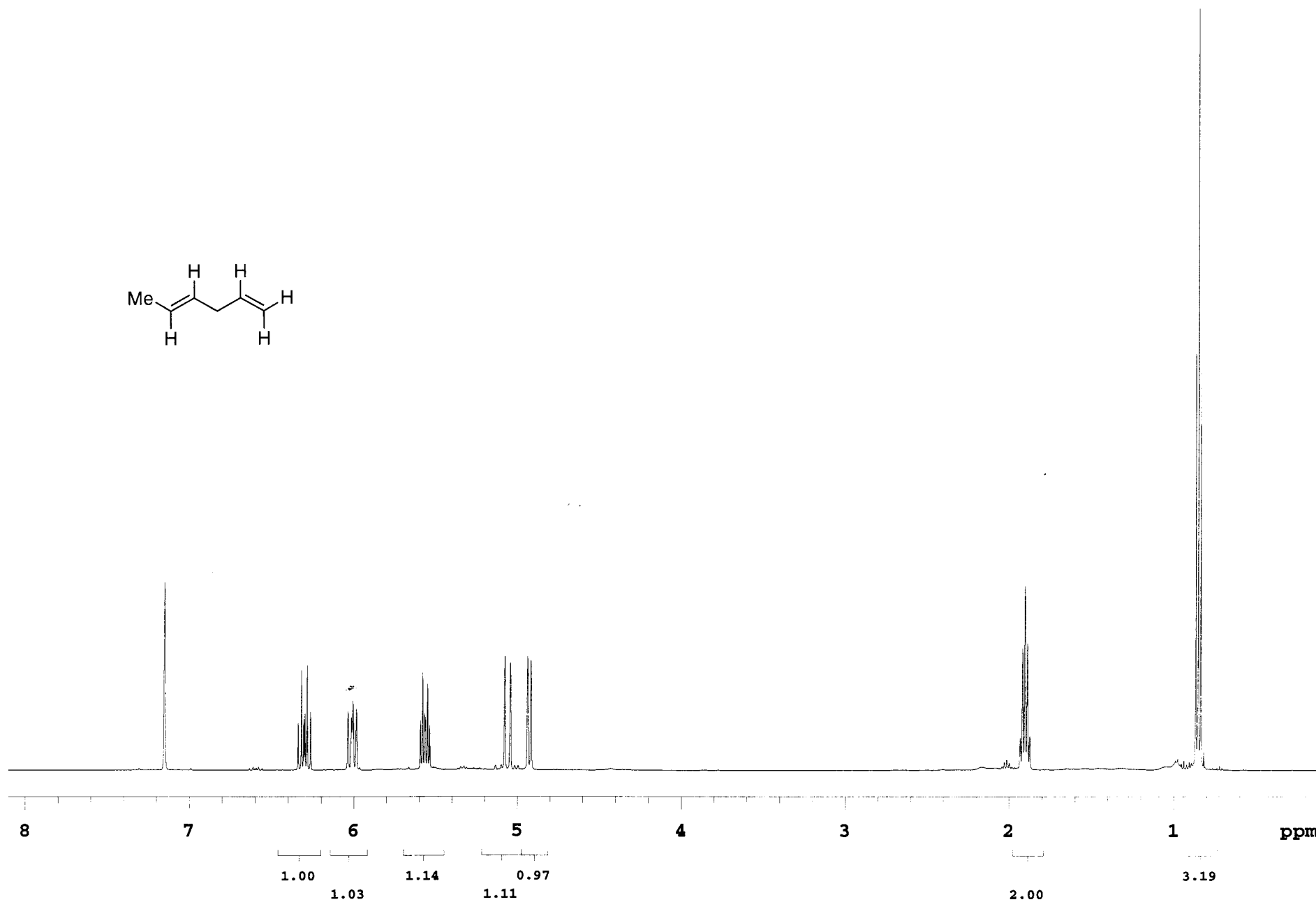
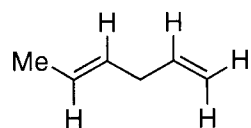
Pulse Sequence: s2pul

S97



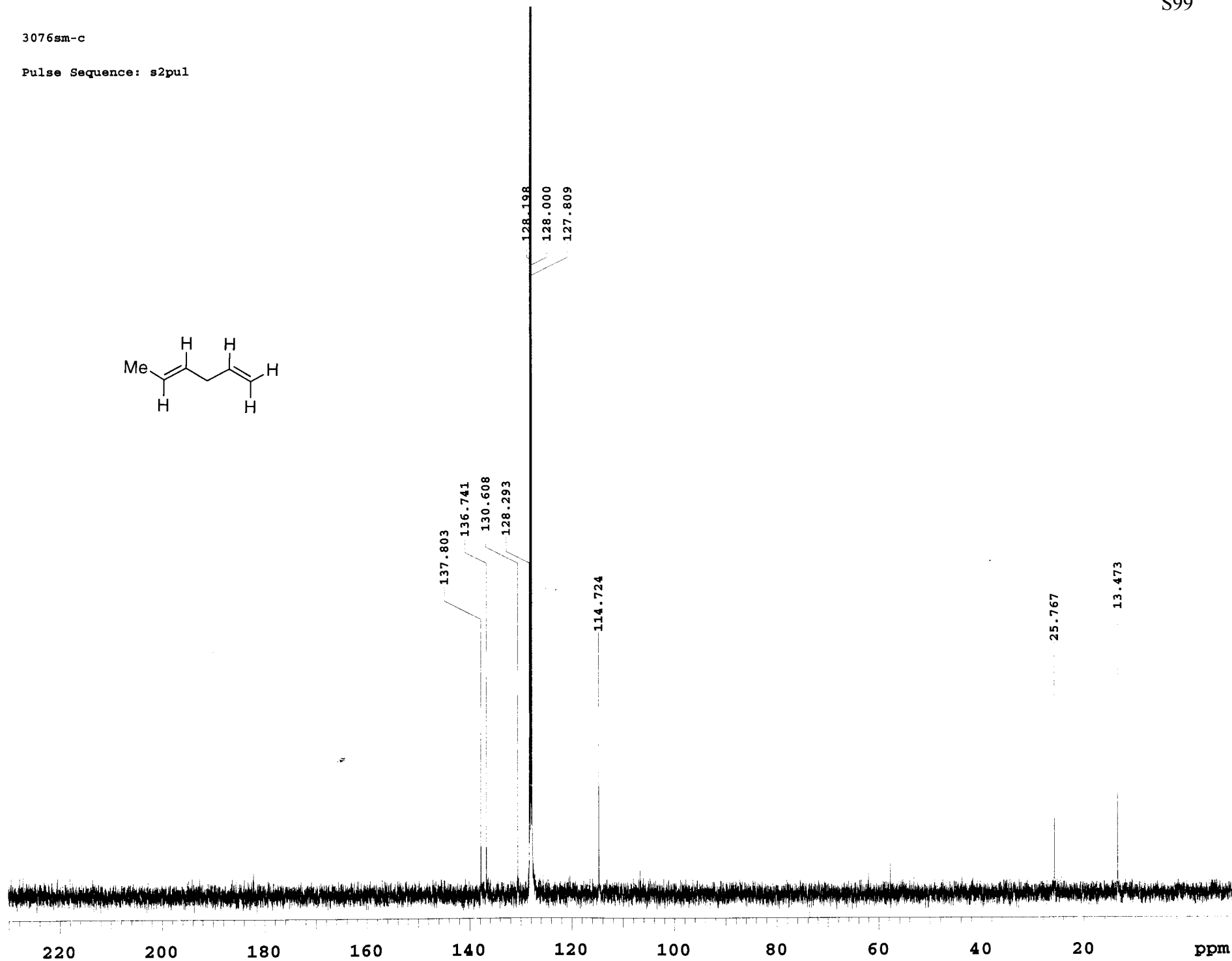
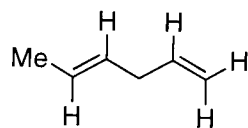
3076sm-h

Pulse Sequence: s2pul



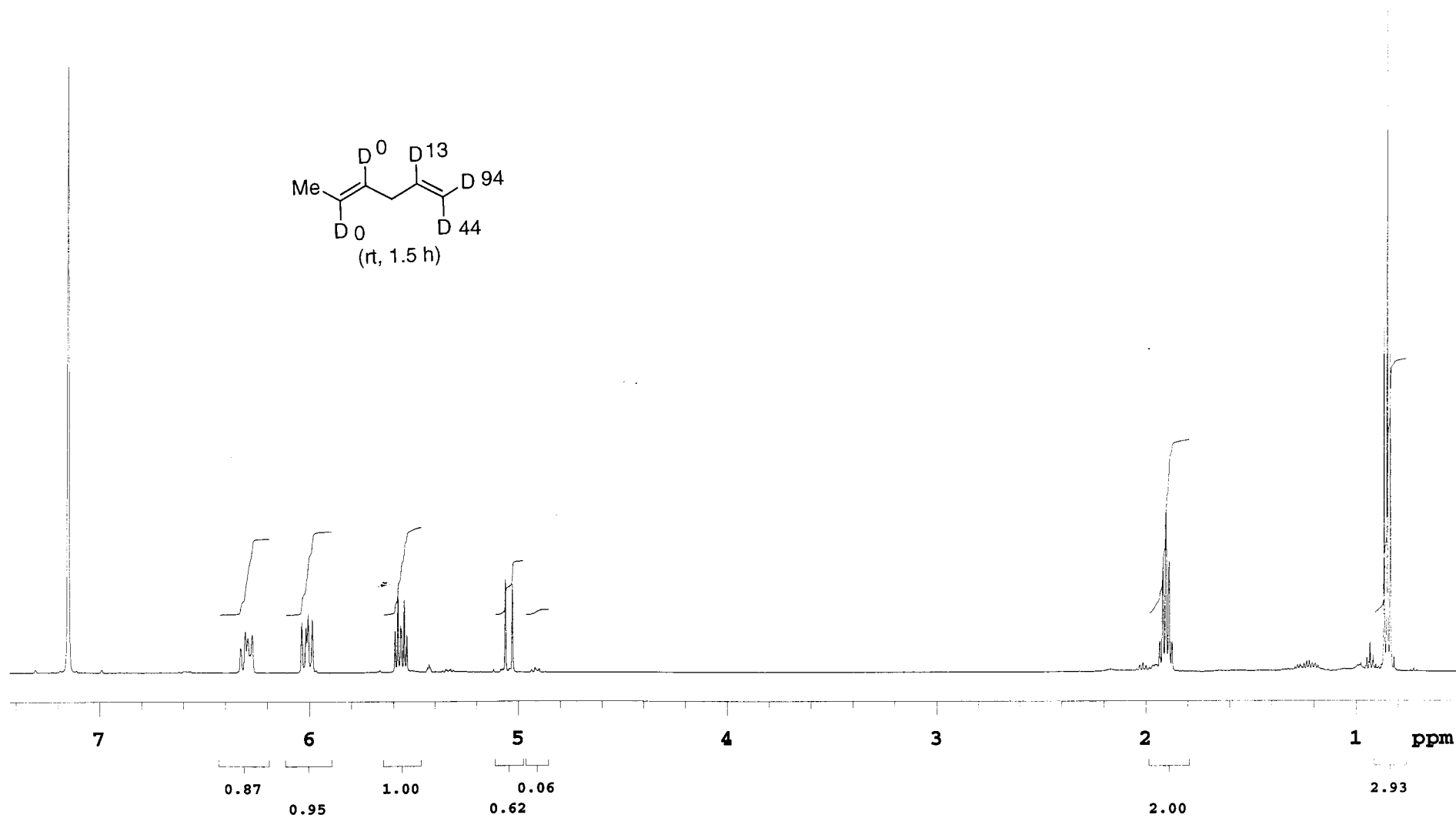
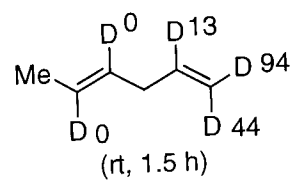
3076sm-c

Pulse Sequence: s2pul



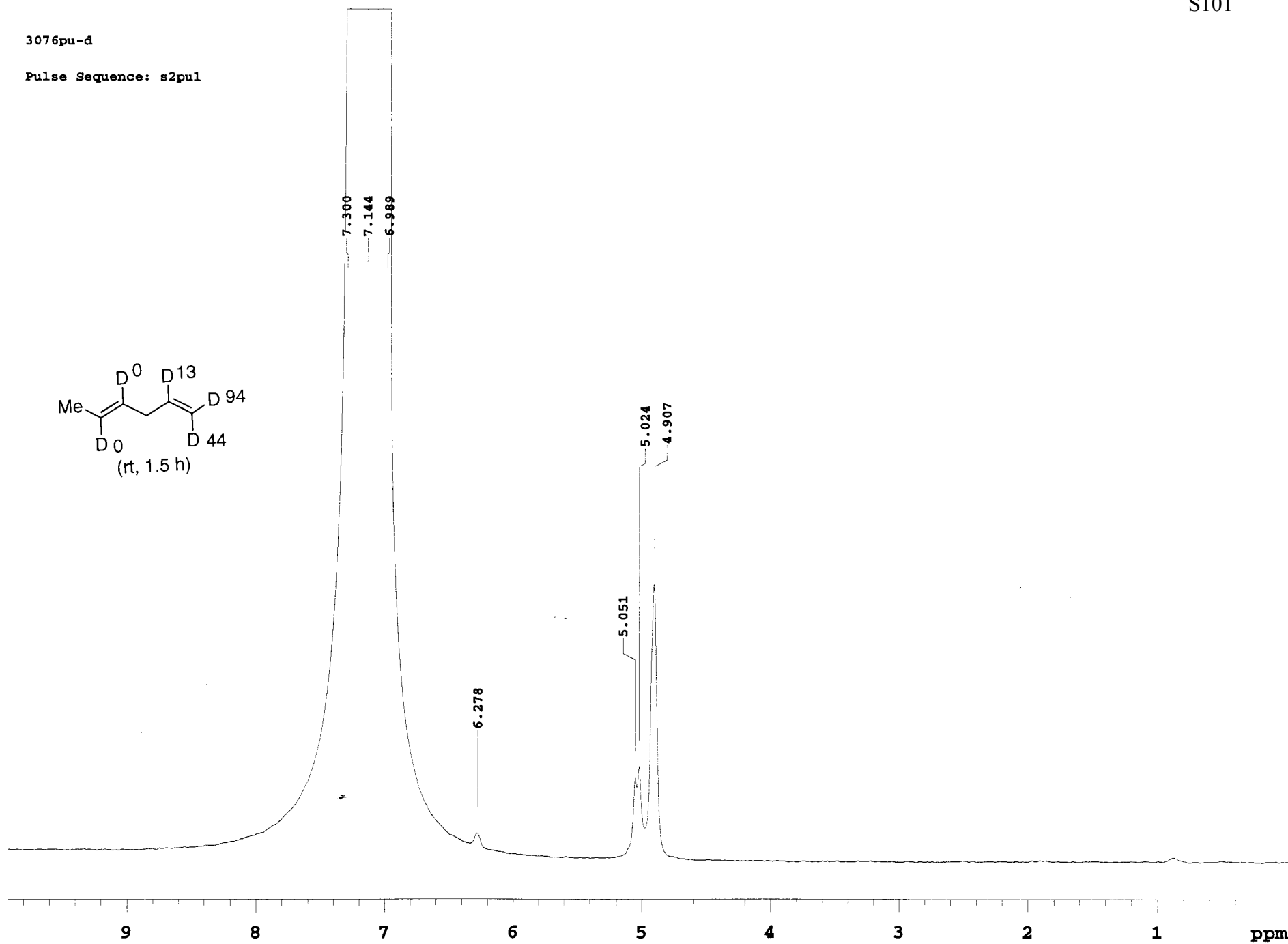
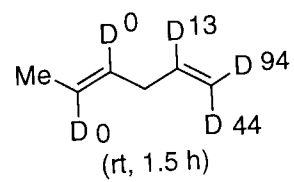
3076pu-h

Pulse Sequence: s2pul



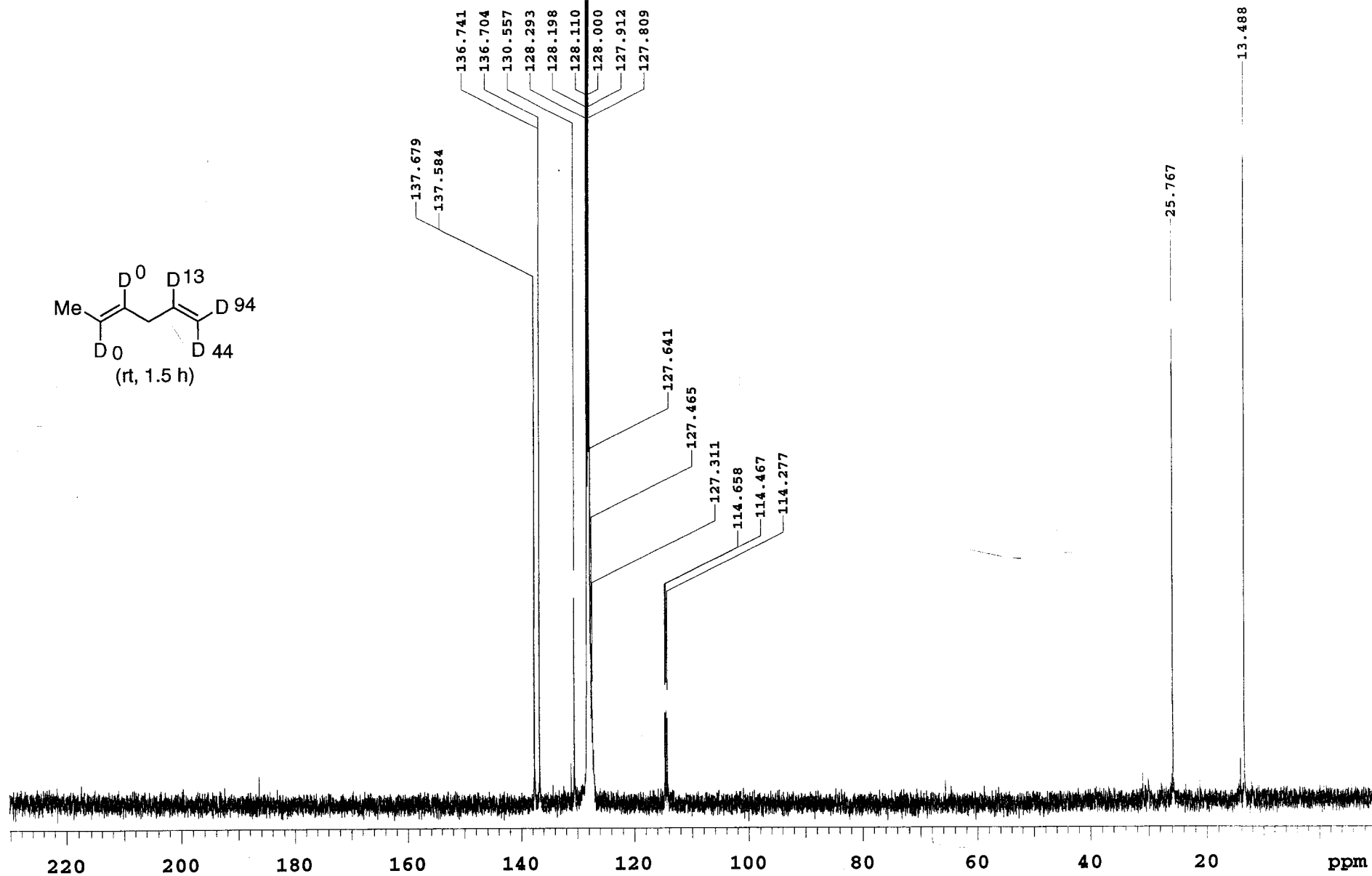
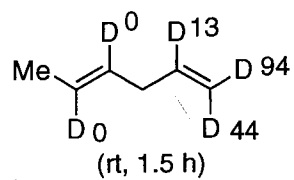
3076pu-d

Pulse Sequence: s2pul



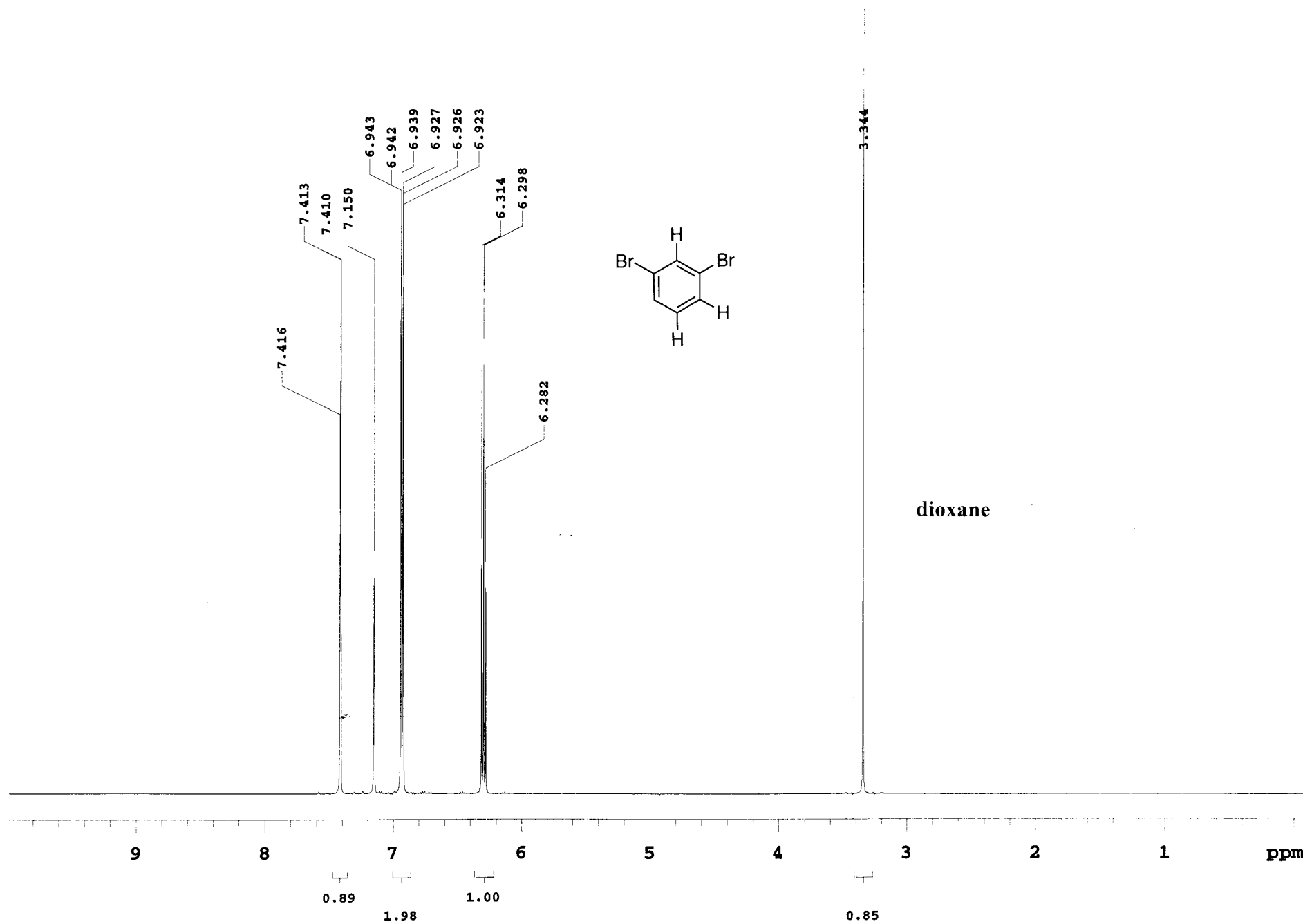
3076pu-c

Pulse Sequence: s2pul



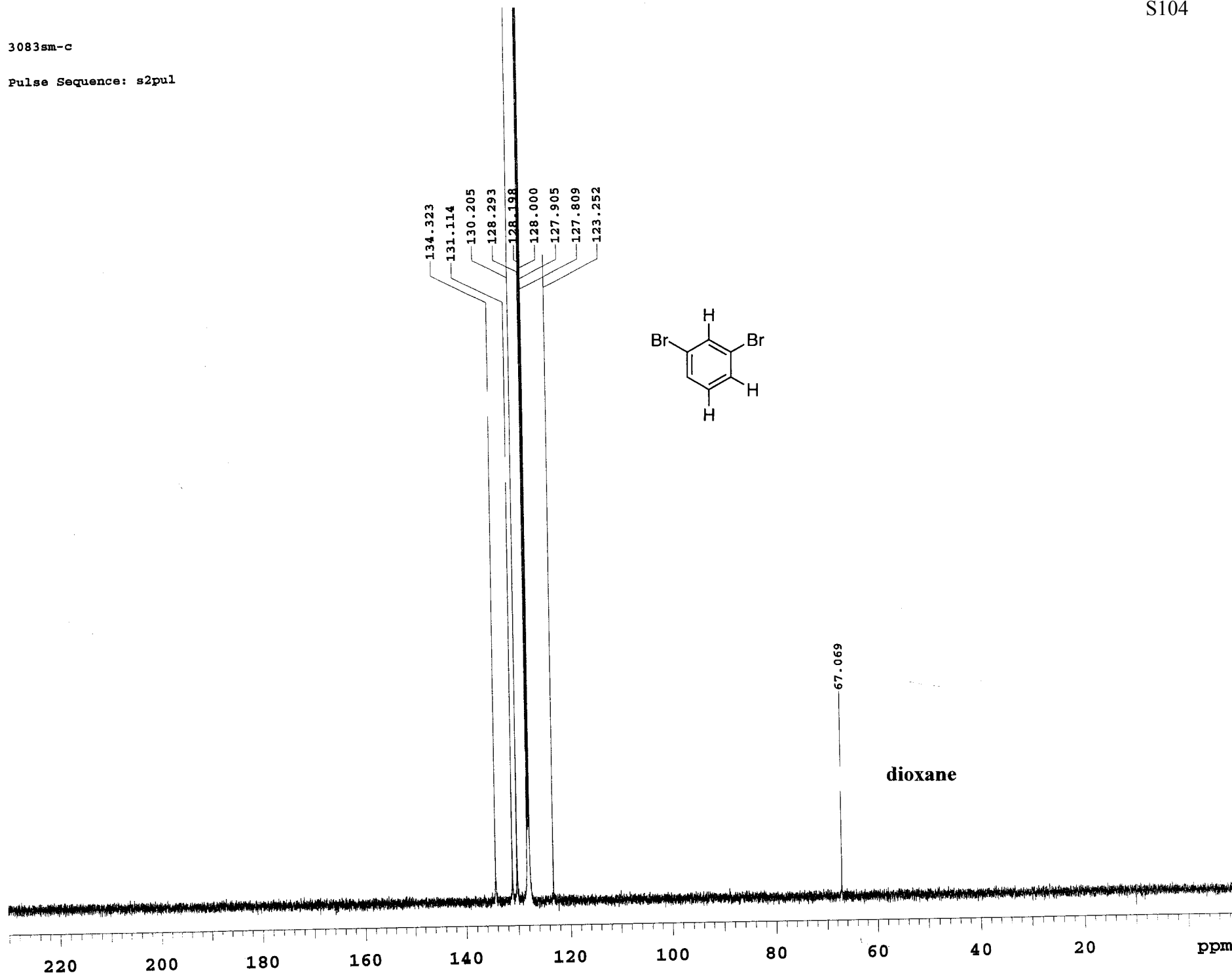
3083sm-h

Pulse Sequence: s2pul



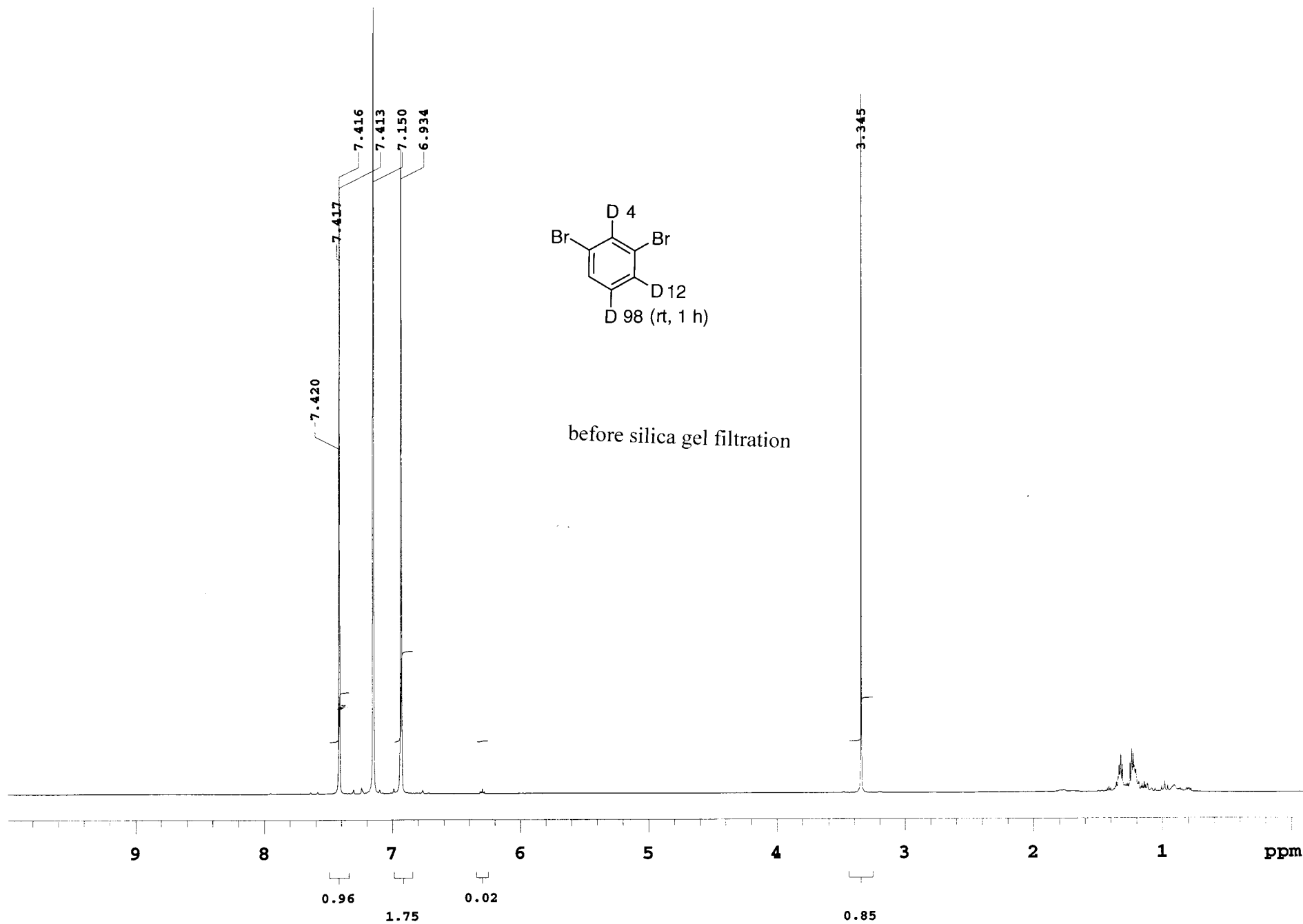
3083sm-c

Pulse Sequence: s2pul



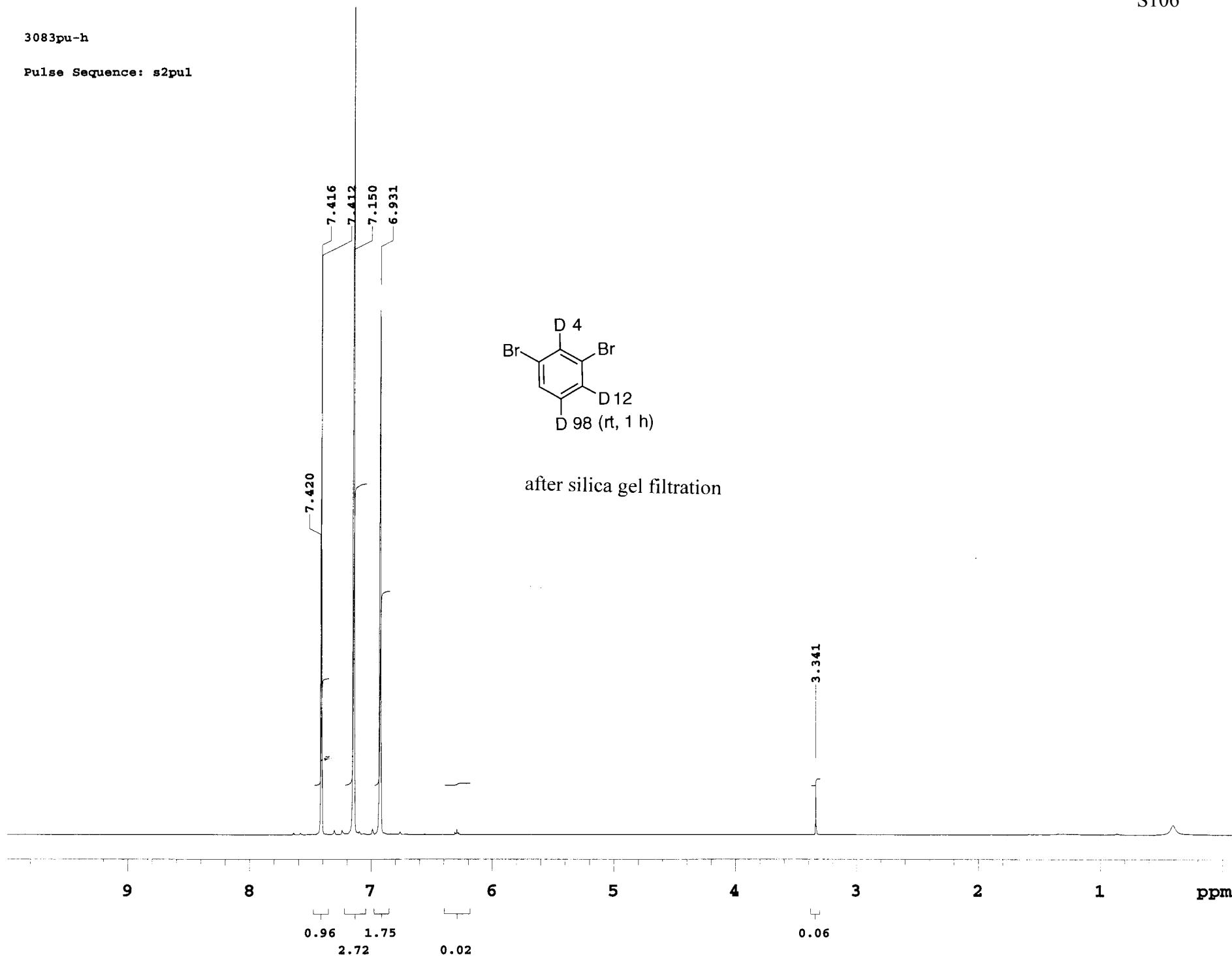
3083-1h

Pulse Sequence: s2pul



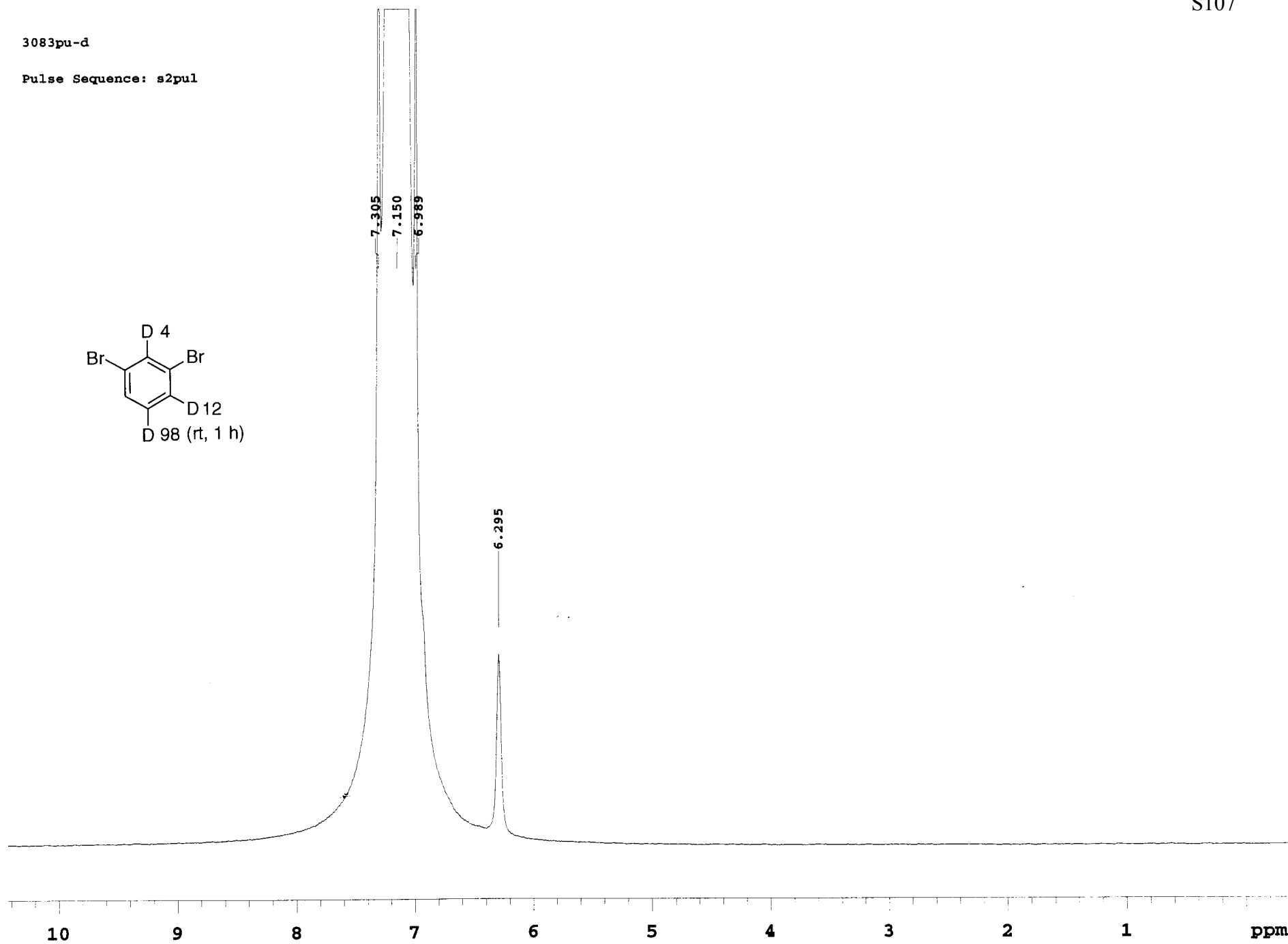
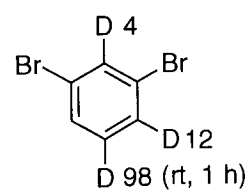
3083pu-h

Pulse Sequence: s2pul



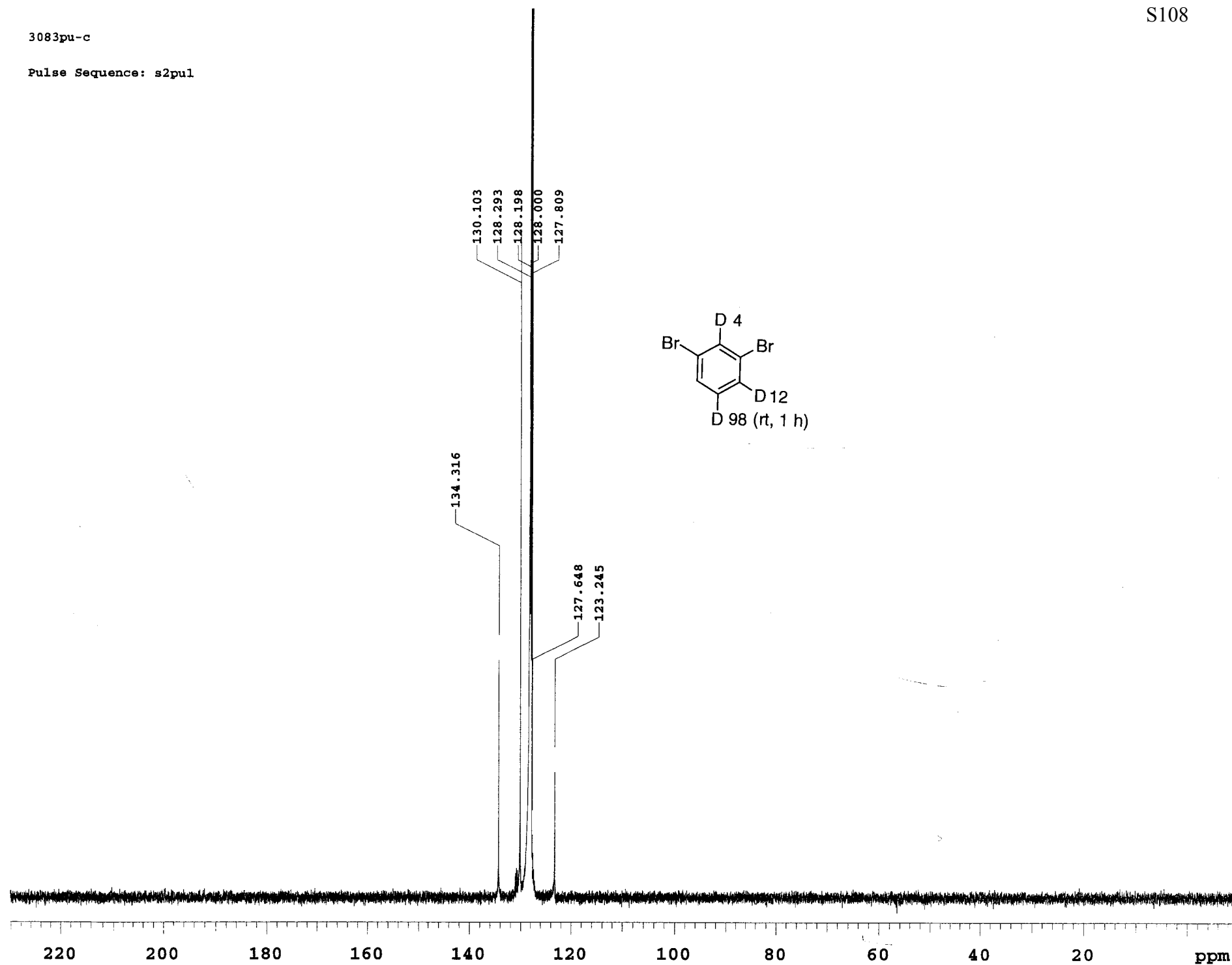
3083pu-d

Pulse Sequence: s2pul



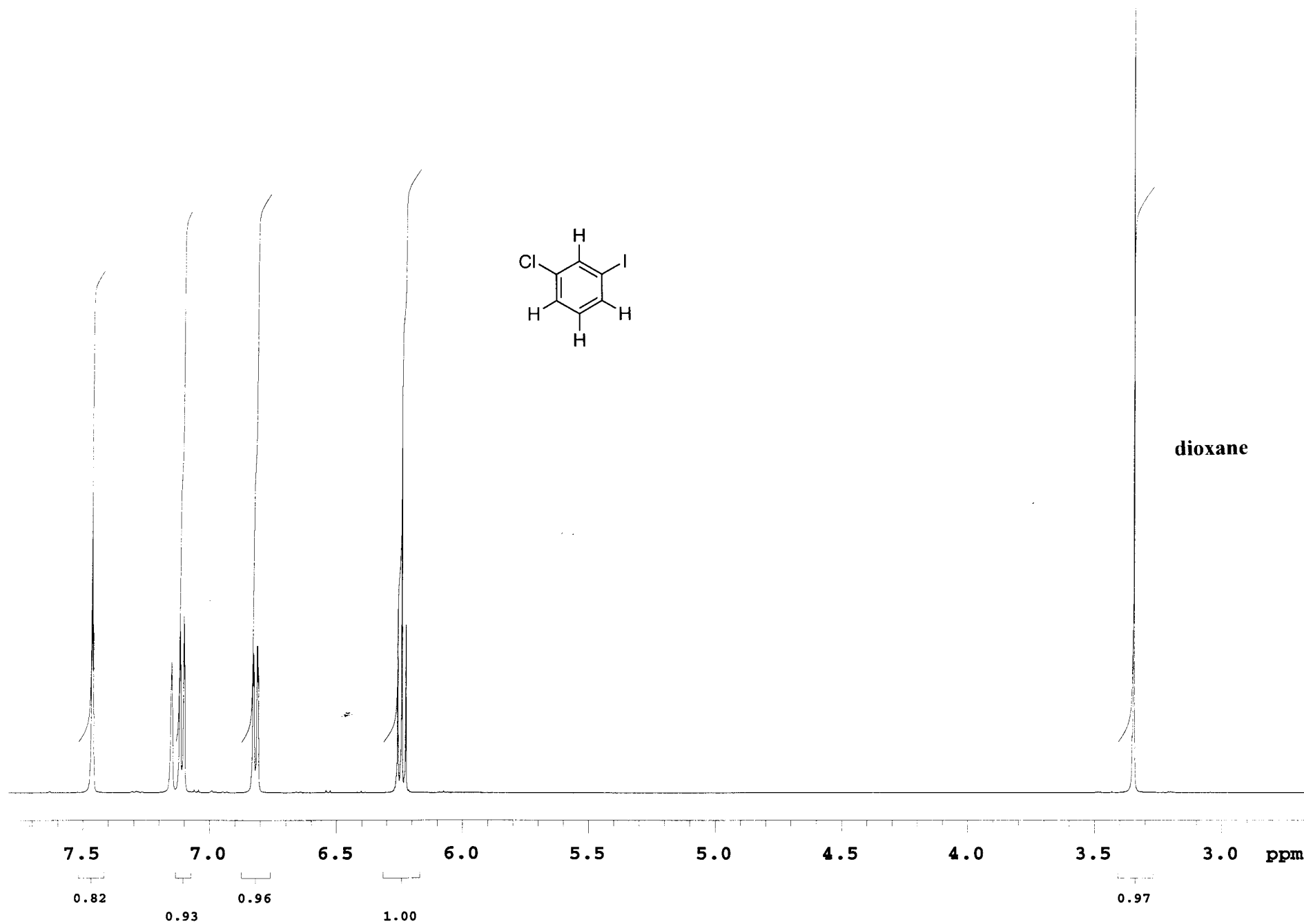
3083pu-c

Pulse Sequence: s2pul



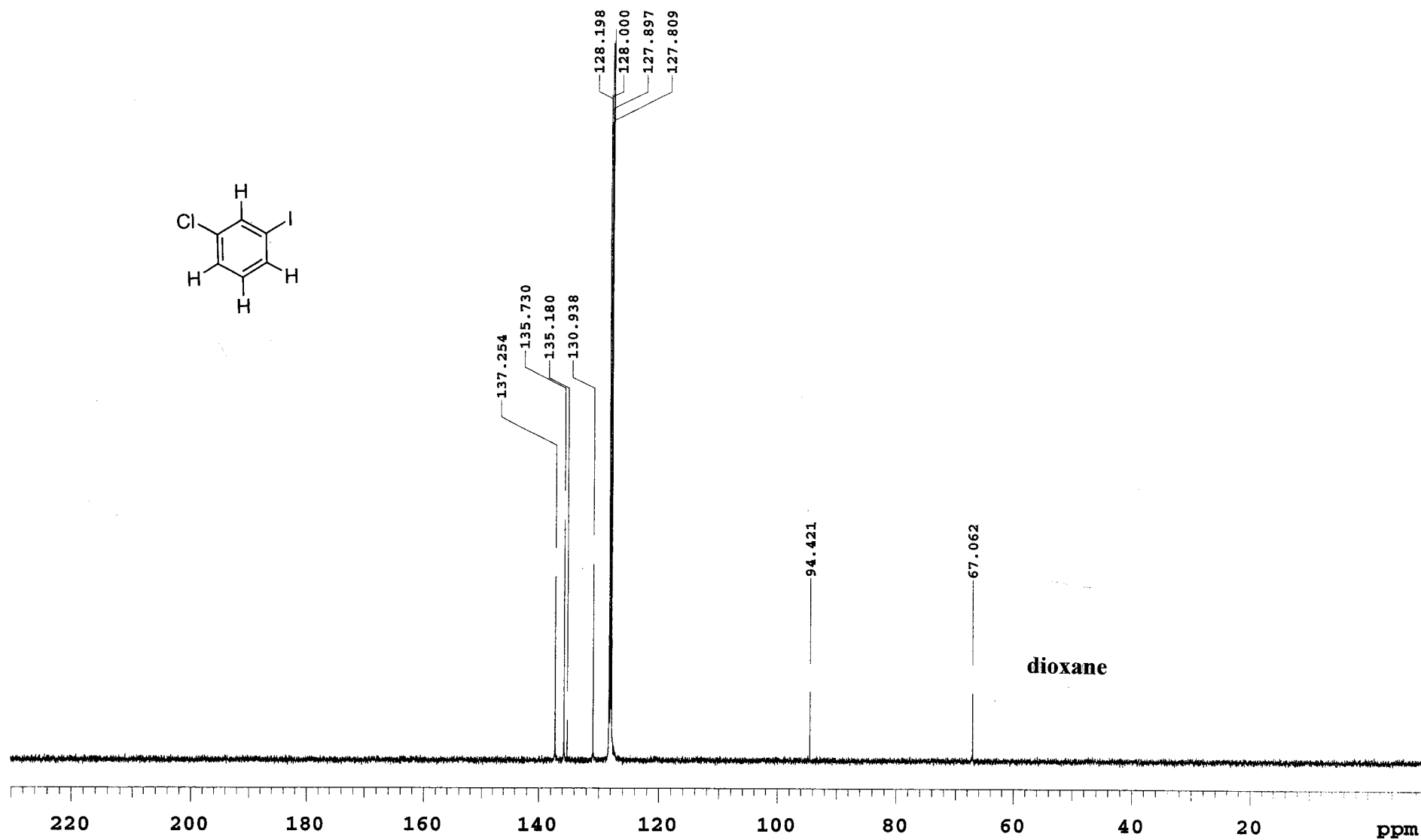
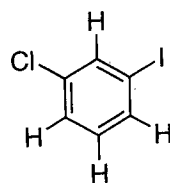
3081sm-h

Pulse Sequence: s2pul



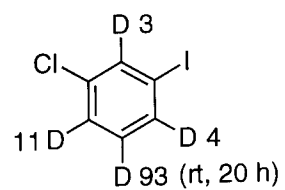
3081sm-c

Pulse Sequence: s2pul

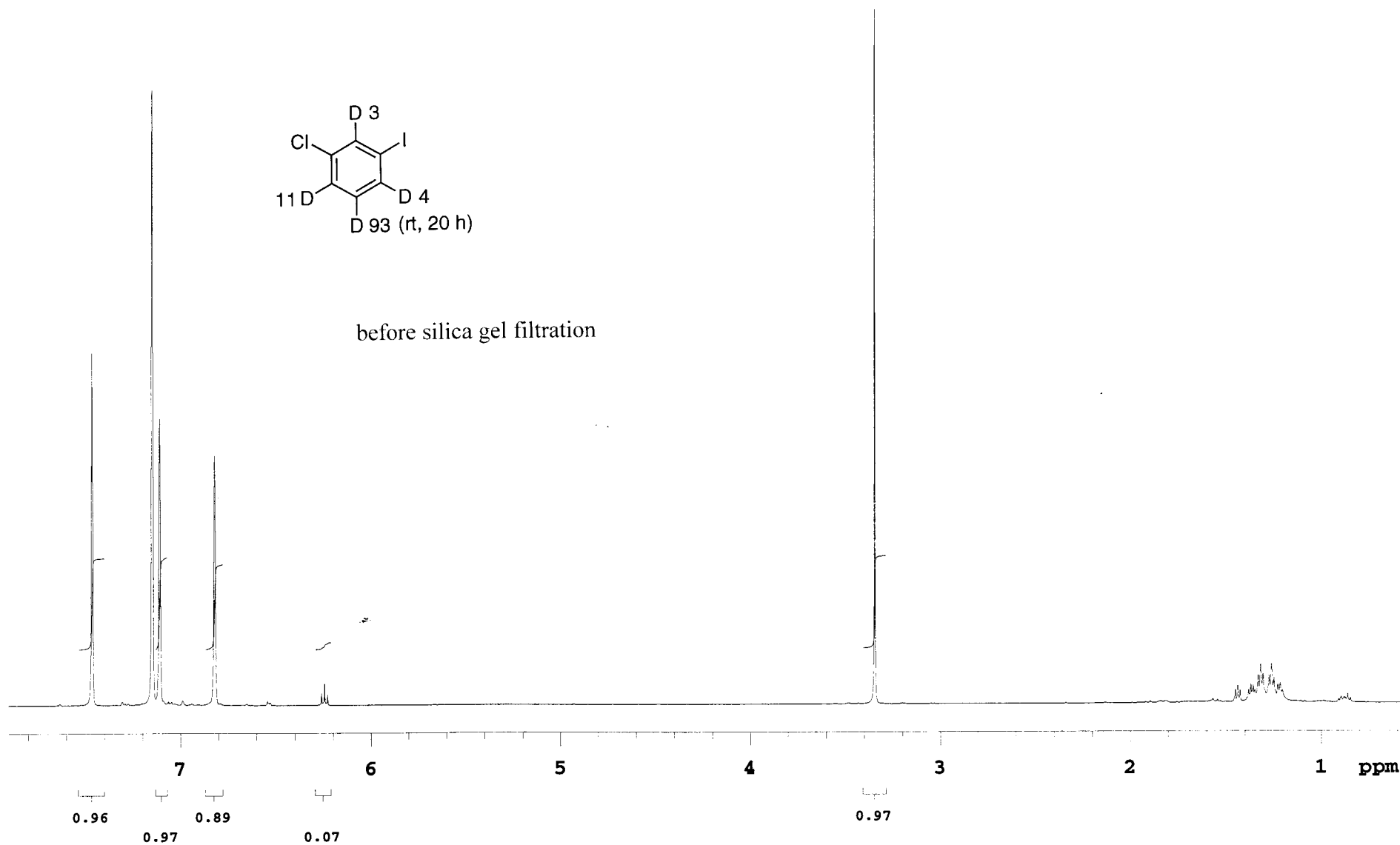


3081-20h

Pulse Sequence: s2pul

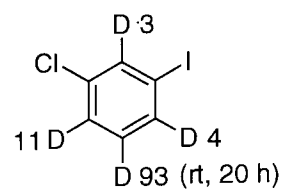


before silica gel filtration

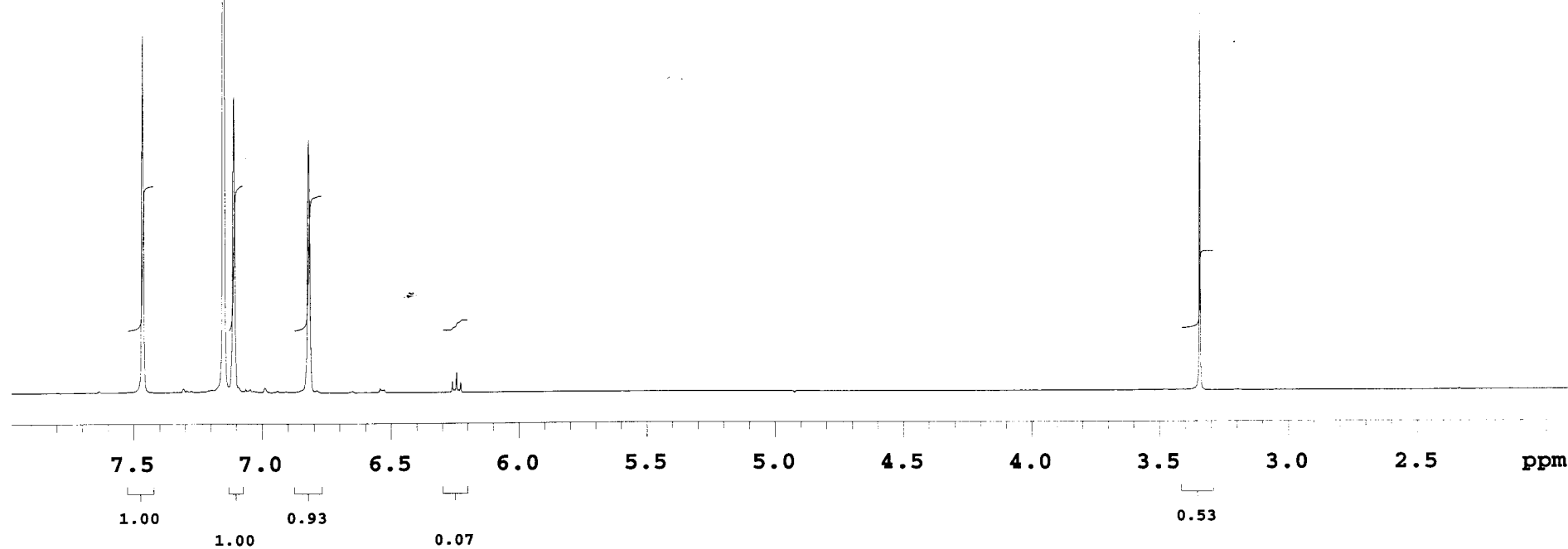


3081pu-h

Pulse Sequence: s2pul

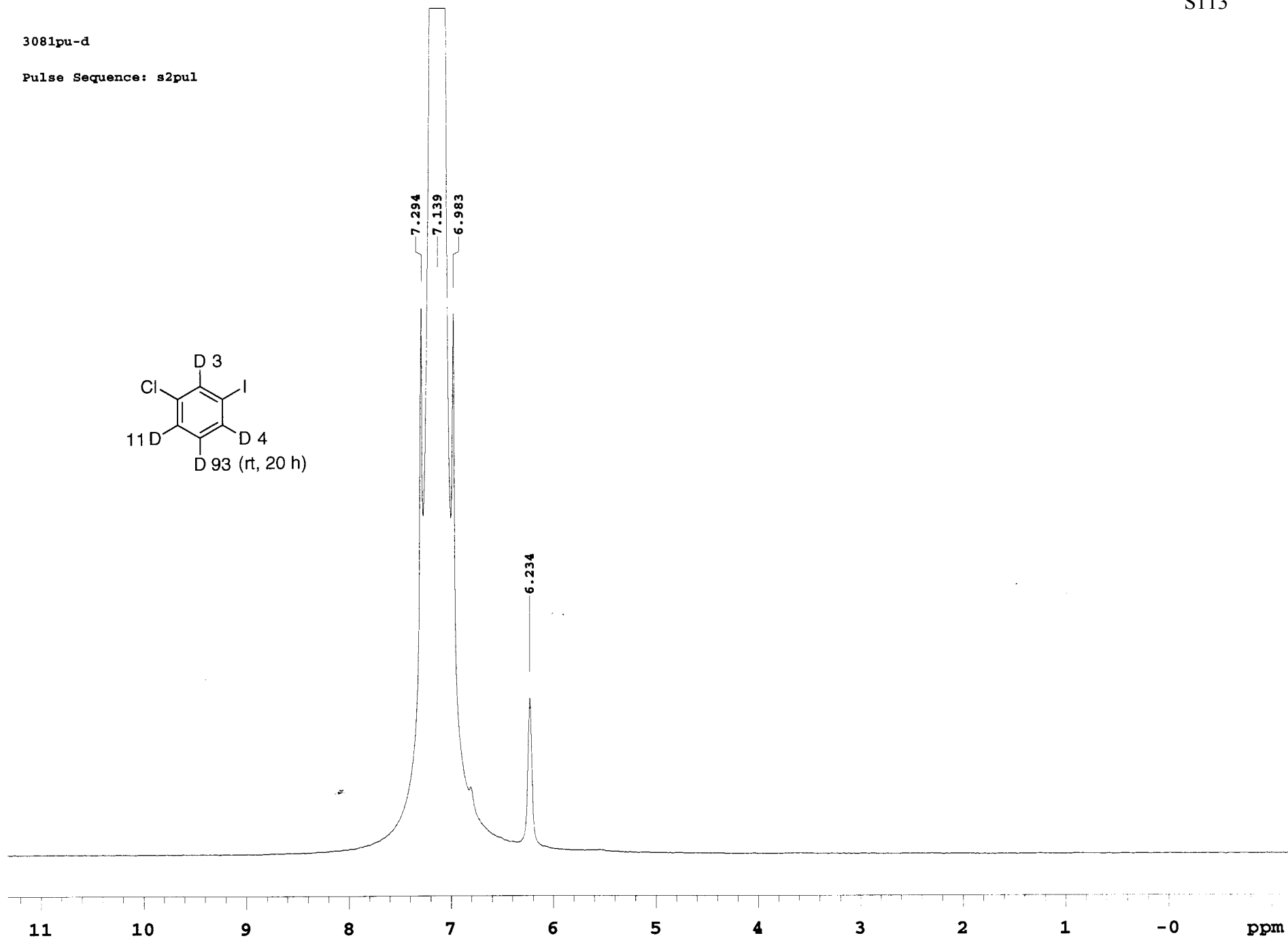
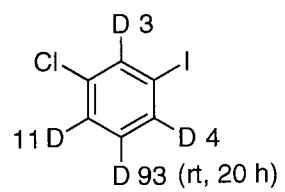


after silica gel filtration



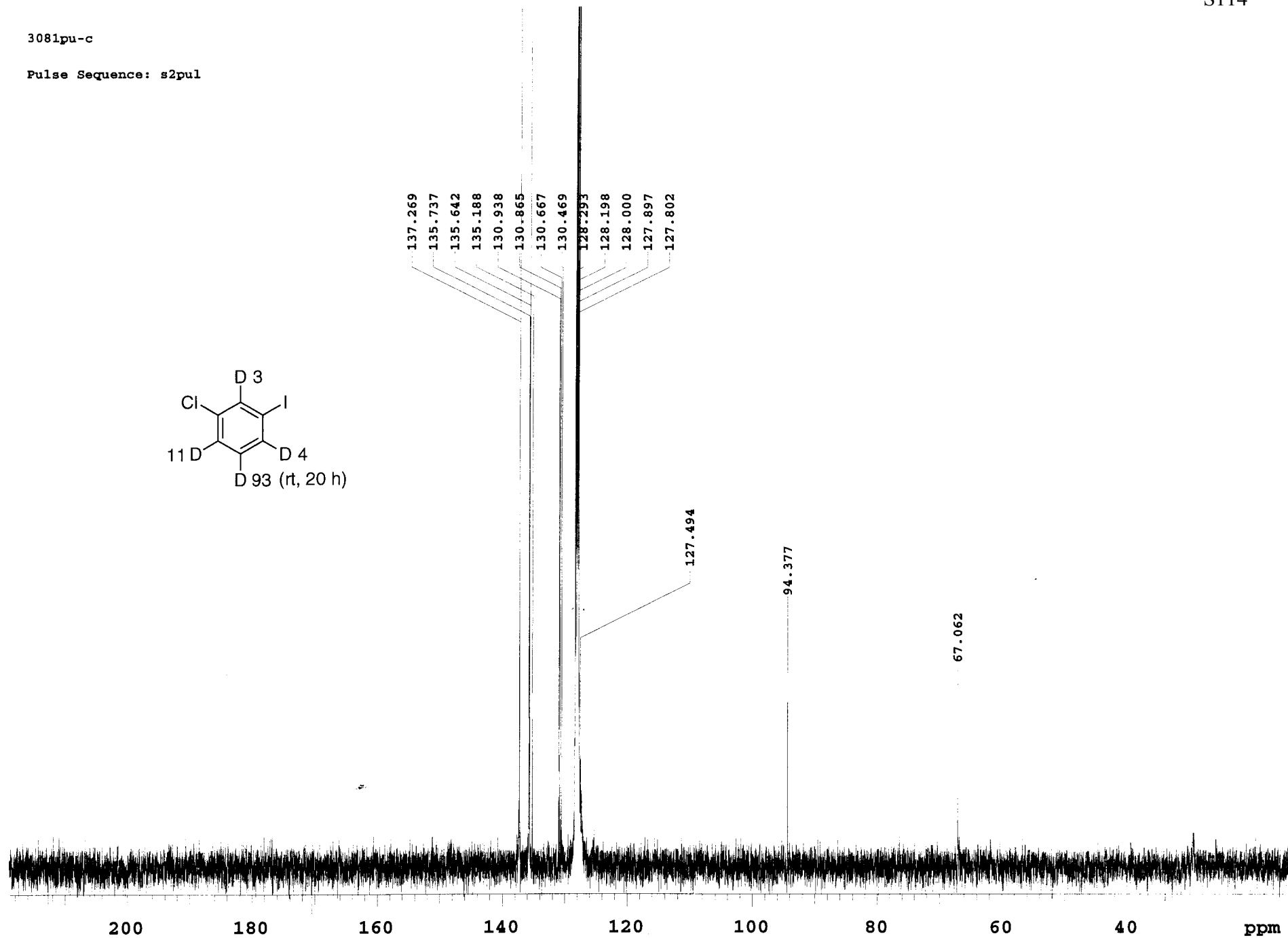
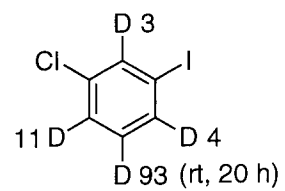
3081pu-d

Pulse Sequence: s2pul



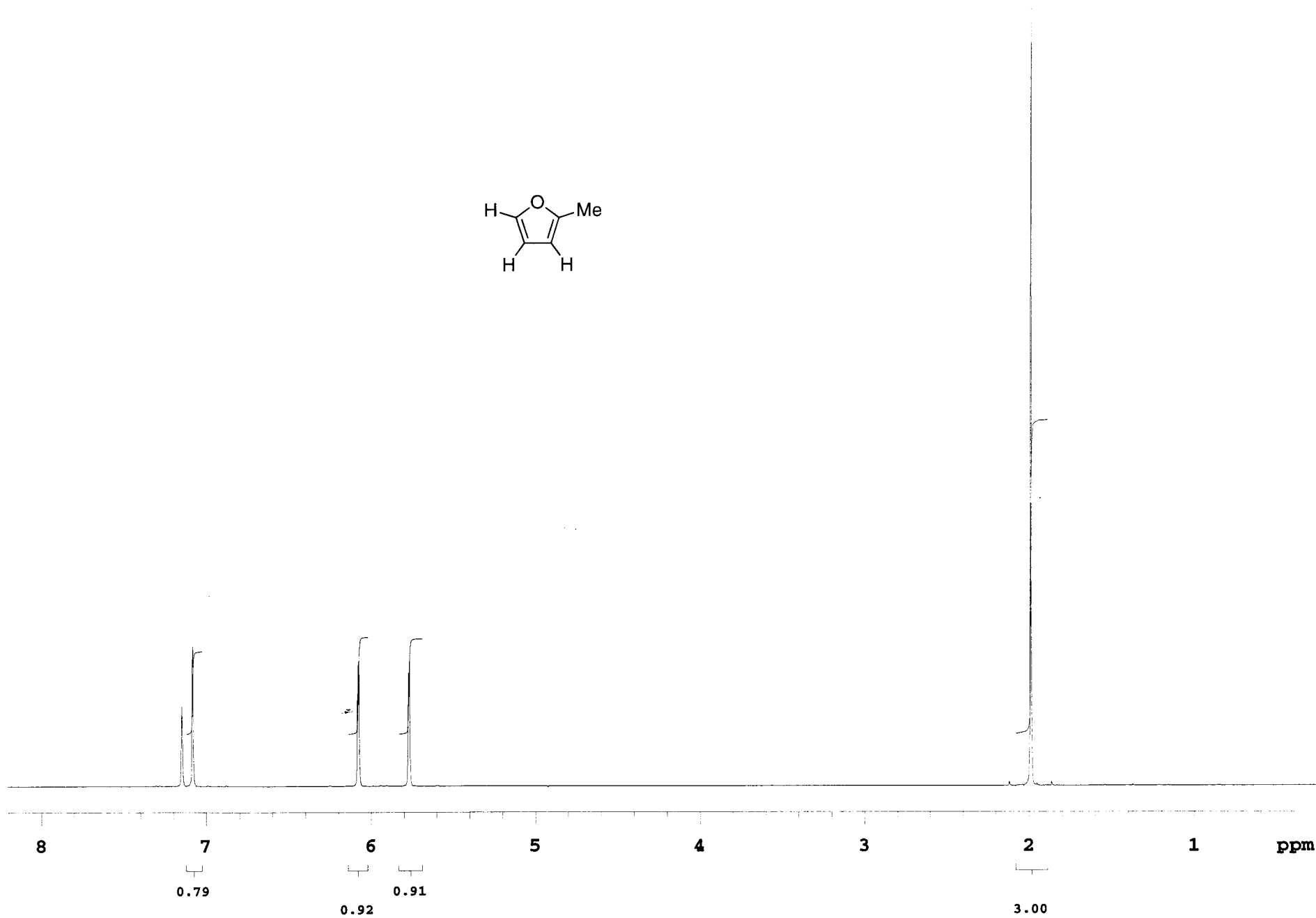
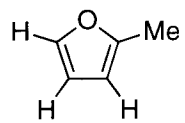
3081pu-c

Pulse Sequence: s2pul



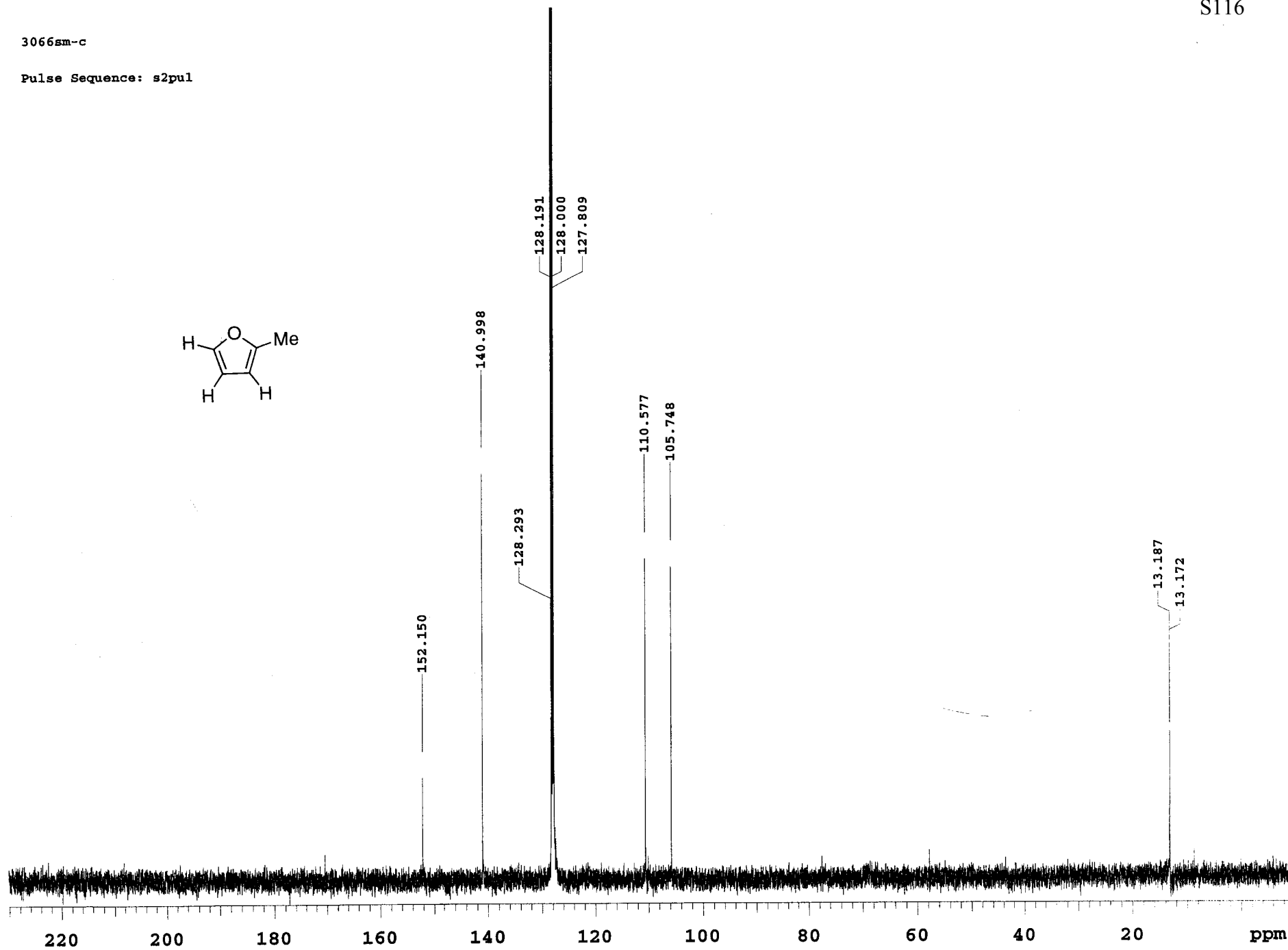
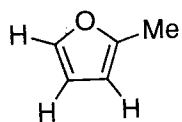
3066sm-h

Pulse Sequence: s2pul



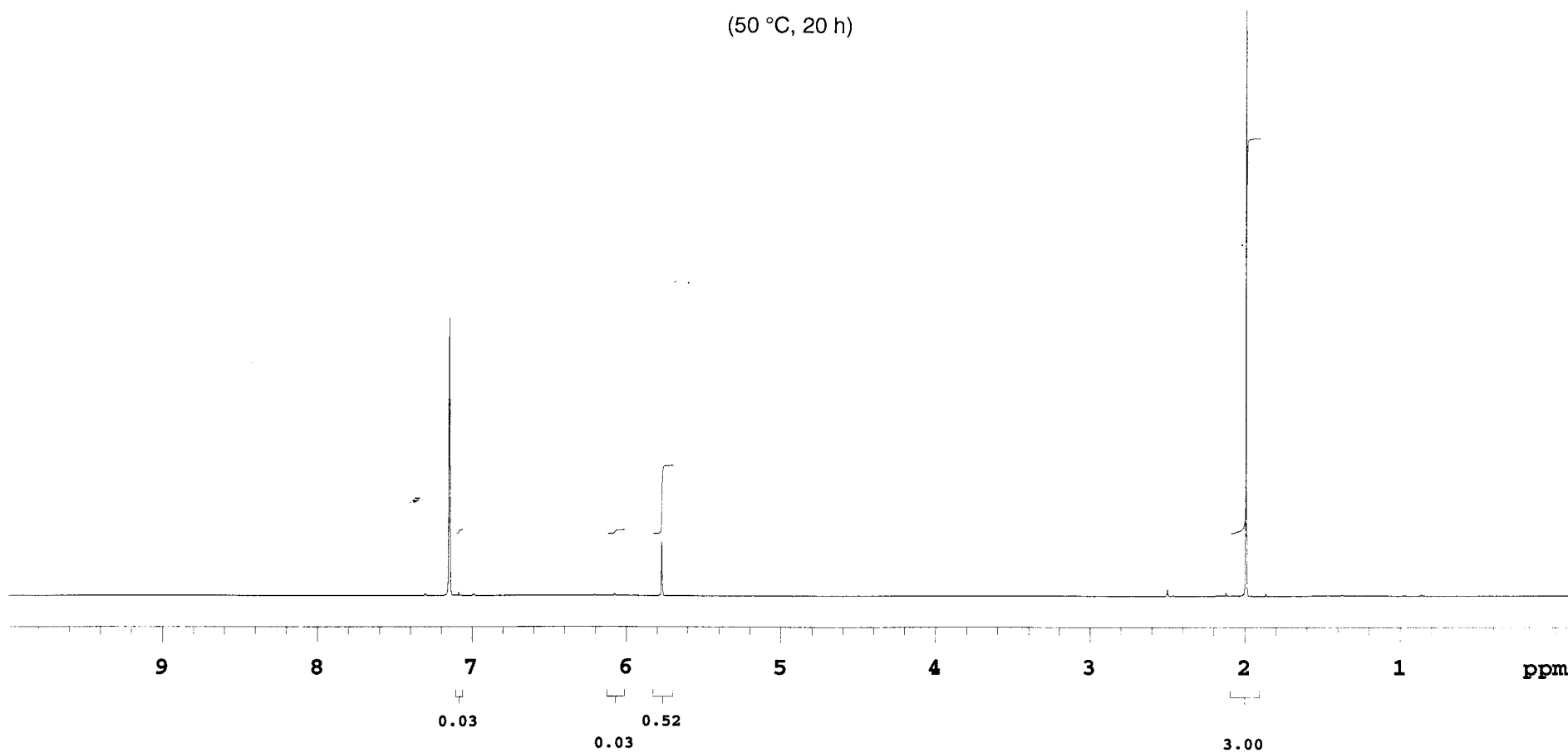
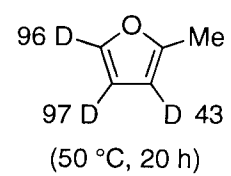
3066sm-c

Pulse Sequence: s2pul



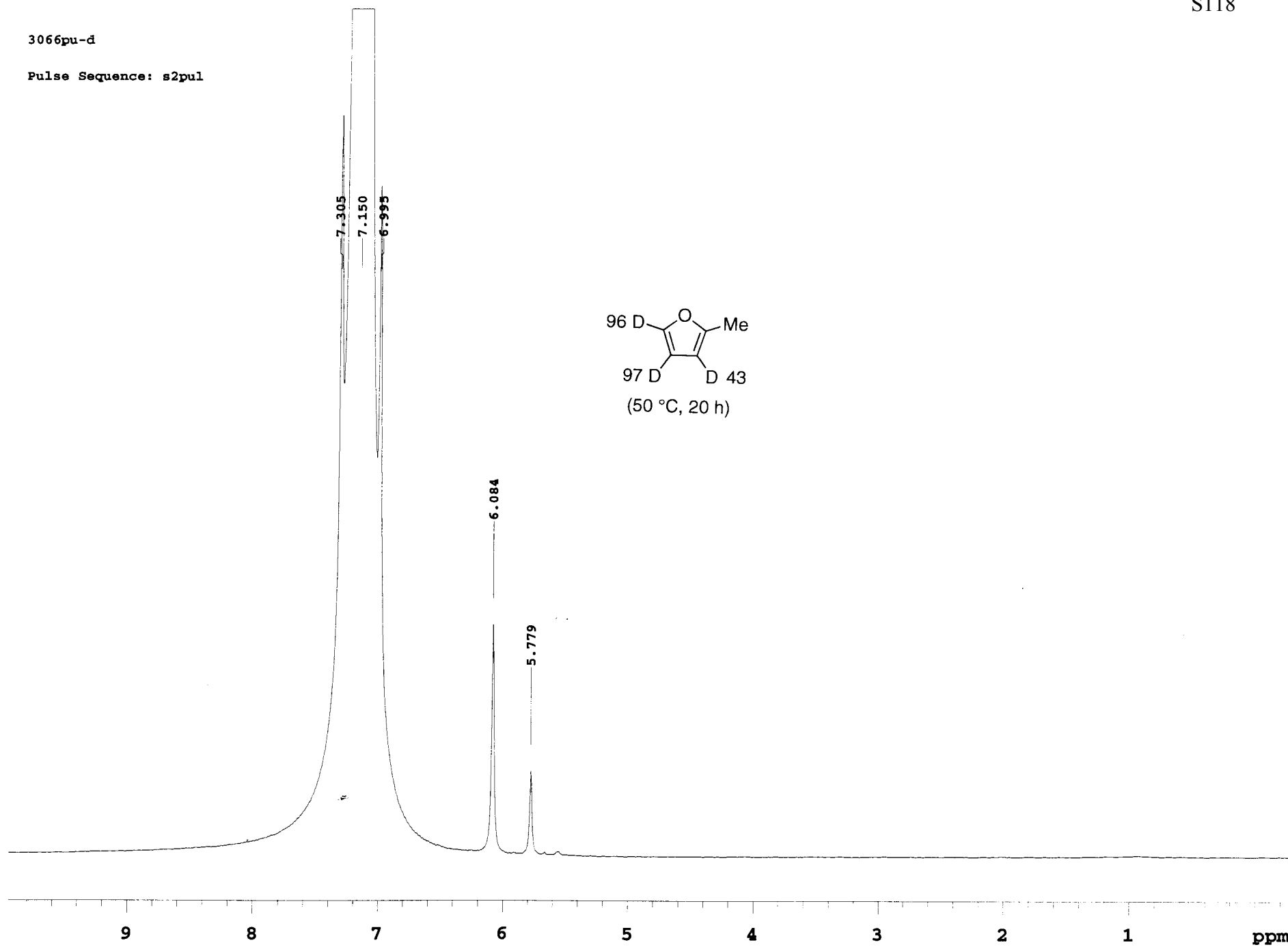
3066.

Pulse Sequence: s2pul



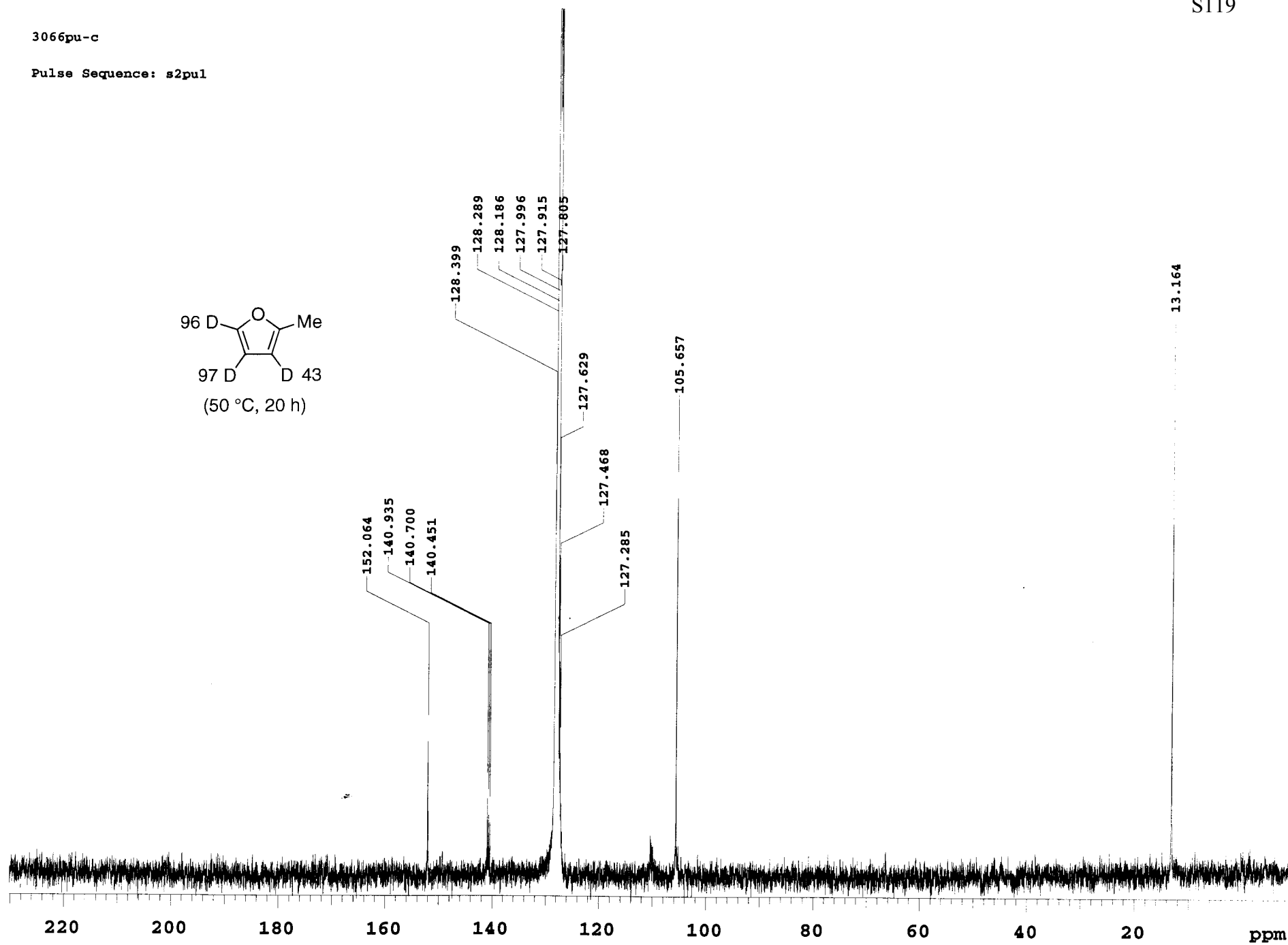
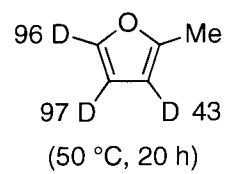
3066pu-d

Pulse Sequence: s2pul



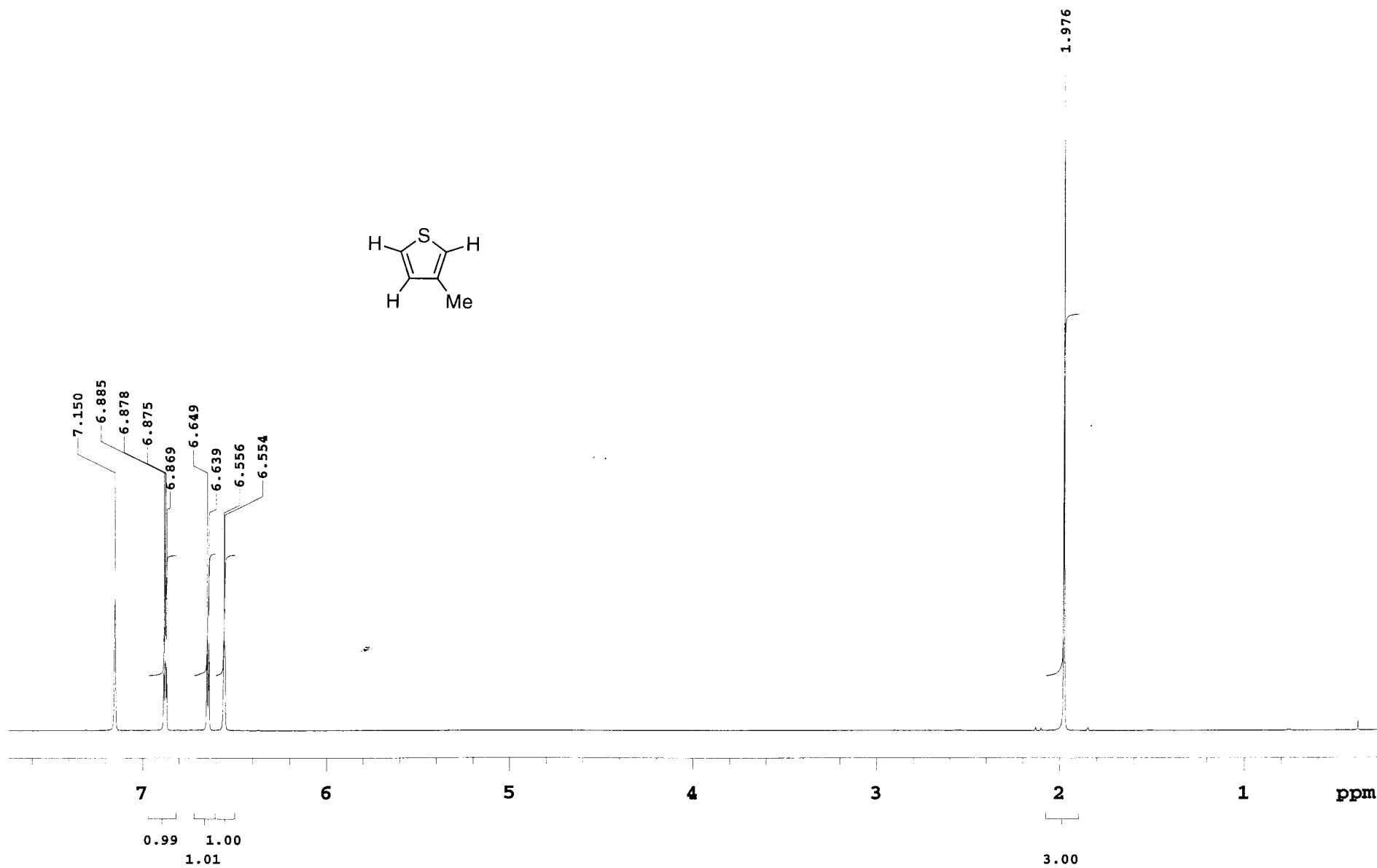
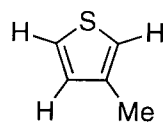
3066pu-c

Pulse Sequence: s2pul



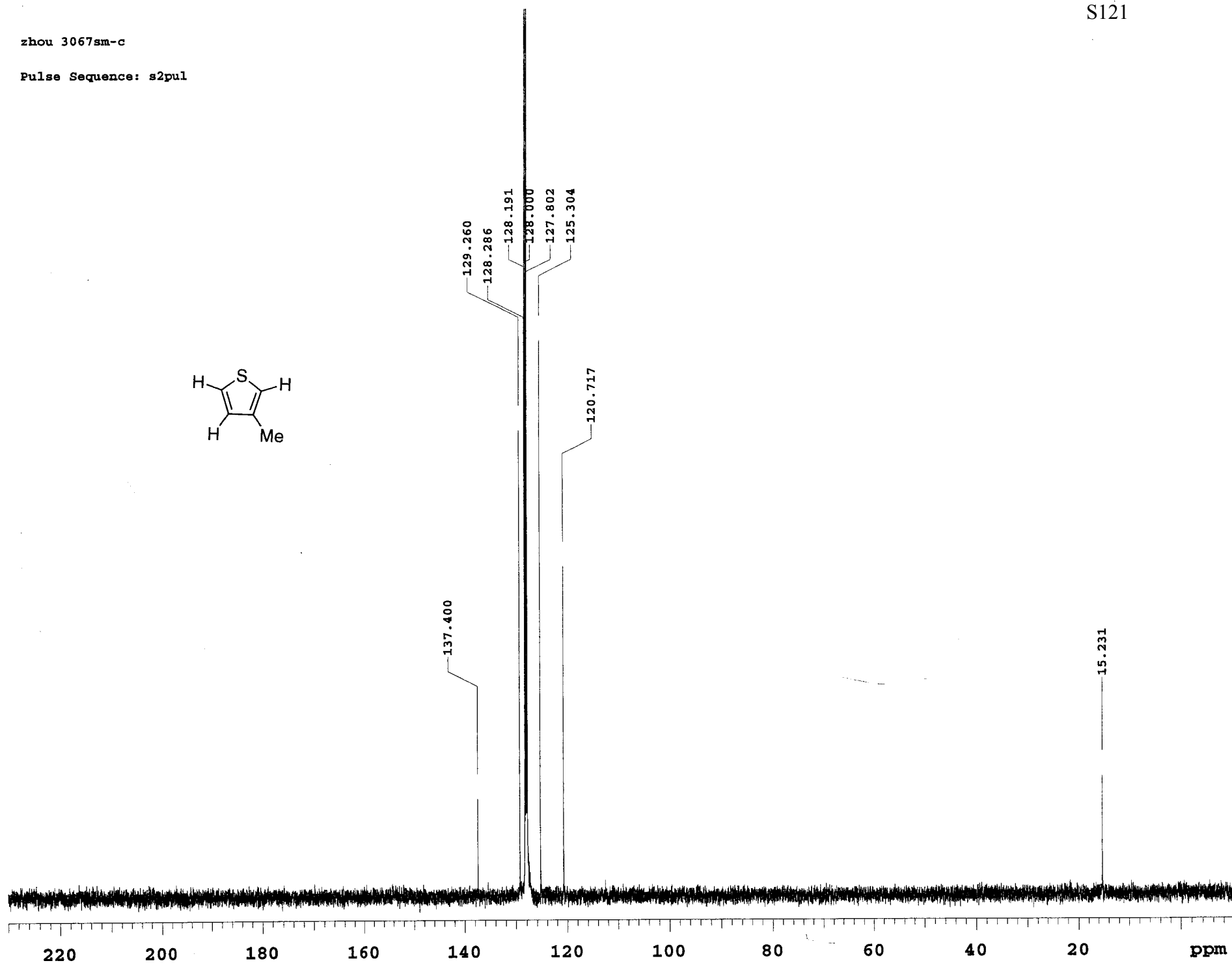
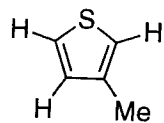
3067sm-h

Pulse Sequence: s2pul



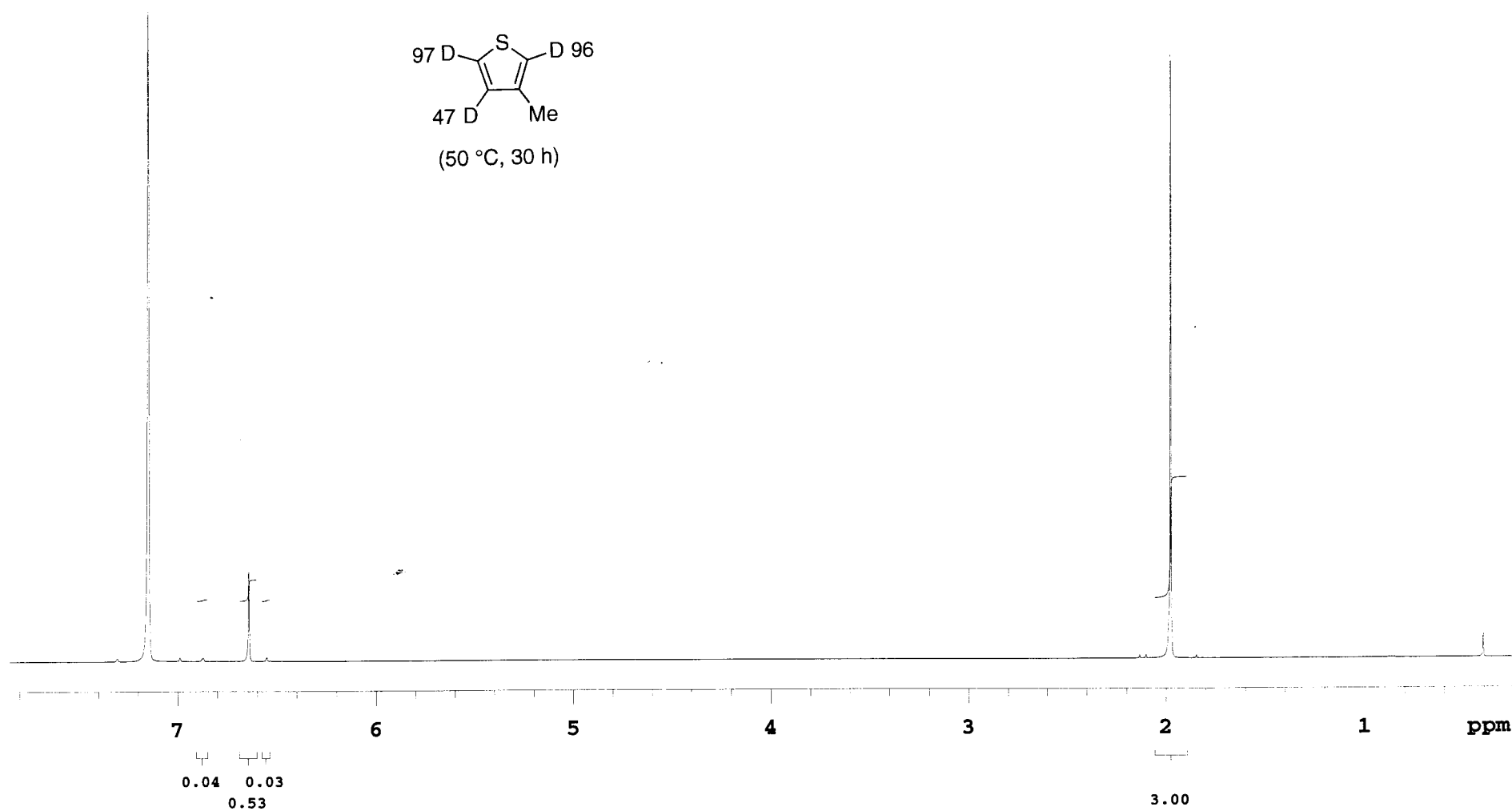
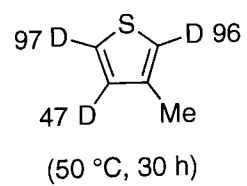
zhou 3067sm-c

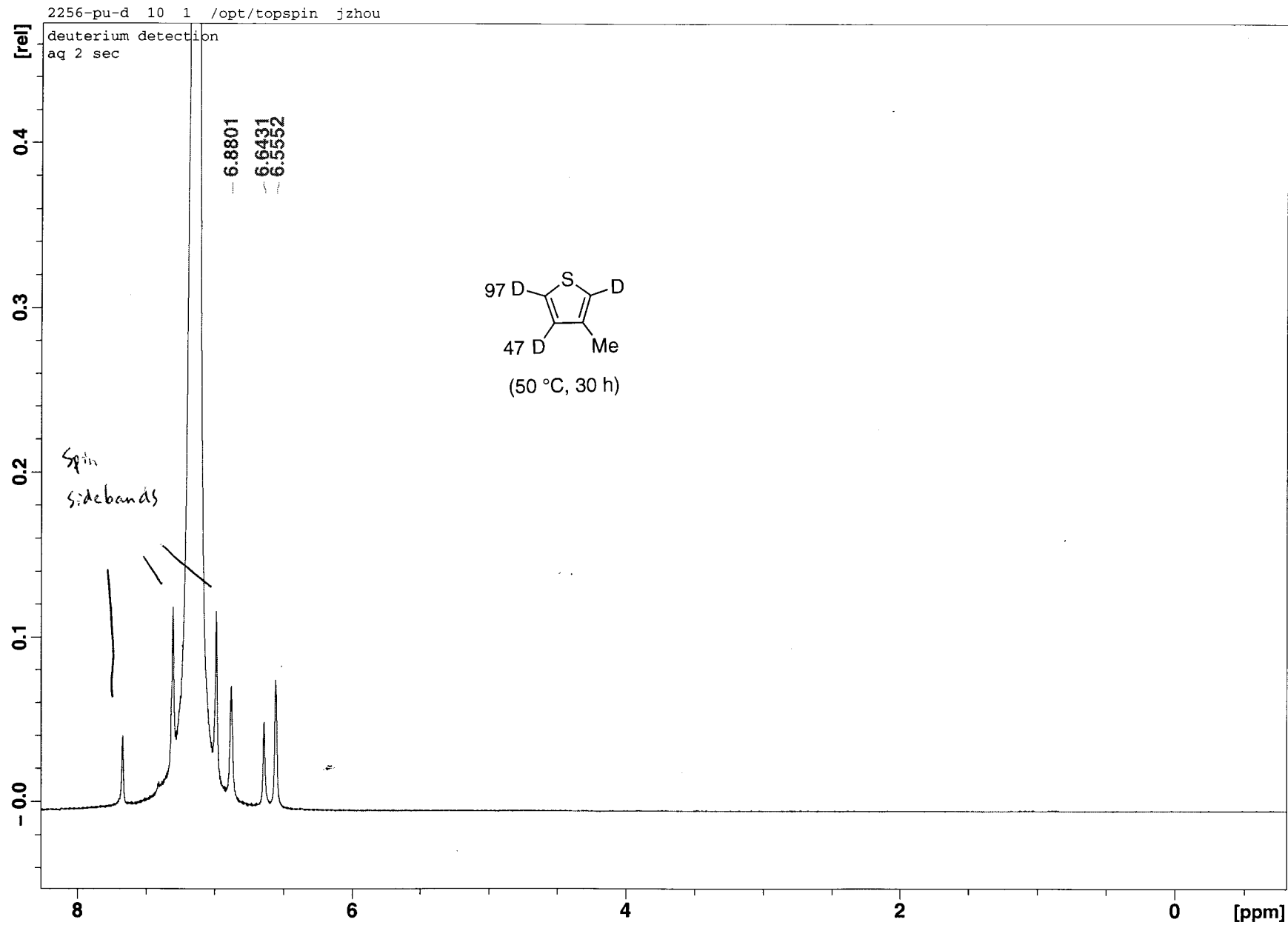
Pulse Sequence: s2pul



3067pu-h

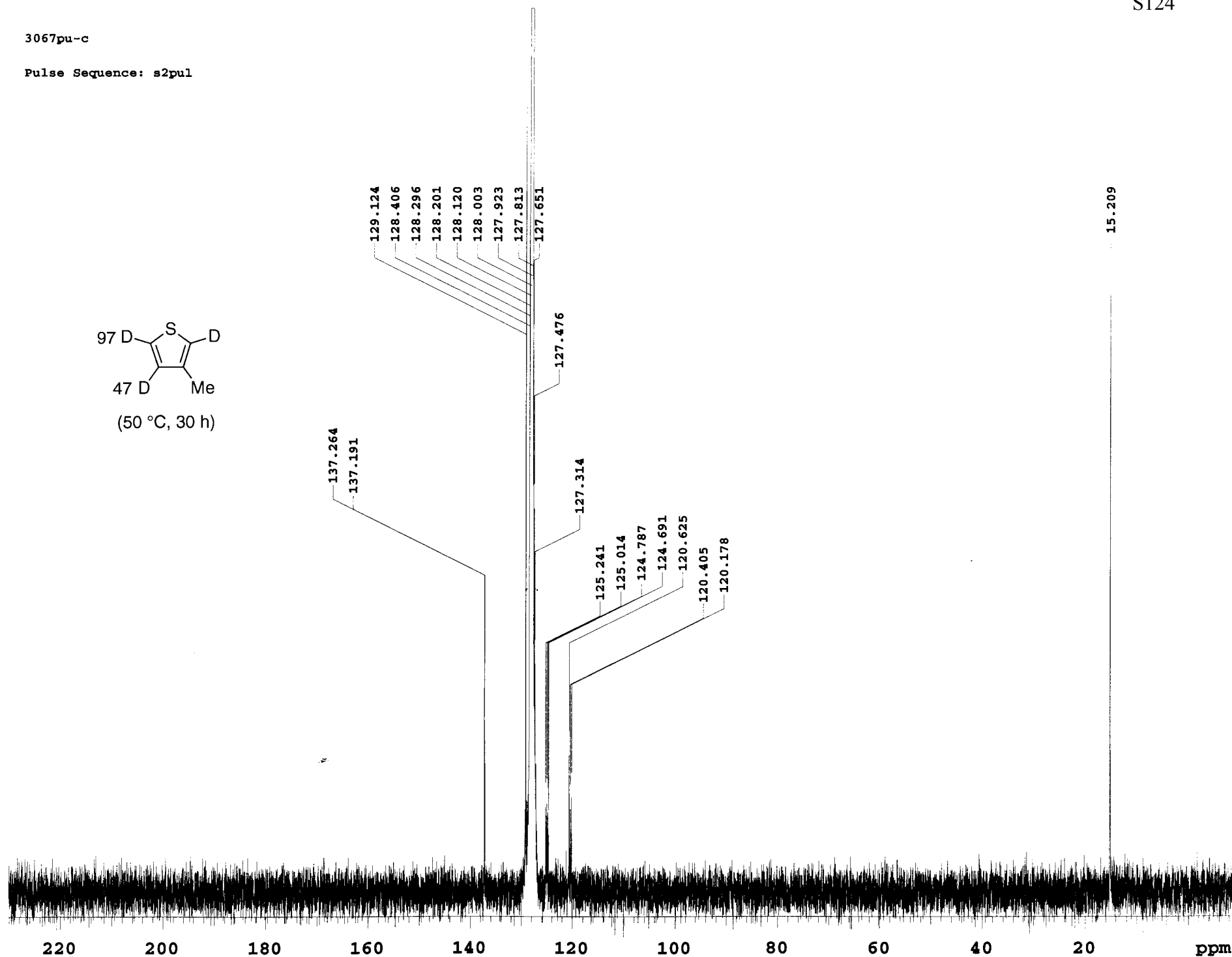
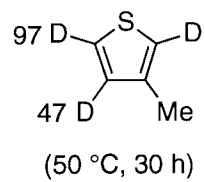
Pulse Sequence: s2pul





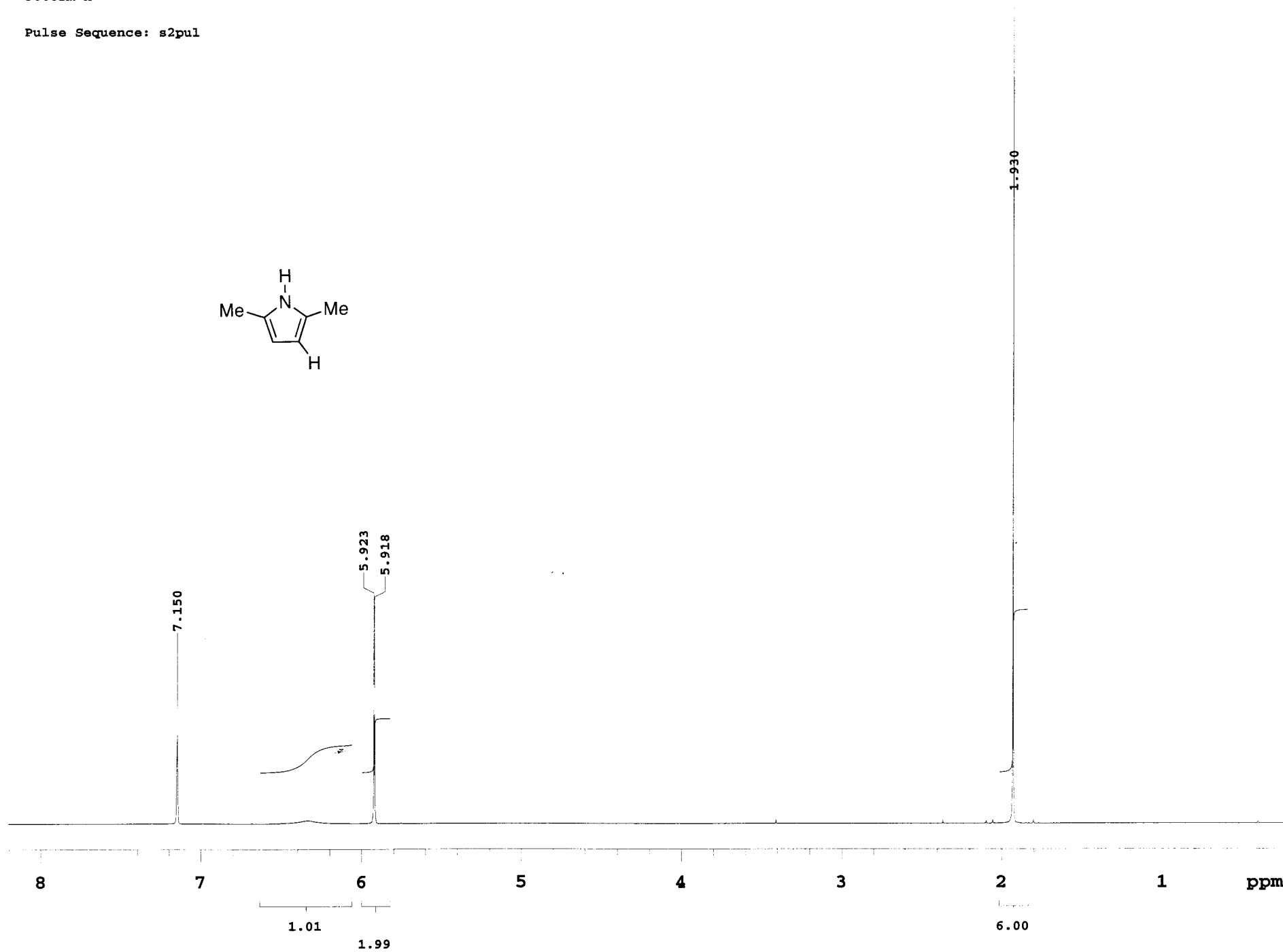
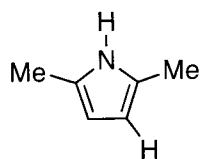
3067pu-c

Pulse Sequence: s2pul



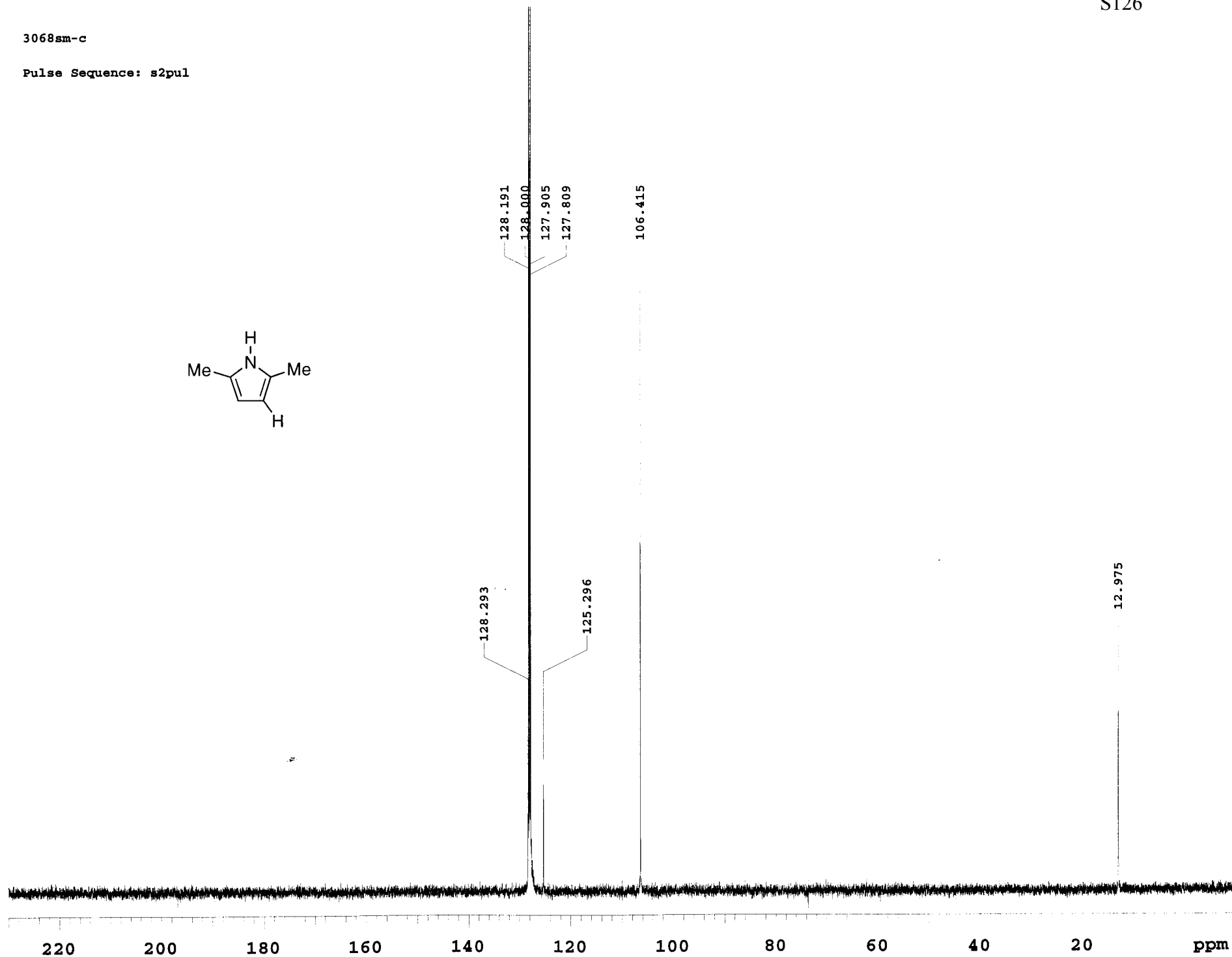
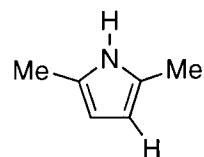
3068sm-h

Pulse Sequence: s2pul



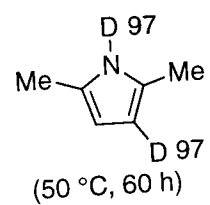
3068sm-c

Pulse Sequence: s2pul

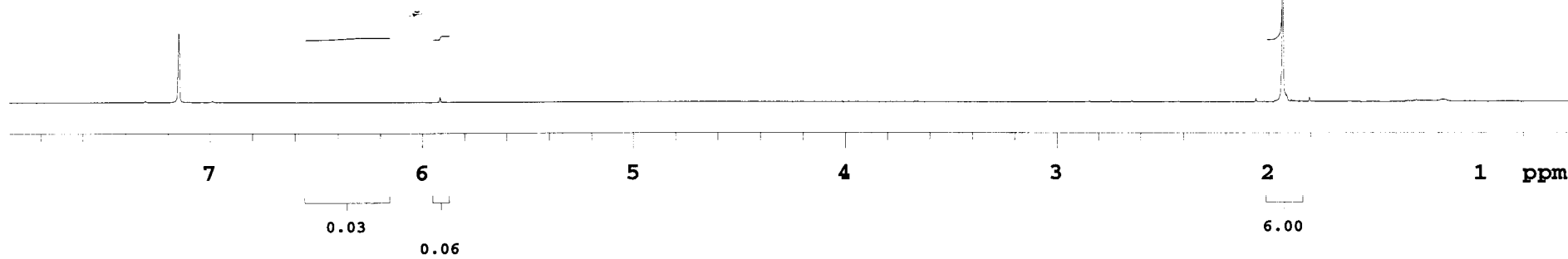


3068-60h

Pulse Sequence: s2pul

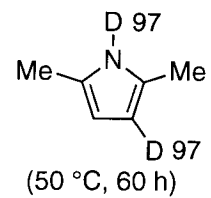


before silica gel filtration

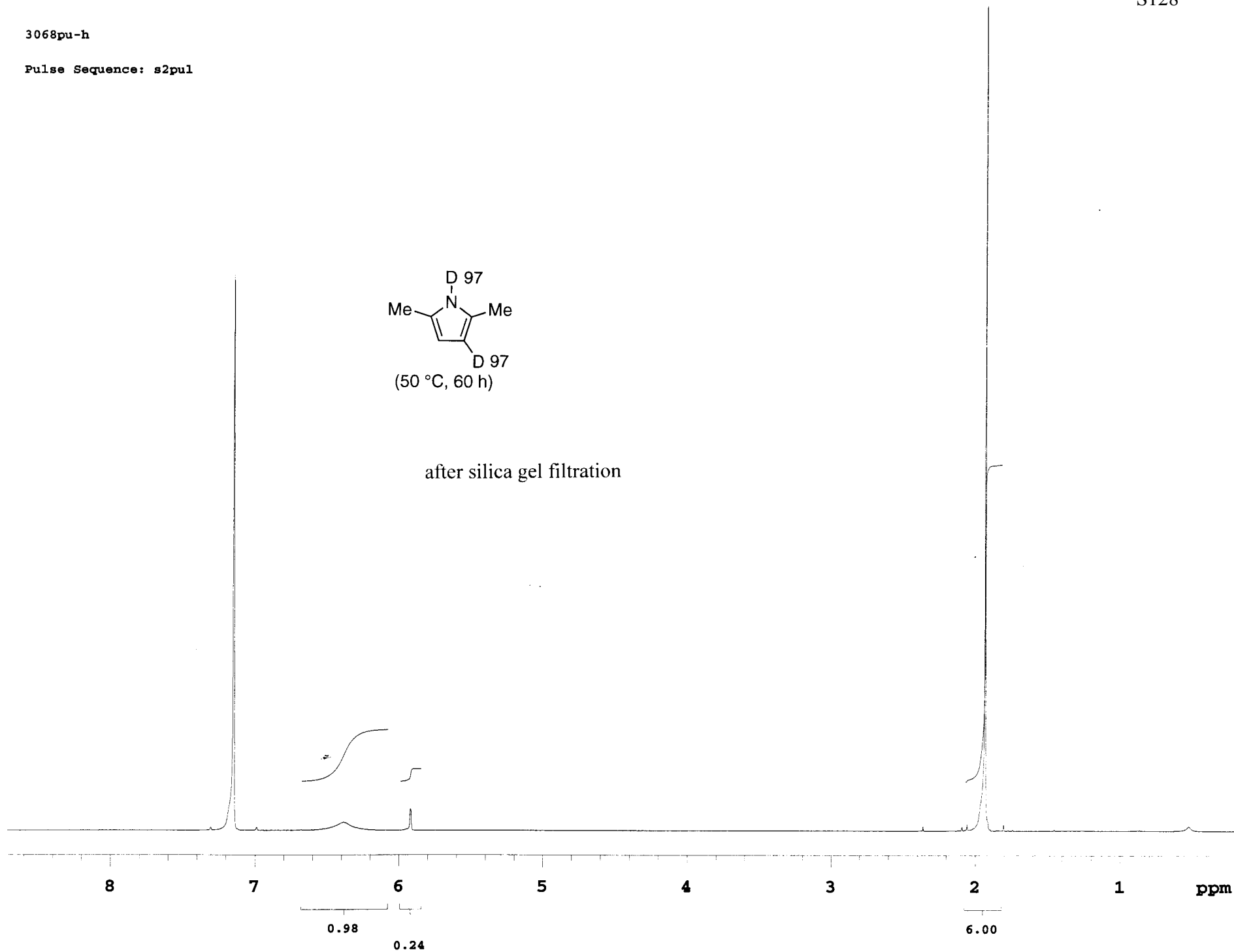


3068pu-h

Pulse Sequence: s2pul

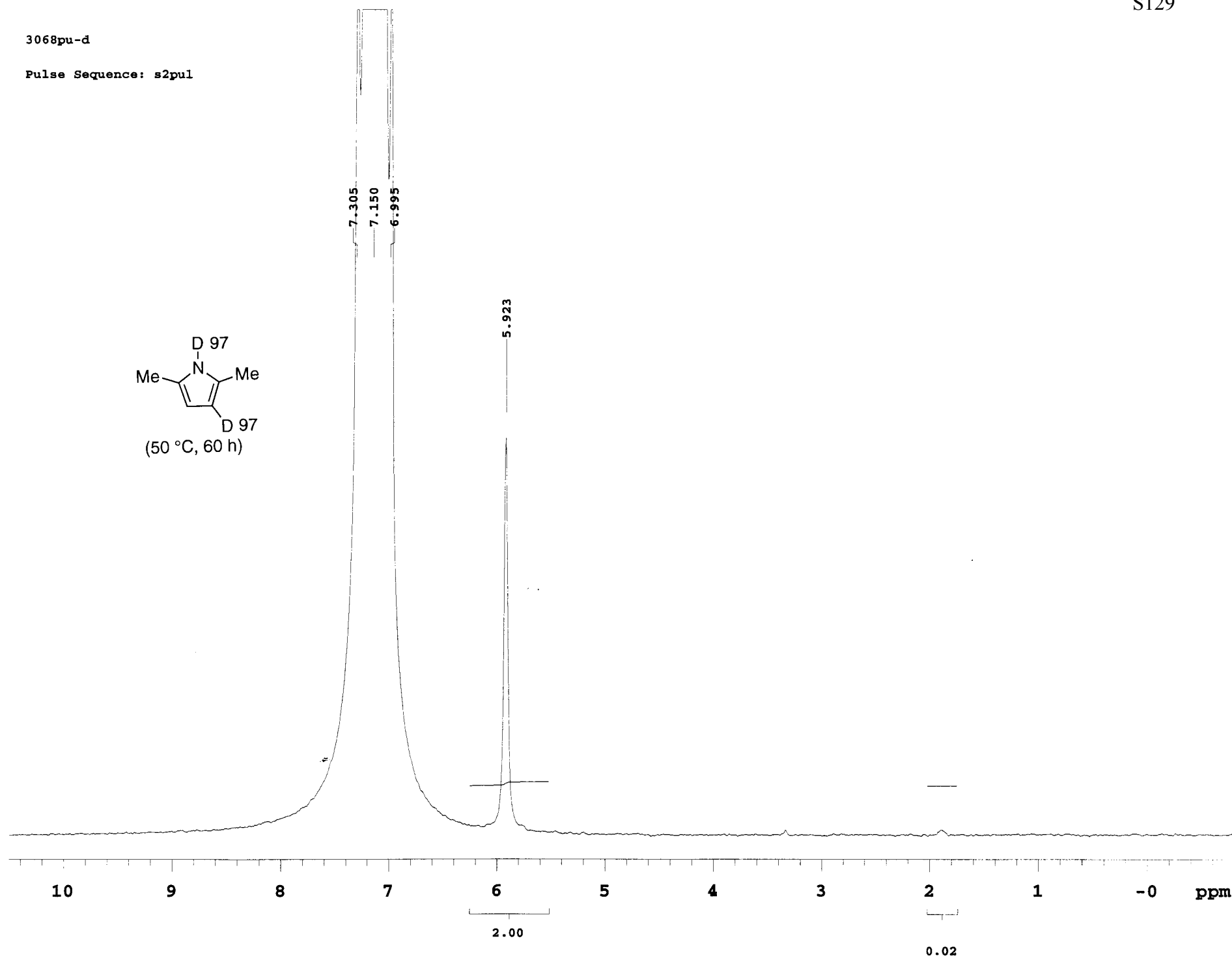


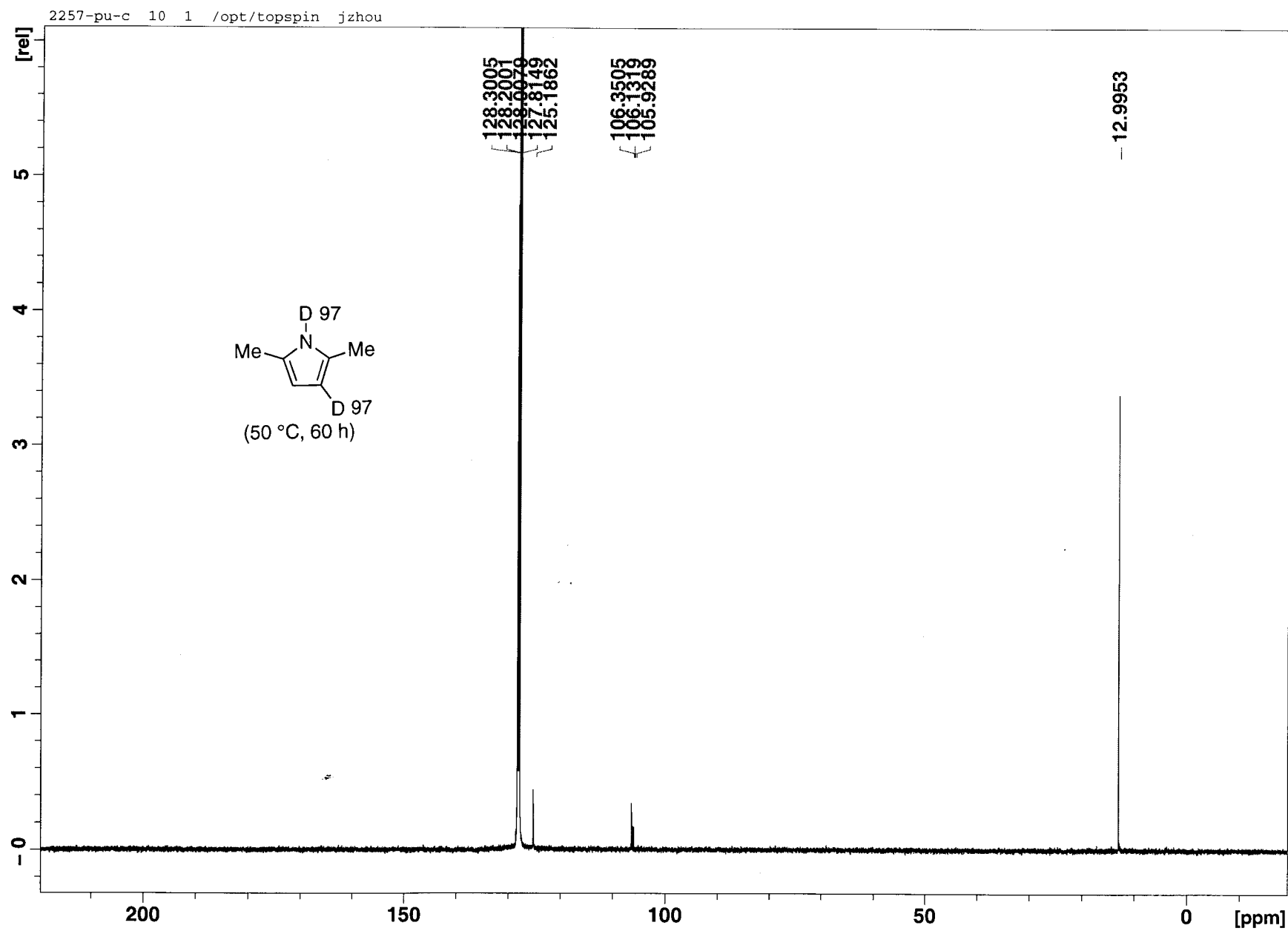
after silica gel filtration



3068pu-d

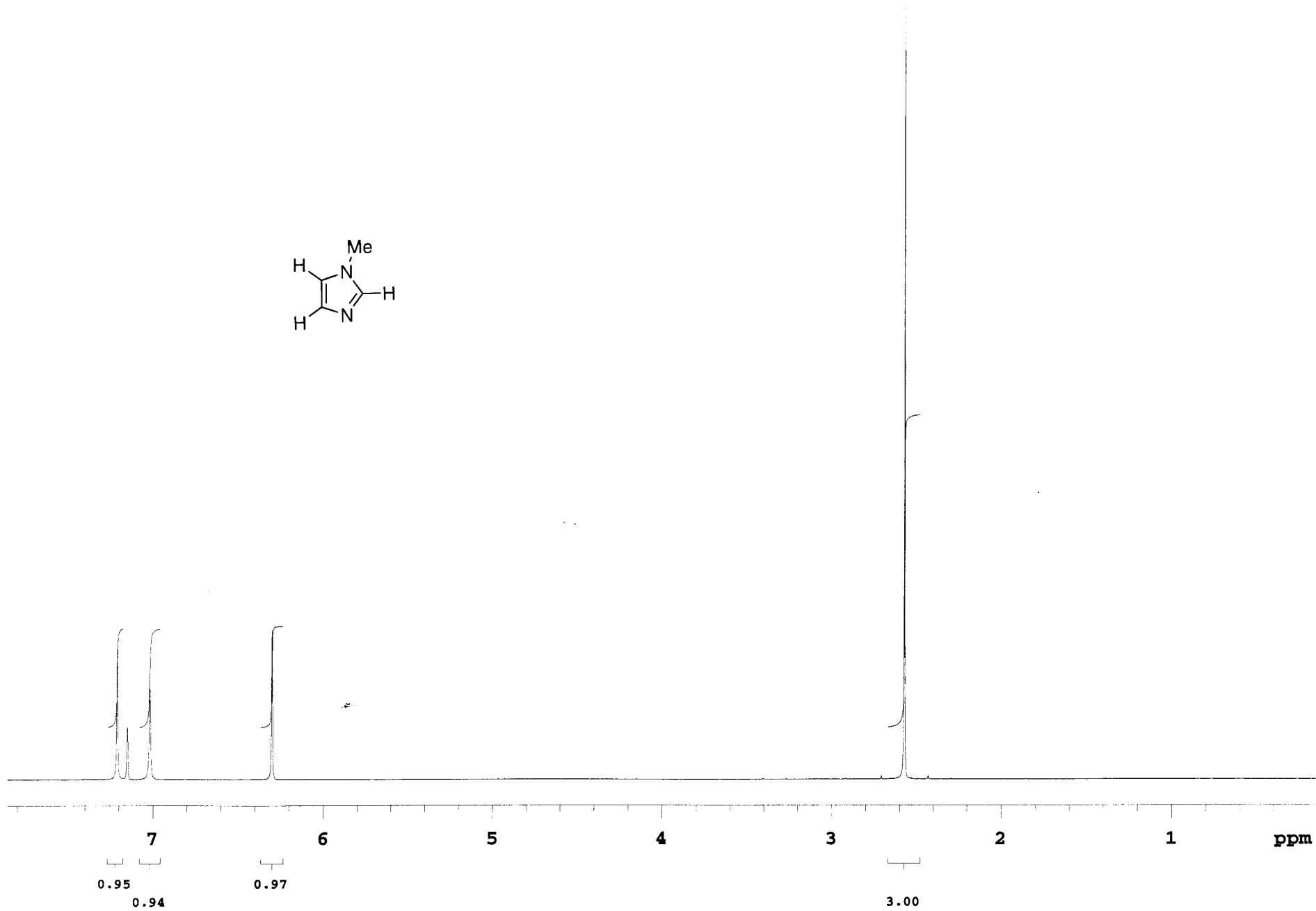
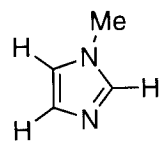
Pulse Sequence: s2pul





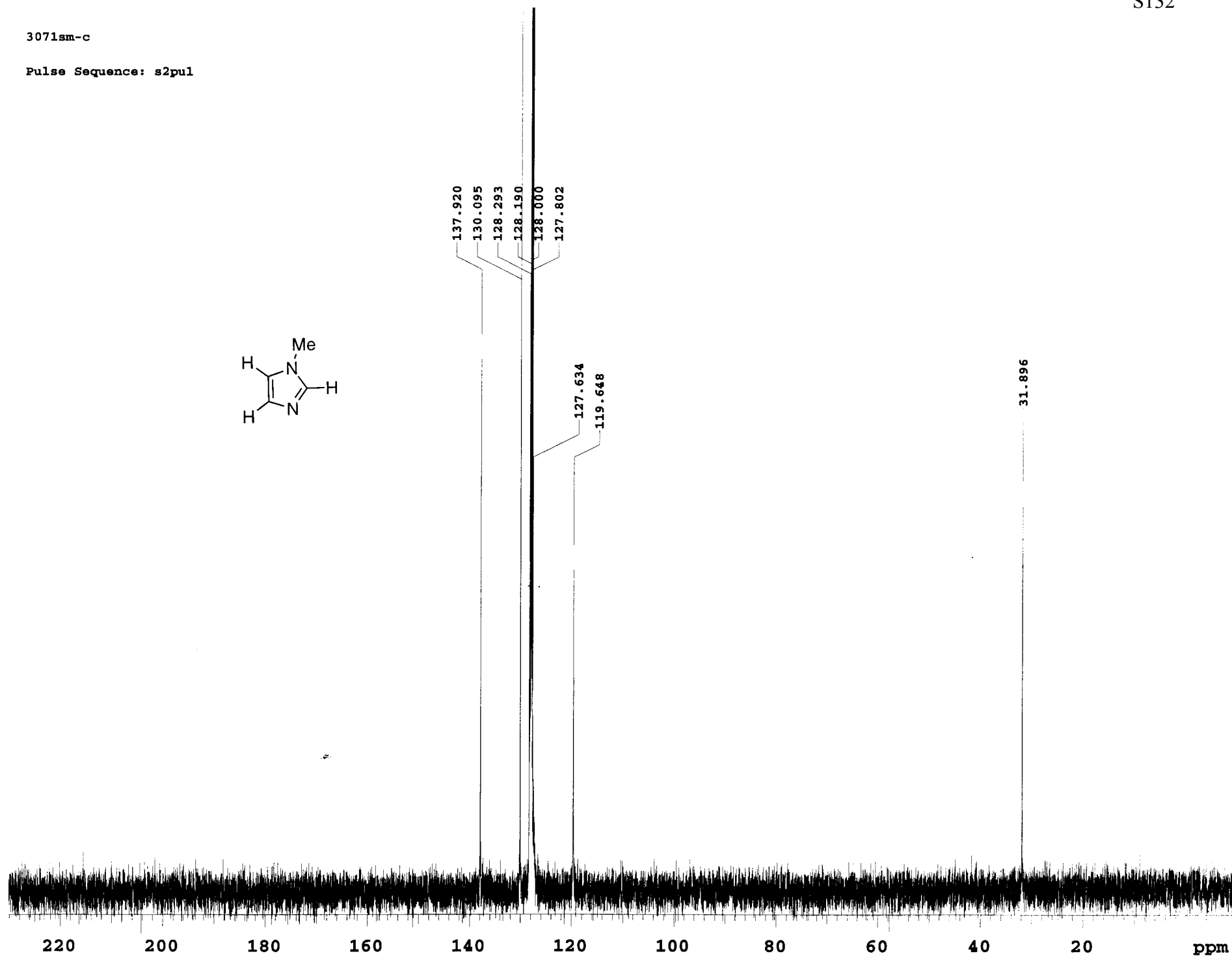
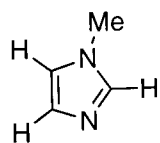
3071sm-h

Pulse Sequence: s2pul



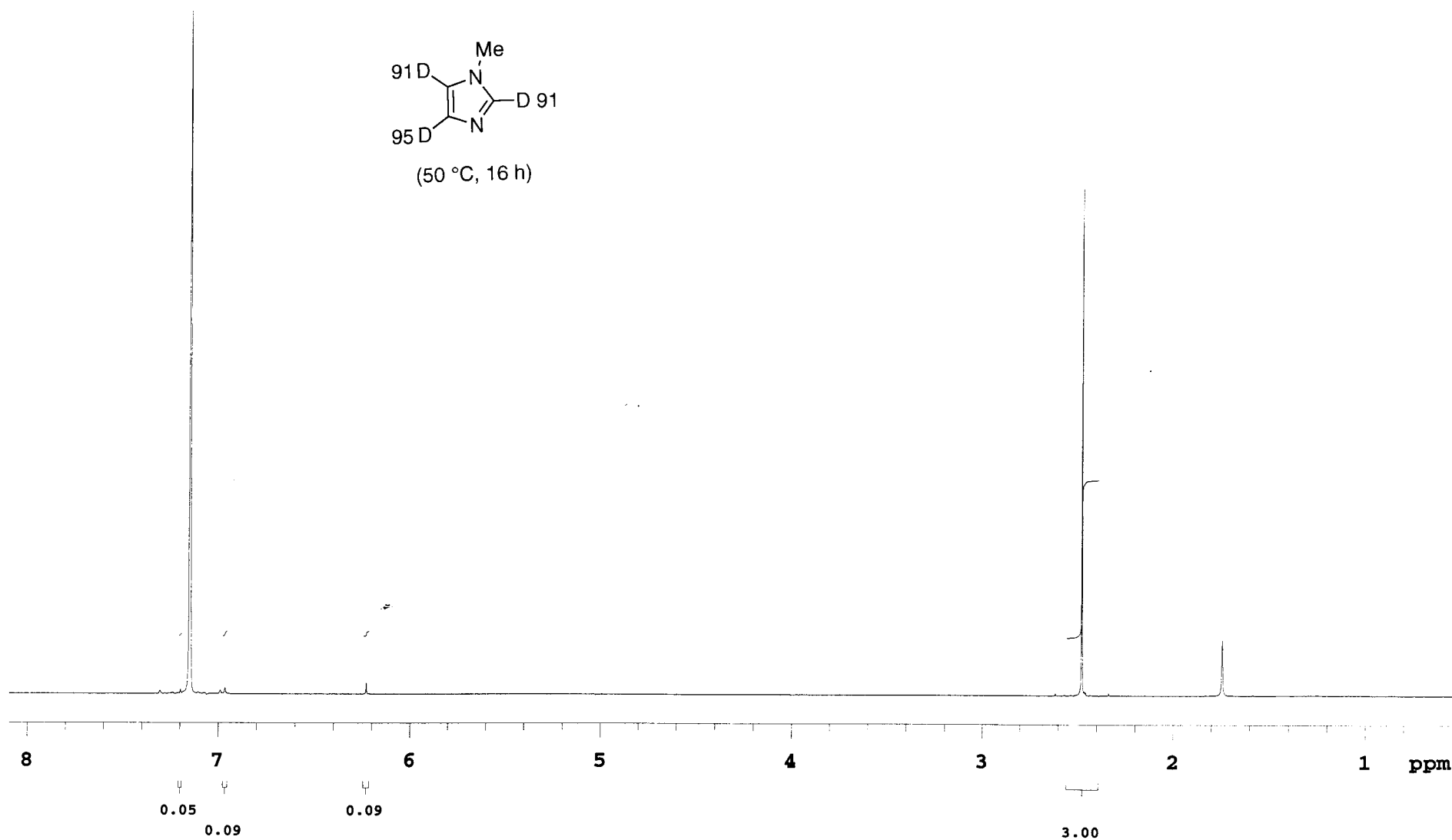
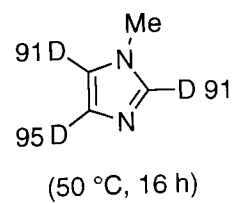
3071sm-c

Pulse Sequence: s2pul



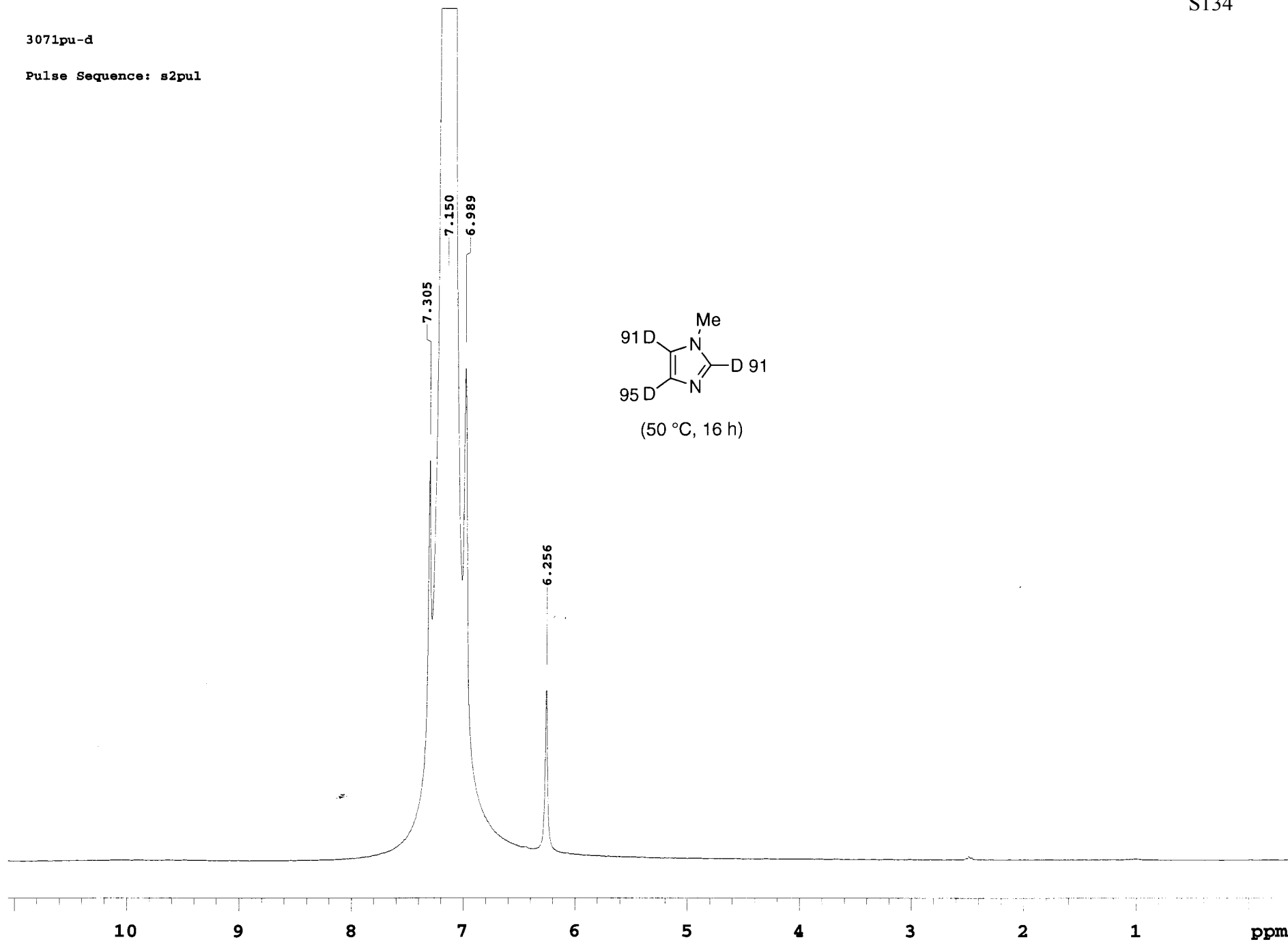
3071pu-h

Pulse Sequence: s2pul



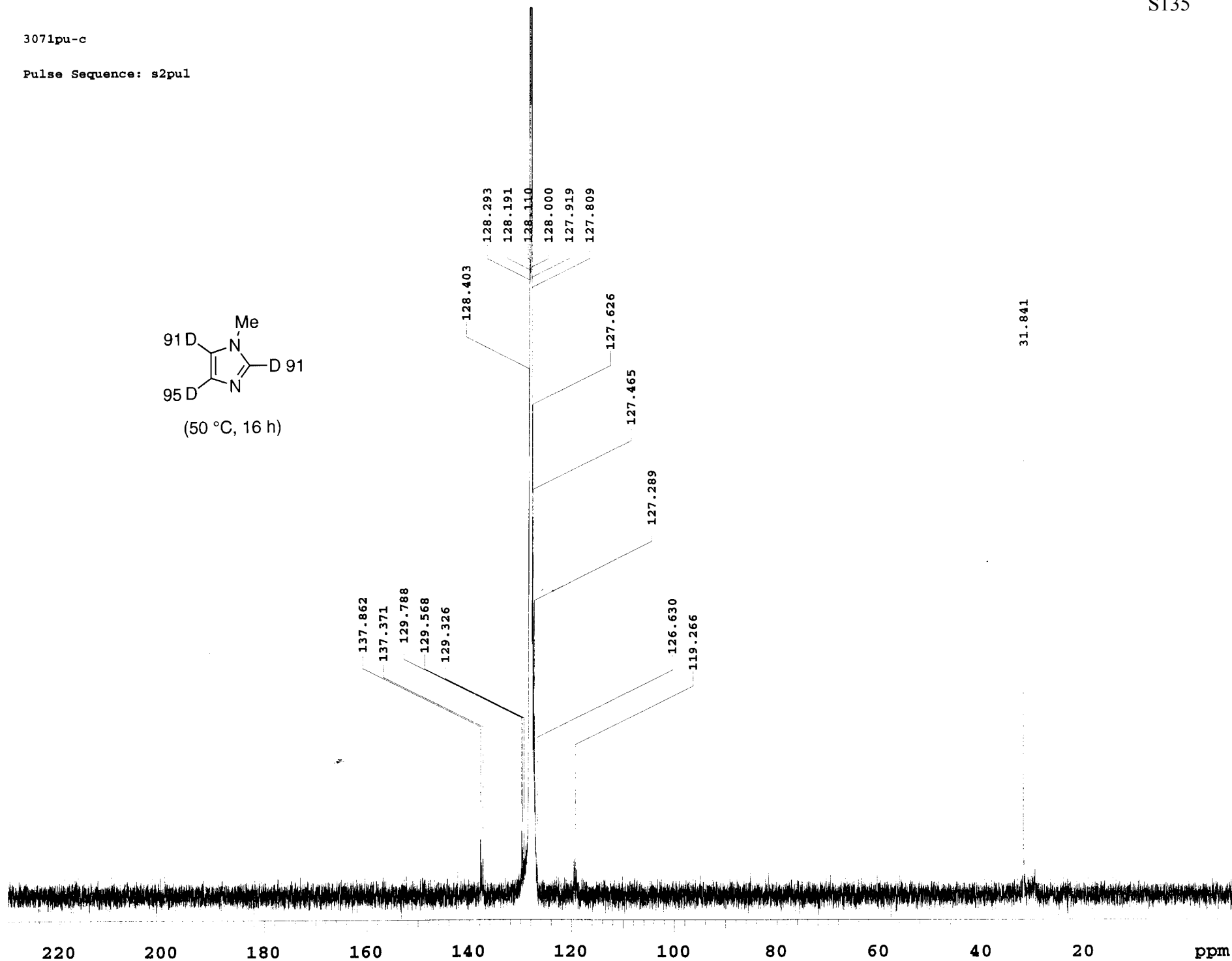
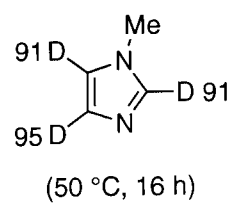
3071pu-d

Pulse Sequence: s2pul



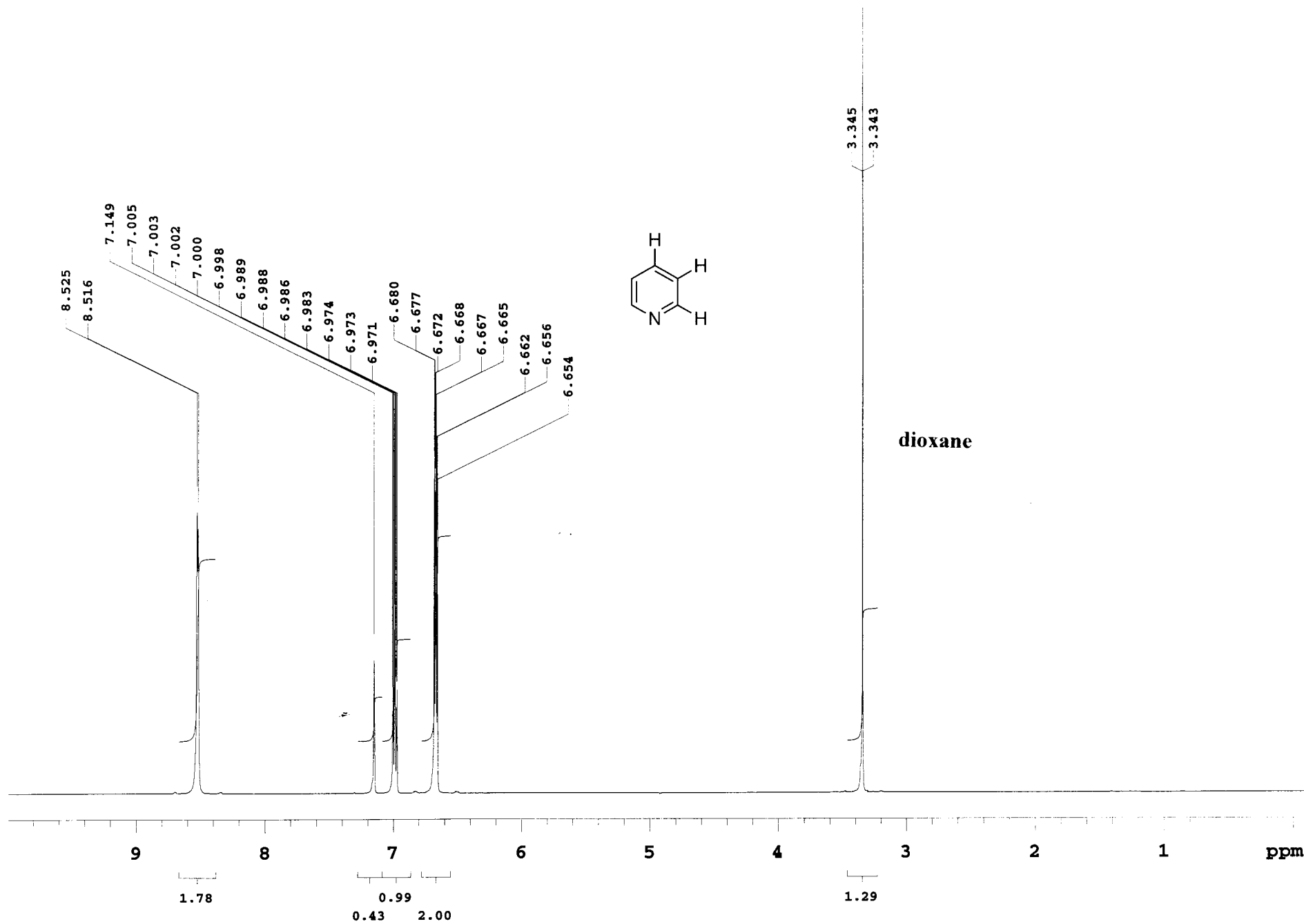
3071pu-c

Pulse Sequence: s2pul



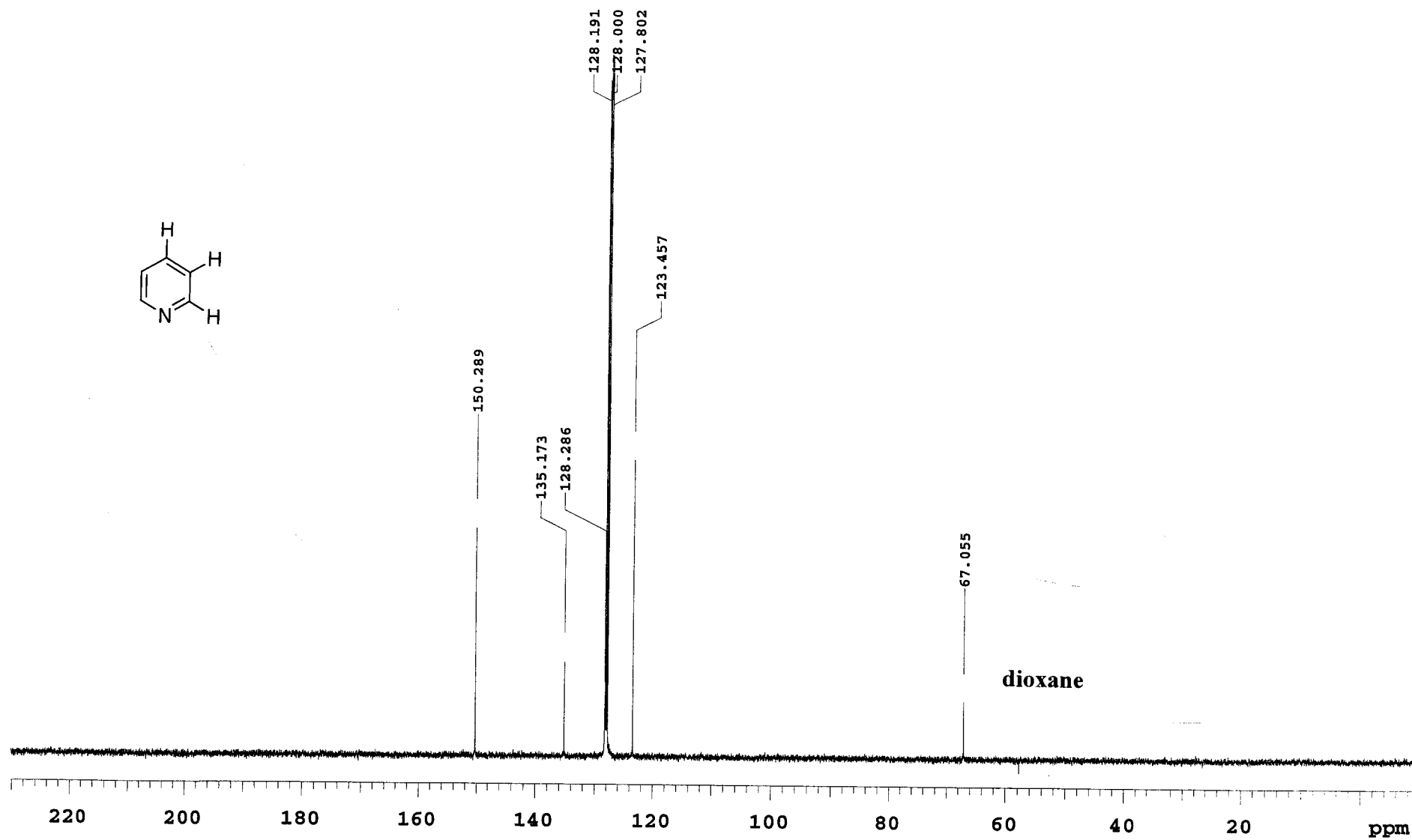
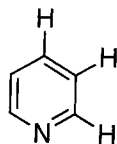
3082sm-h

Pulse Sequence: s2pul



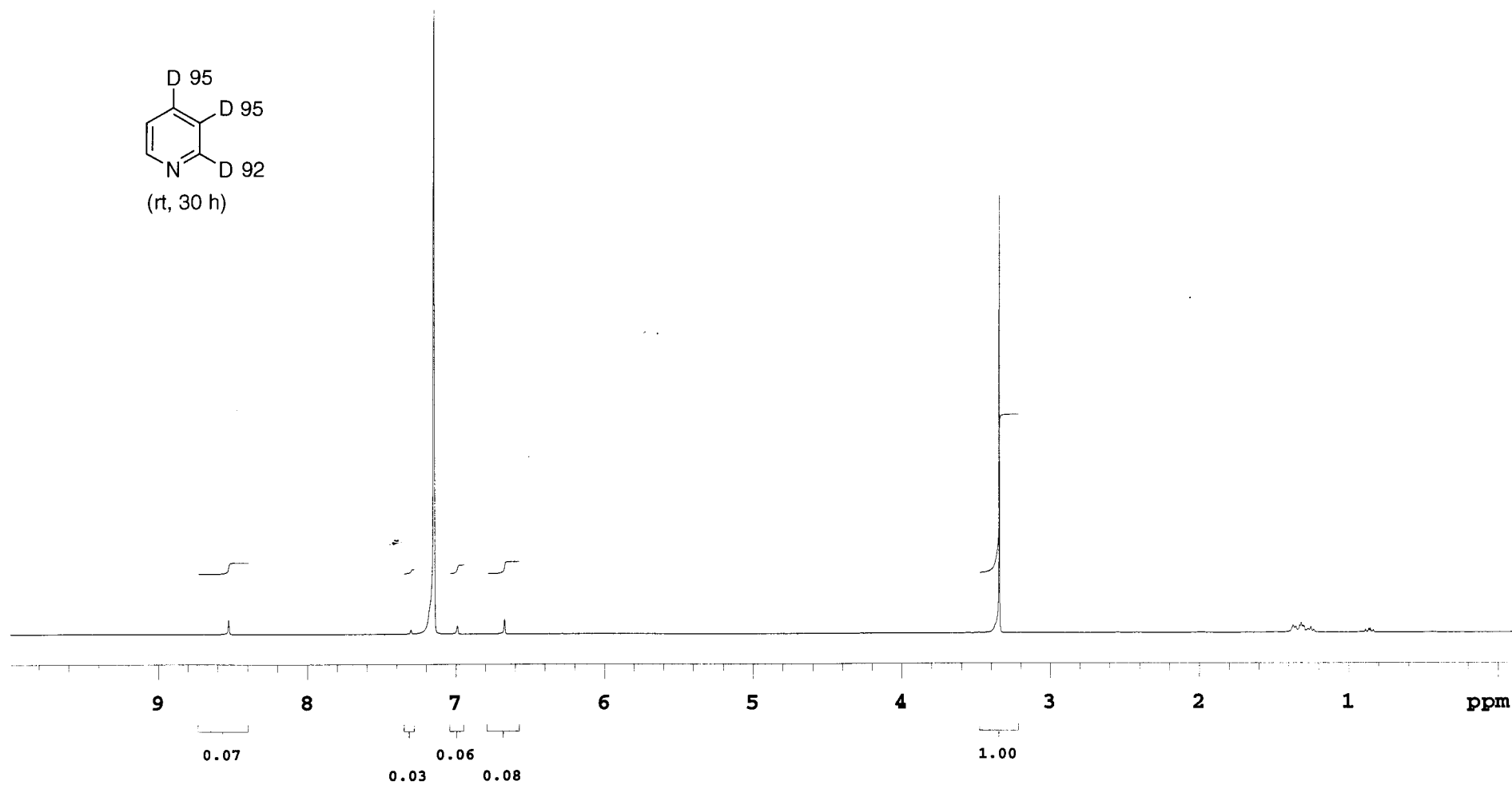
3082sm-c

Pulse Sequence: s2pul



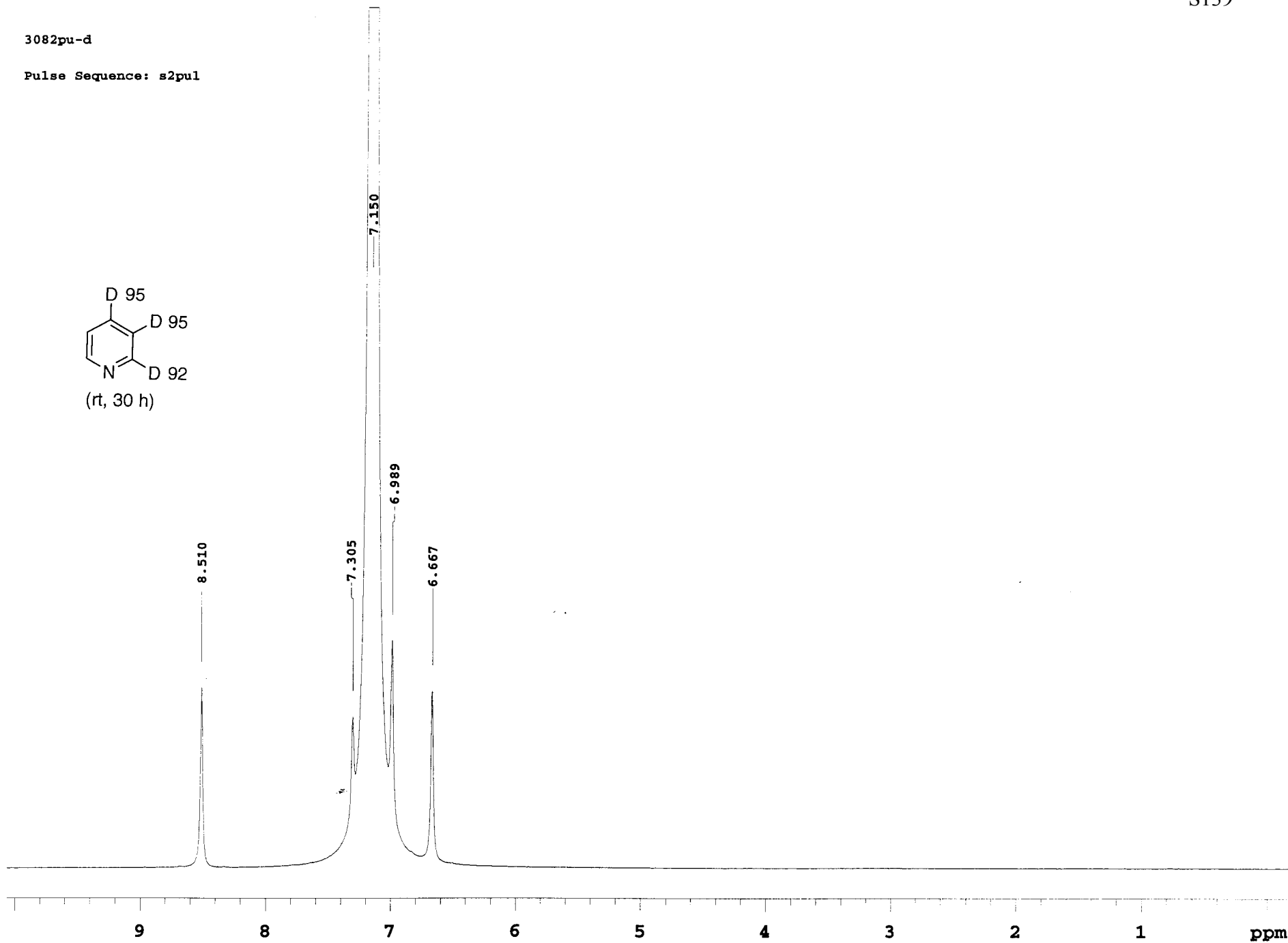
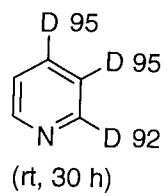
3082-30h

Pulse Sequence: s2pul



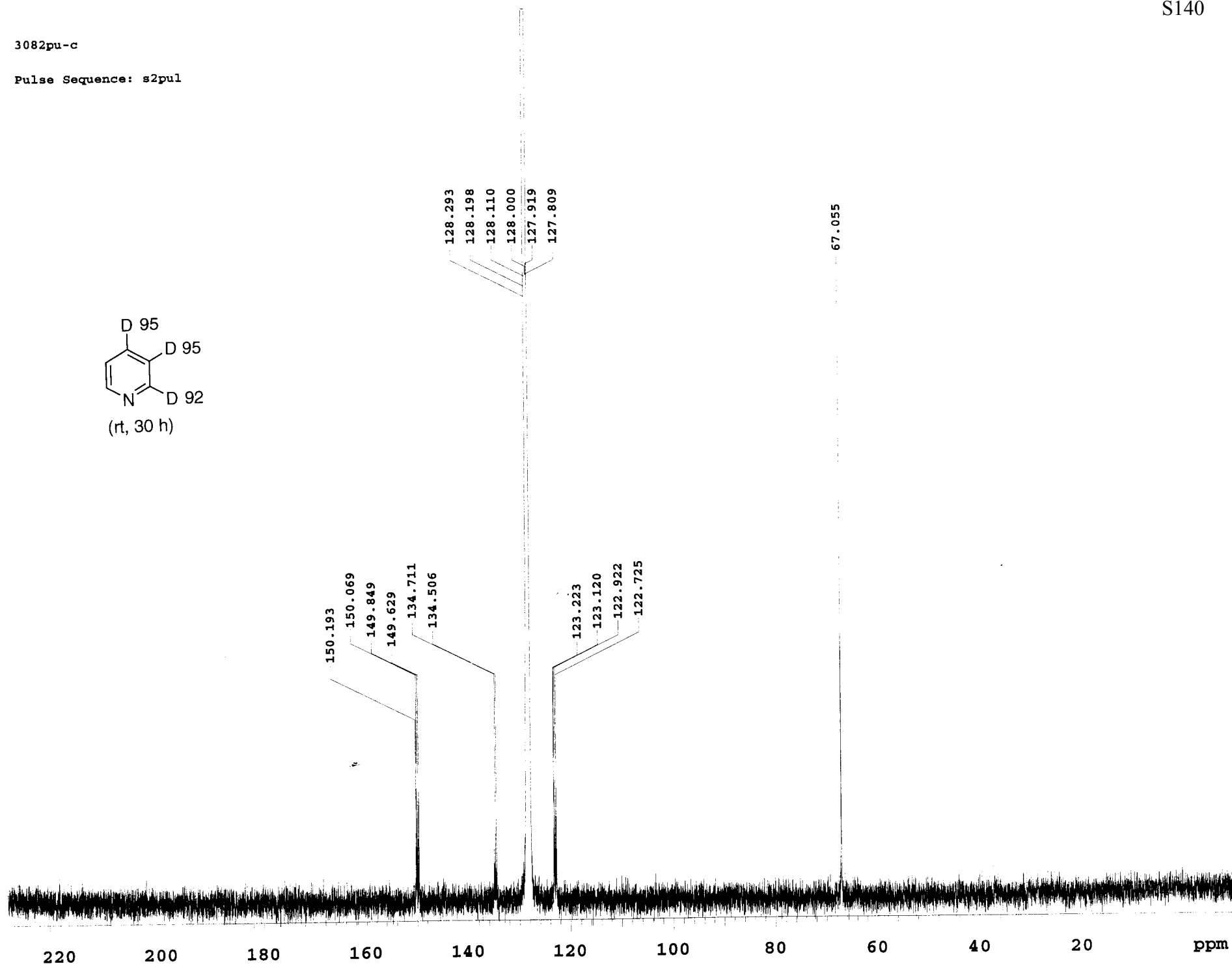
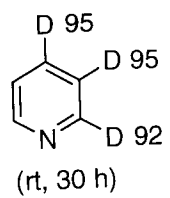
3082pu-d

Pulse Sequence: s2pul



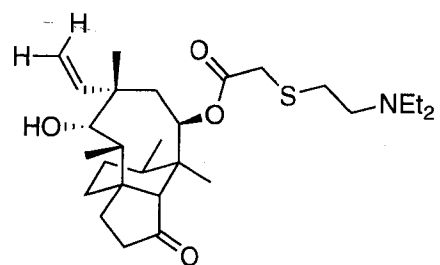
3082pu-c

Pulse Sequence: s2pul

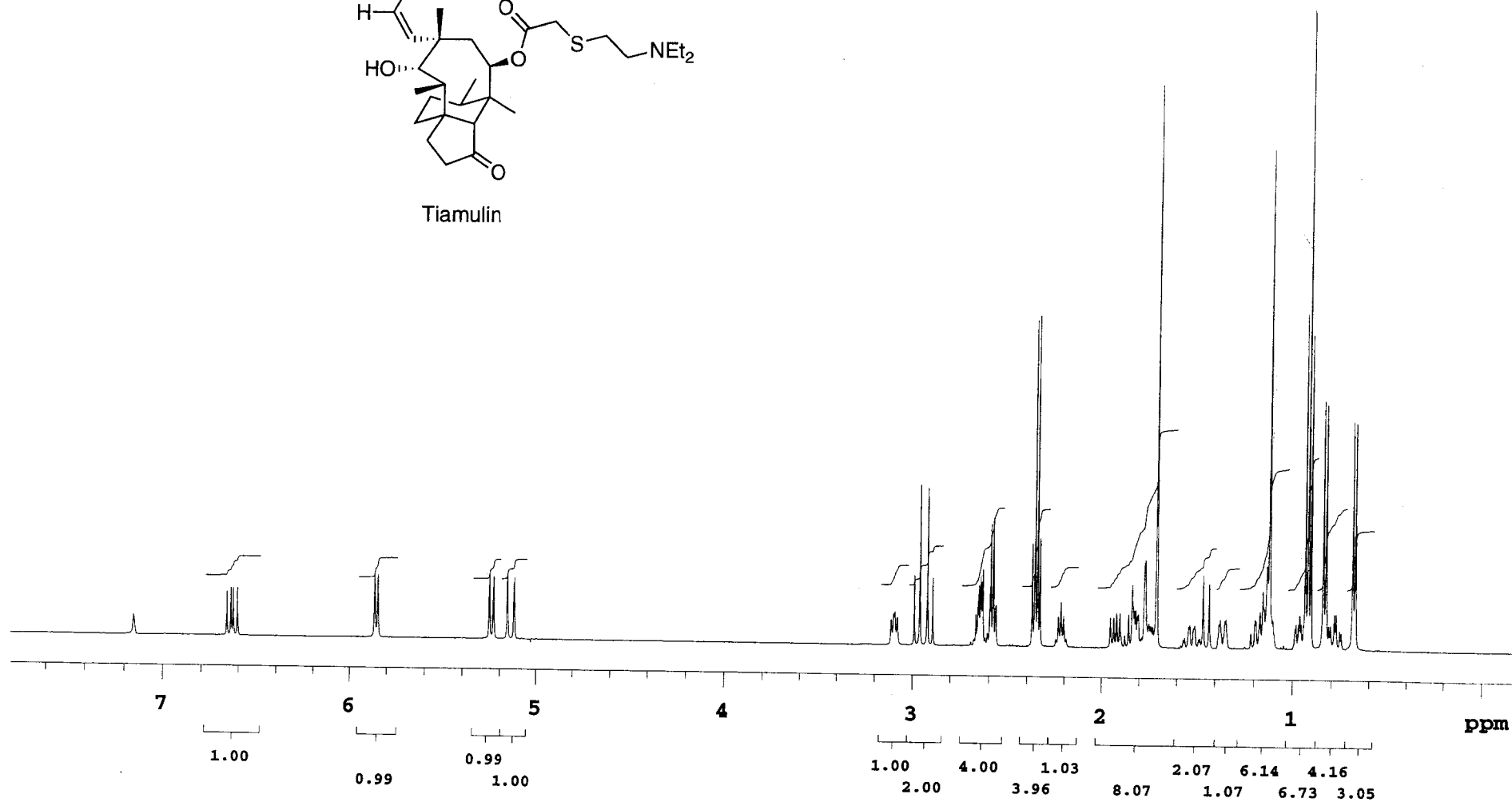


3069sm-h

Pulse Sequence: s2pul

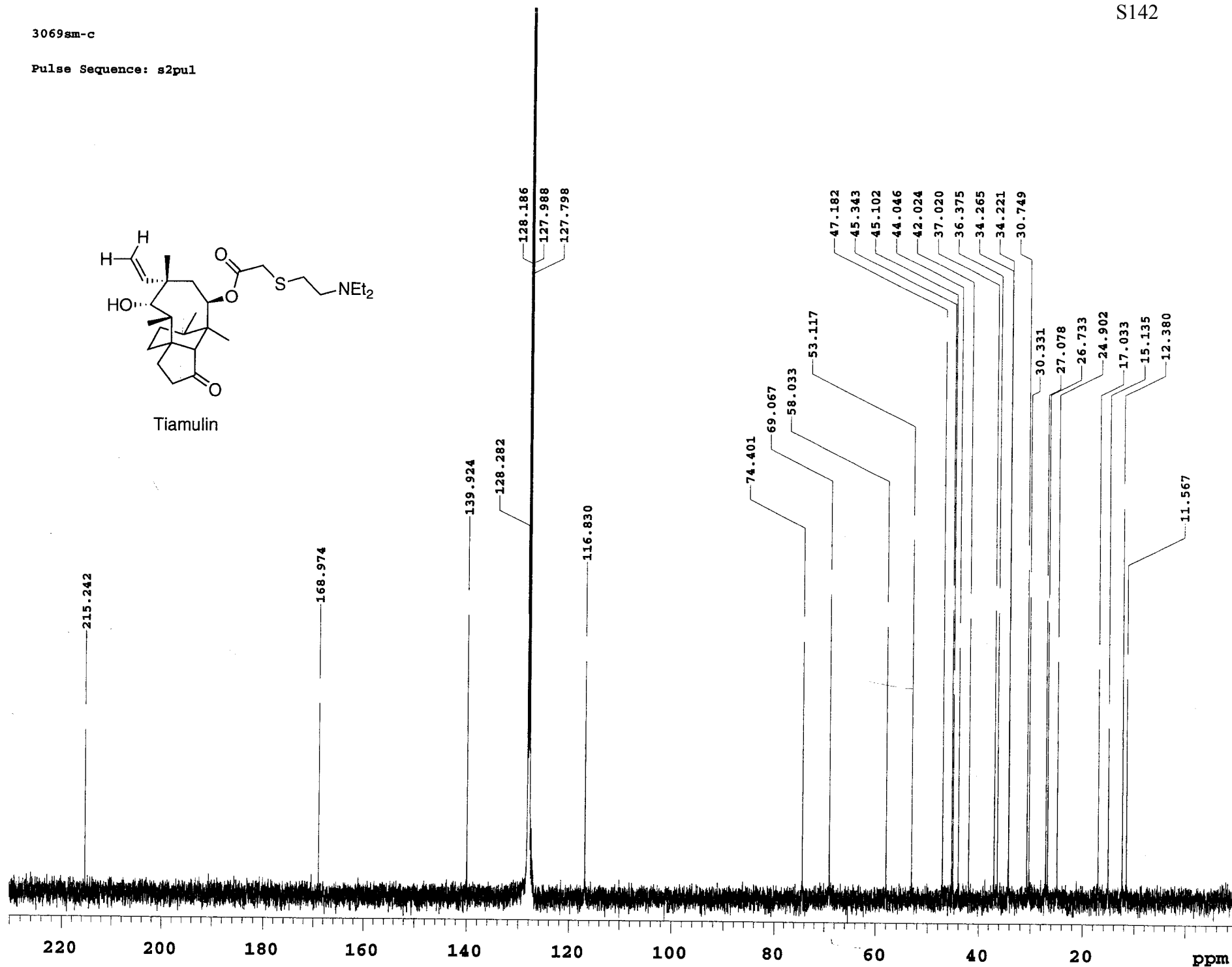
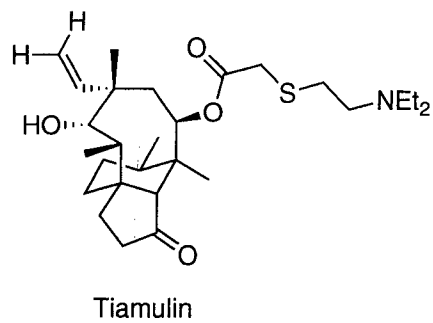


Tiamulin



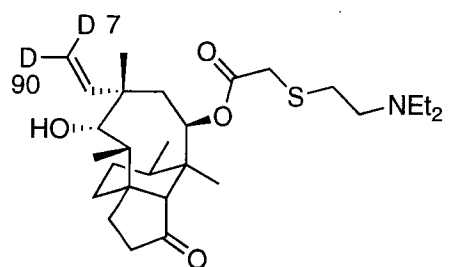
3069sm-c

Pulse Sequence: s2pul1

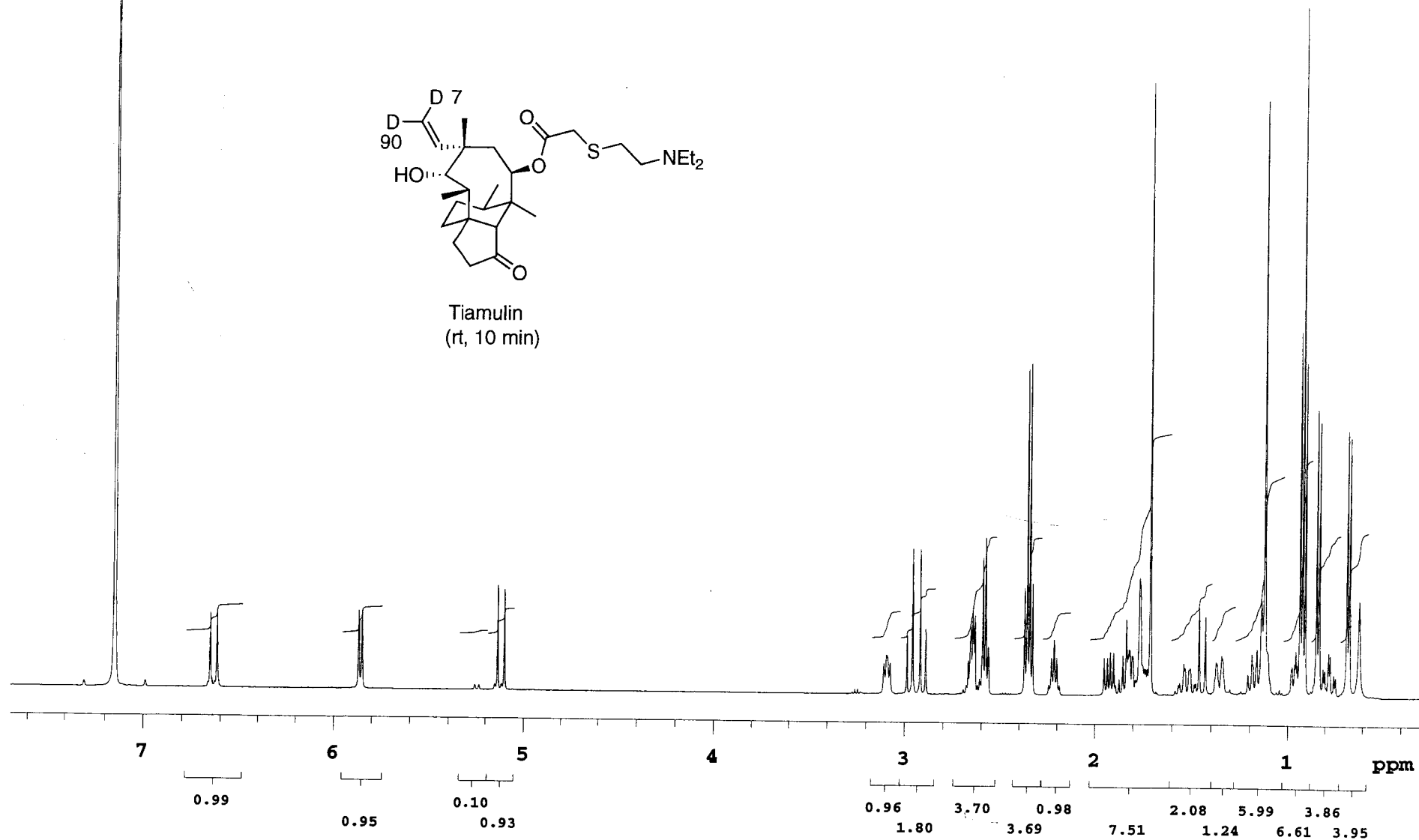


3069pu-h

Pulse Sequence: s2pul

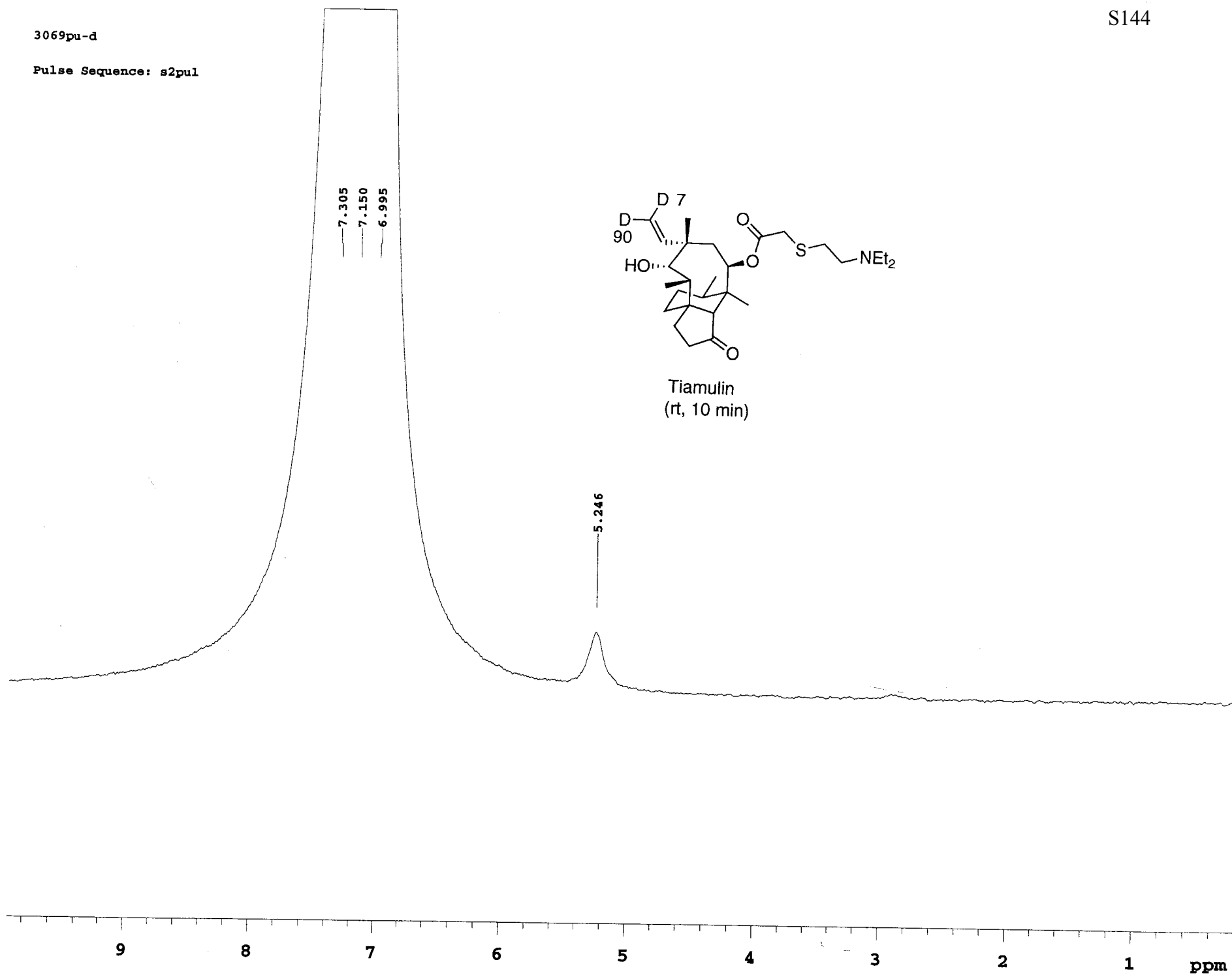


Tiamulin
(rt, 10 min)



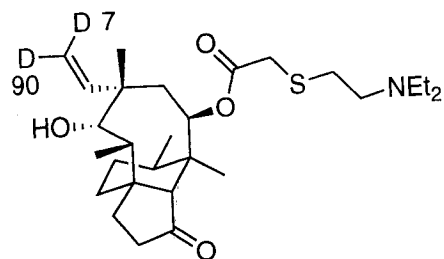
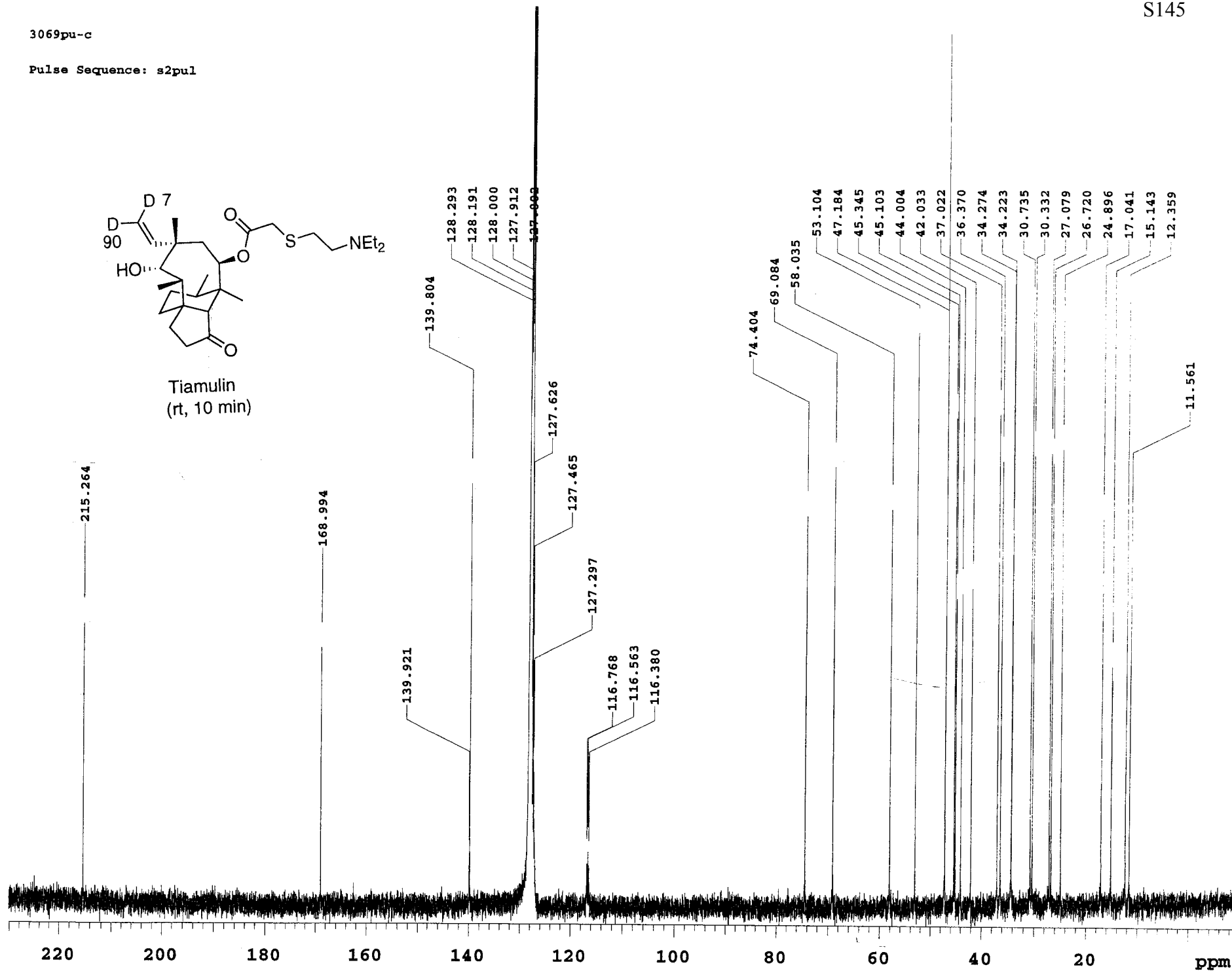
3069pu-d

Pulse Sequence: s2pu1



3069pu-c

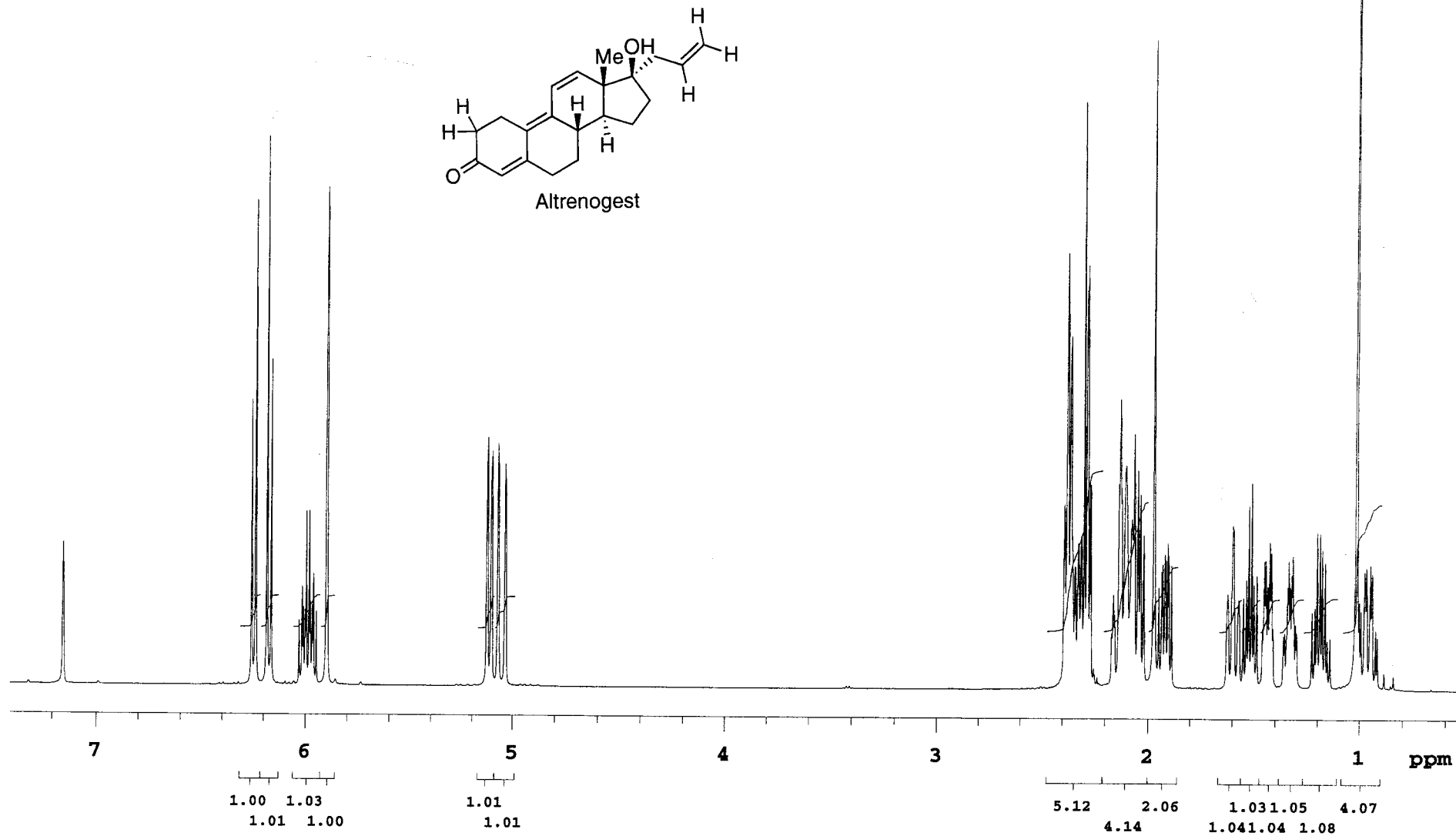
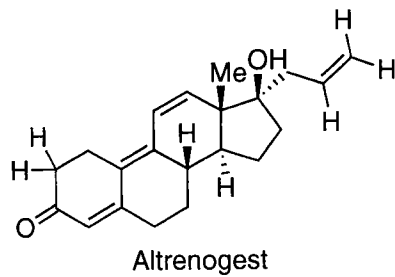
Pulse Sequence: s2pul

Tiamulin
(rt, 10 min)

3070sm-h

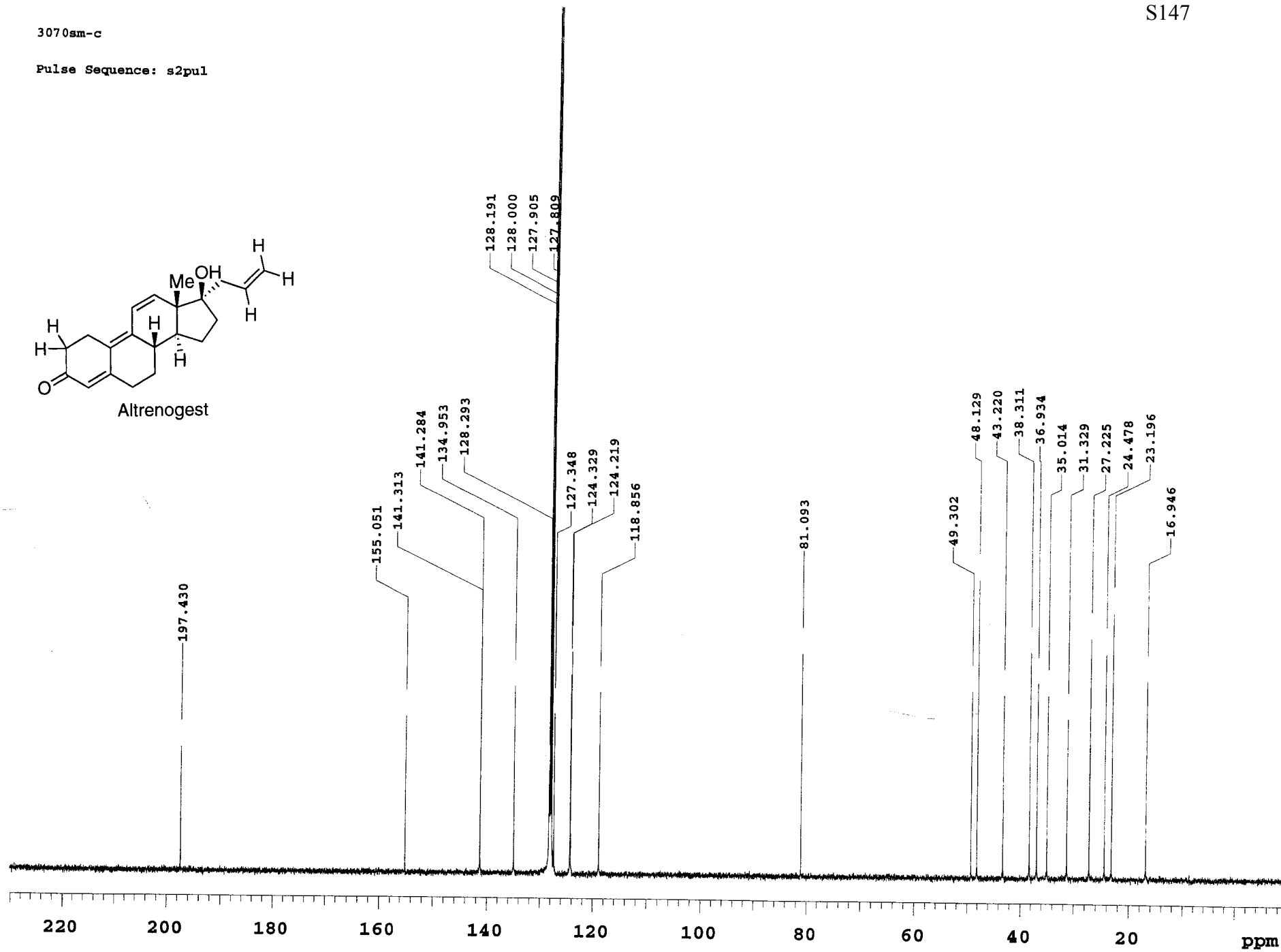
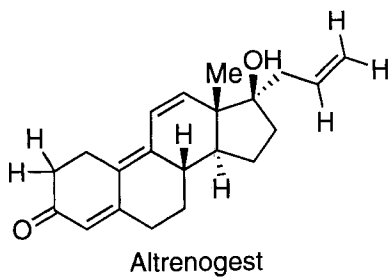
Pulse Sequence: s2pul

S146



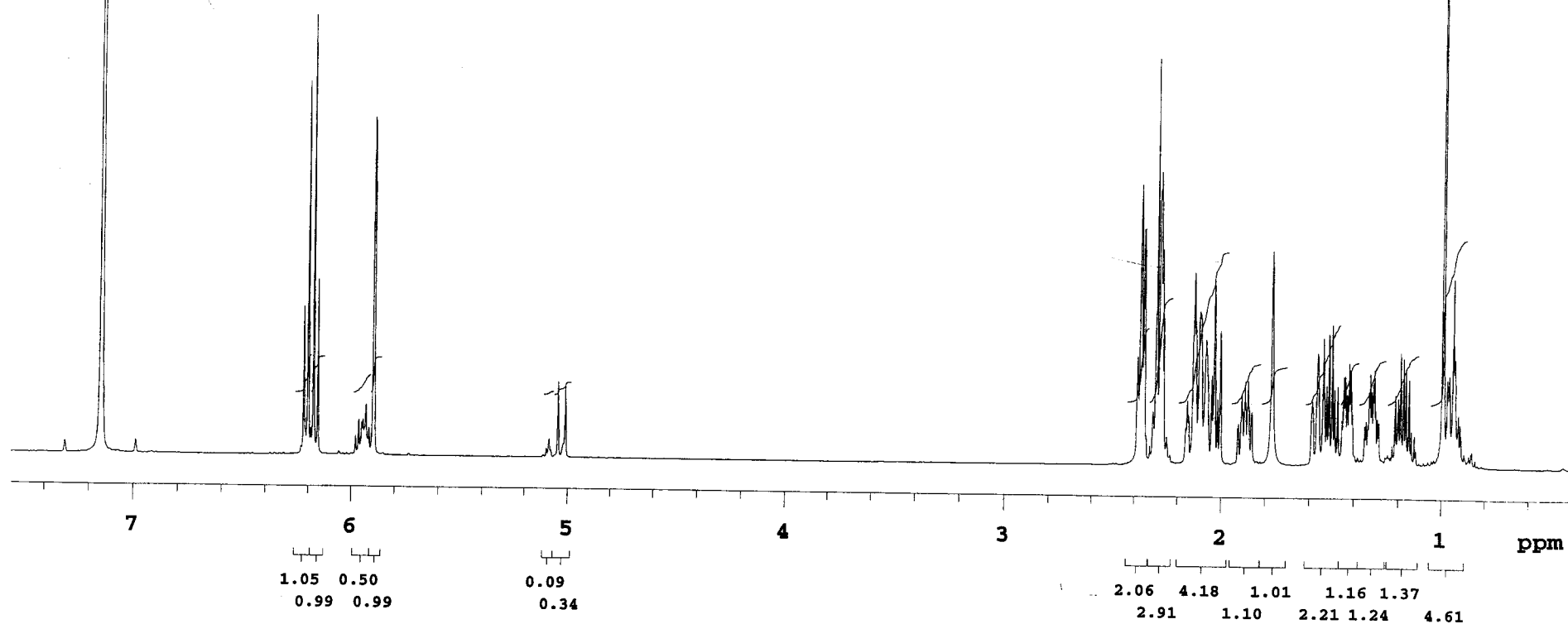
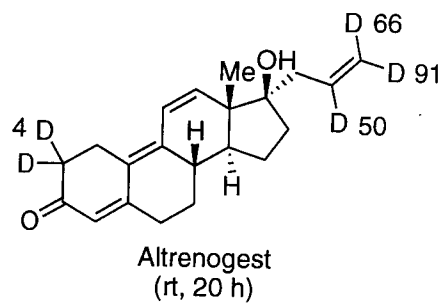
3070sm-c

Pulse Sequence: s2pul



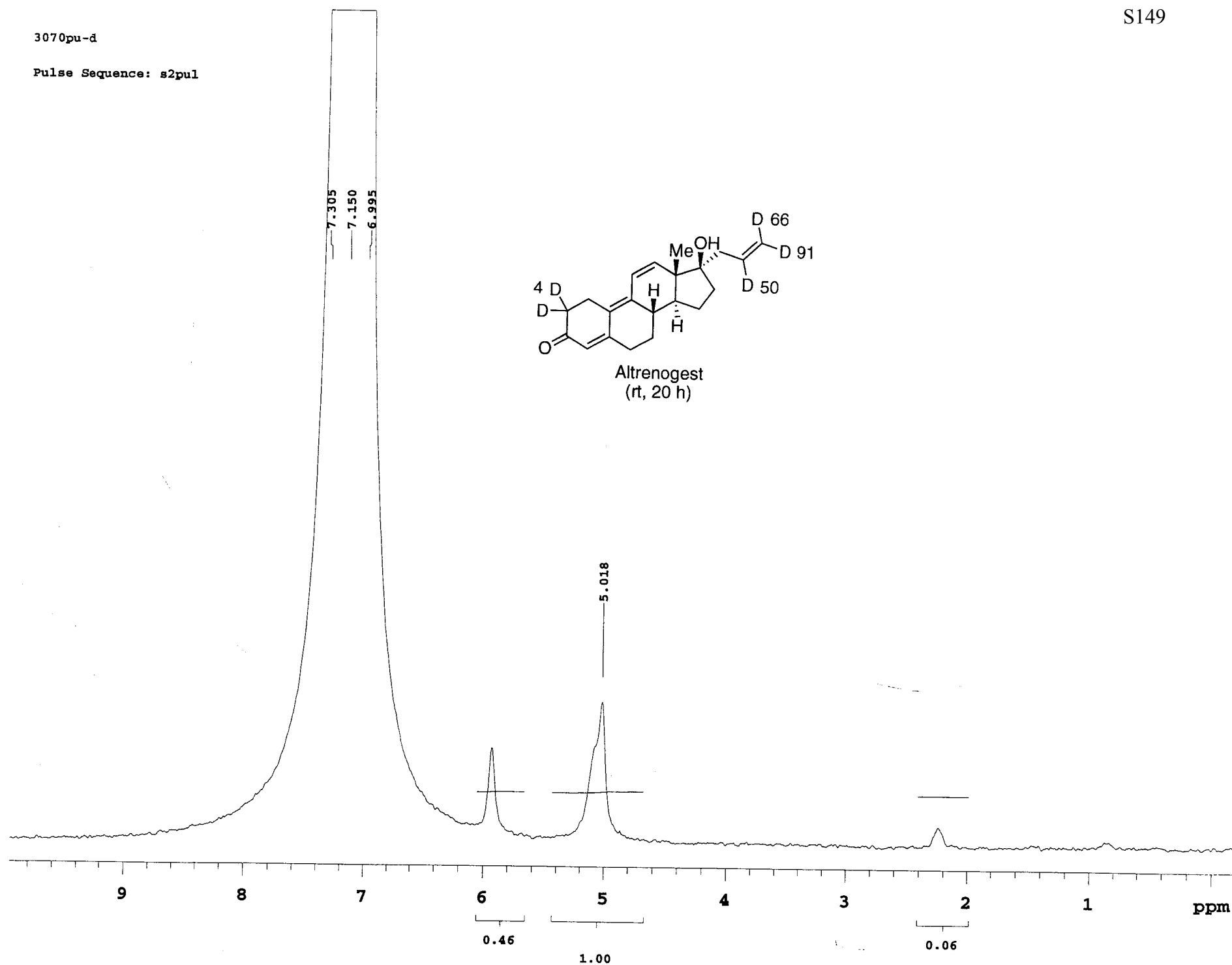
3070pu-h

Pulse Sequence: s2pul



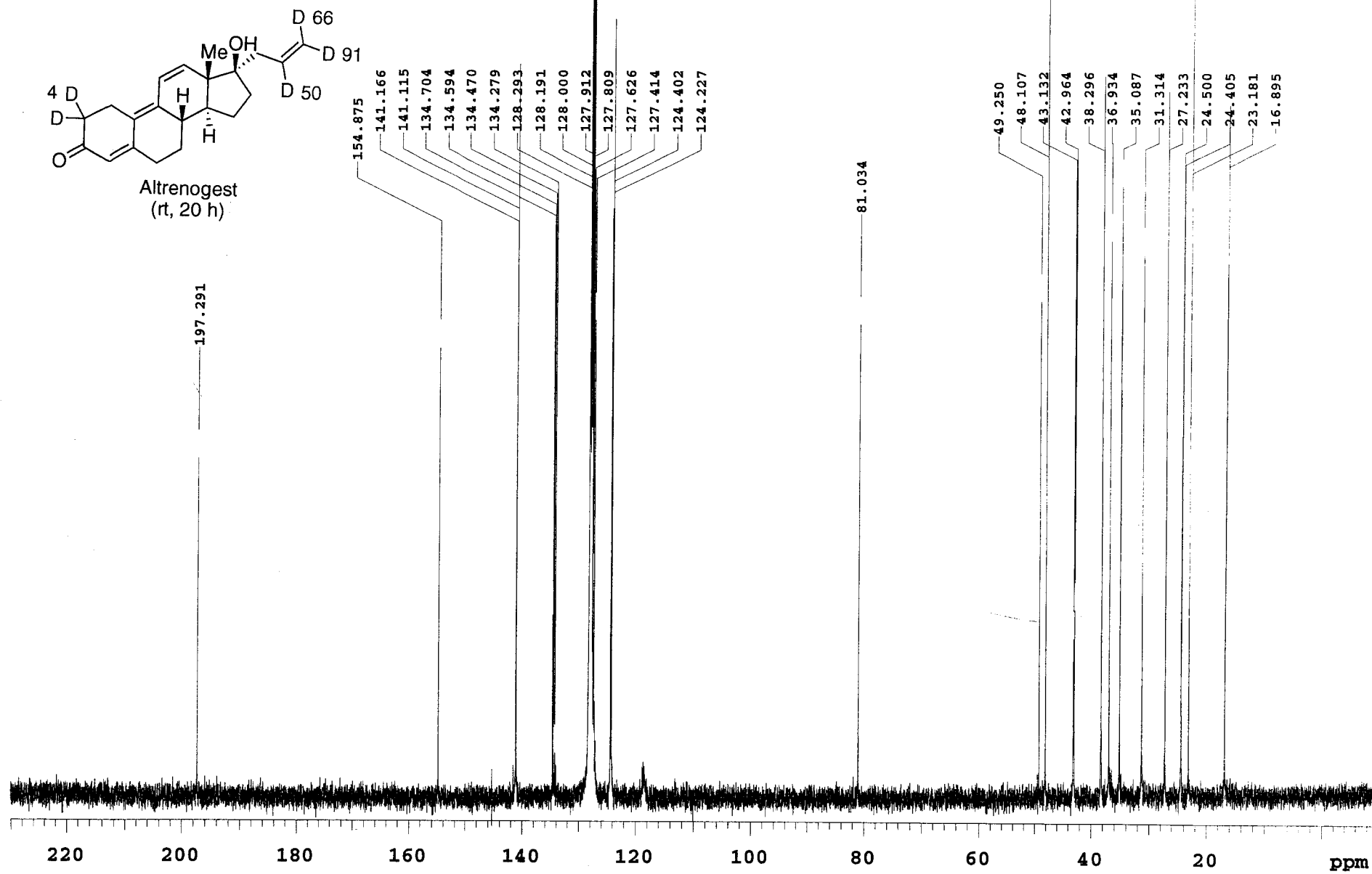
3070pu-d

Pulse Sequence: s2pul



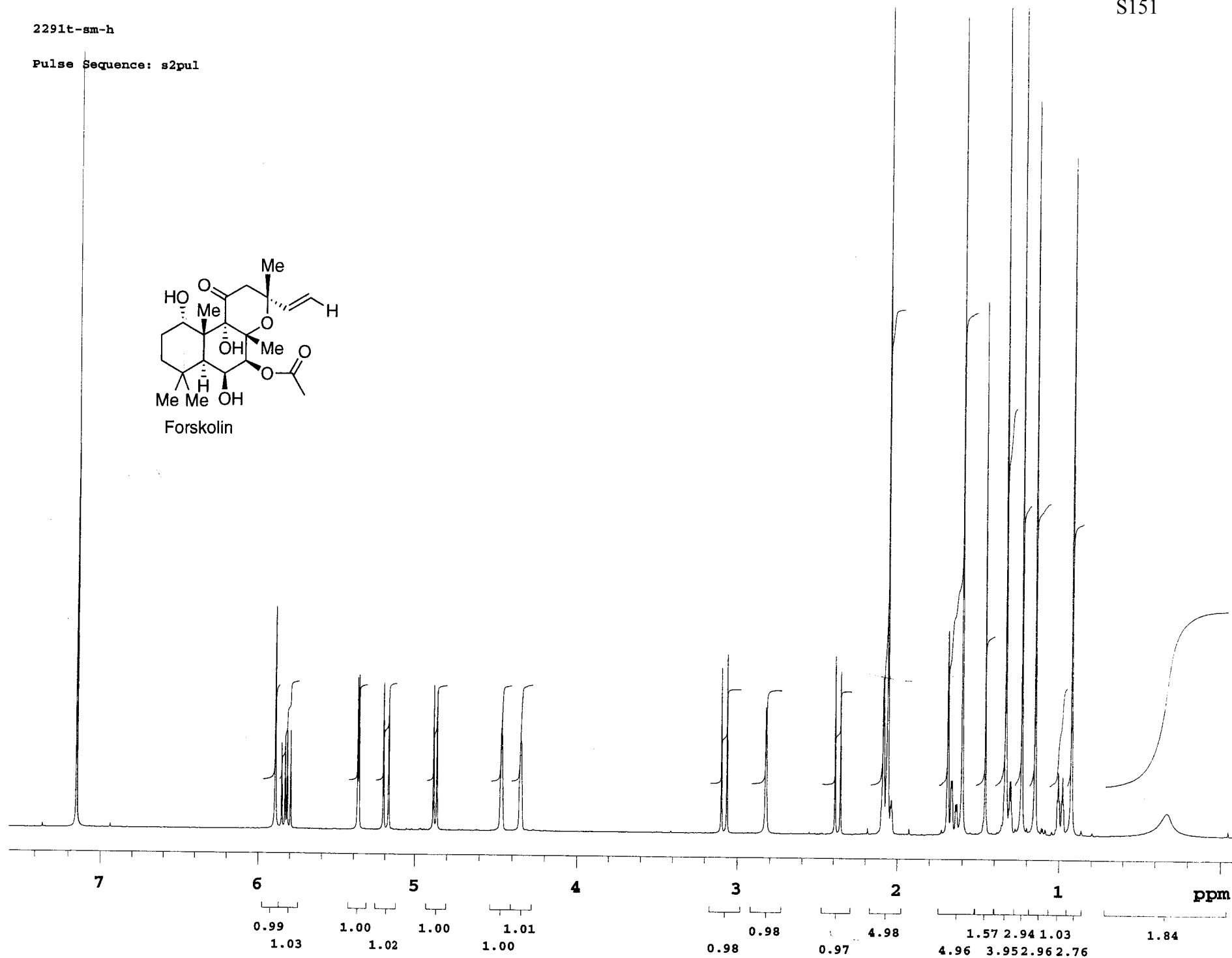
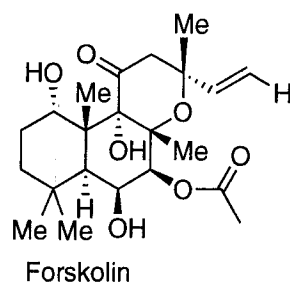
3070pu-c

Pulse Sequence: s2pul



2291t-sm-h

Pulse Sequence: s2pul



2291r-sm-CDCl3-c 20 1 /opt/topspin-1.3 jzhou

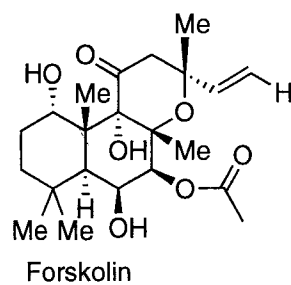
C6D6
aq 2s
dl 20s

-205.3144

-169.6341

-146.2421

-110.7263

82.6222
81.4127
77.2518
76.9974
76.7433
76.4838
74.8846
74.4155
69.939748.6911
42.9668
42.7813
36.0532
34.4236
32.0536
31.3463
26.3111
24.3588
23.1483
19.8287

200

150

100

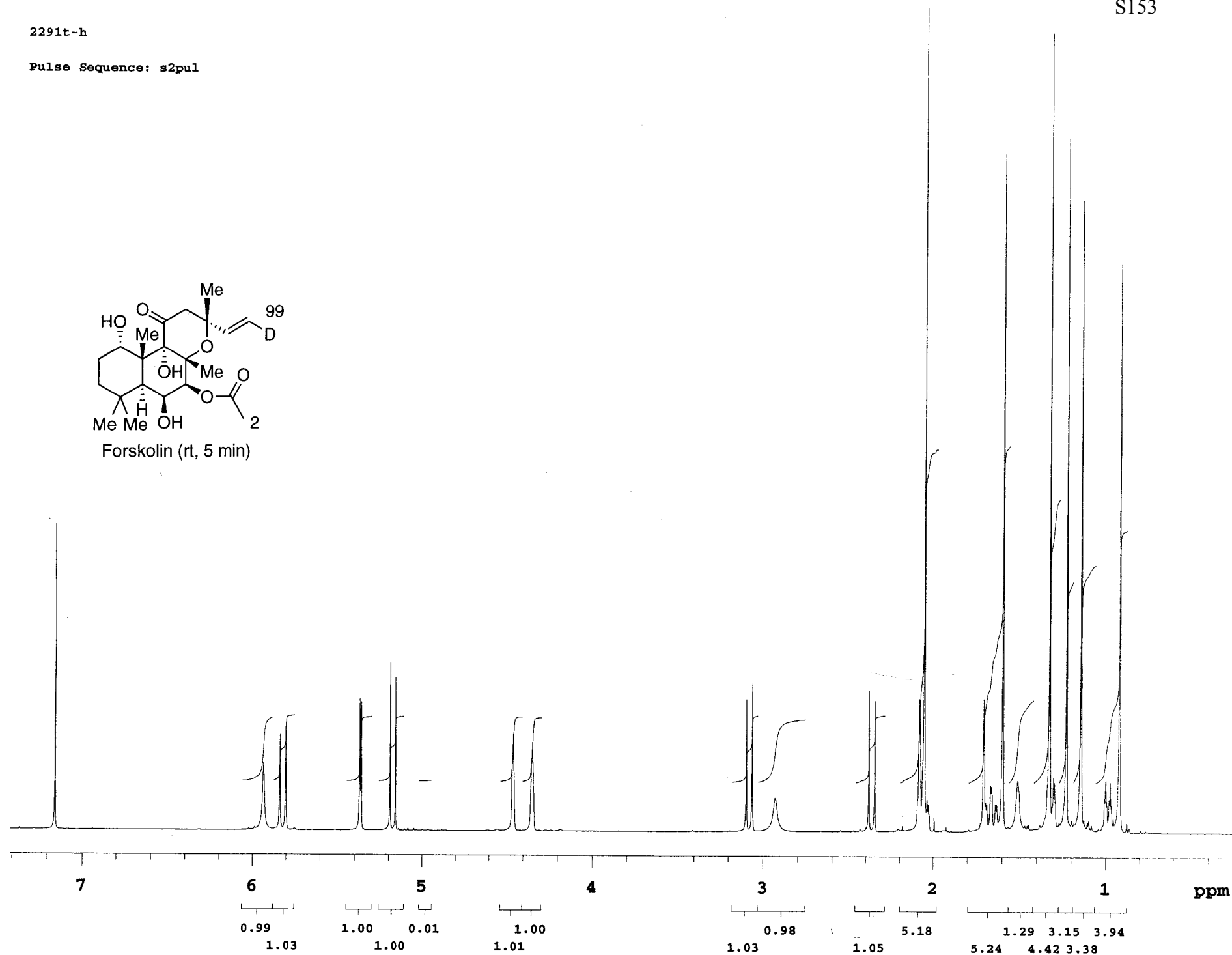
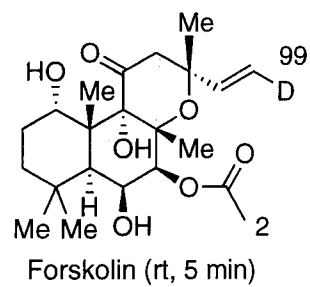
50

0

[ppm]

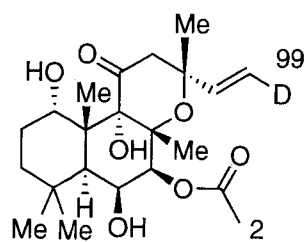
2291t-h

Pulse Sequence: s2pul

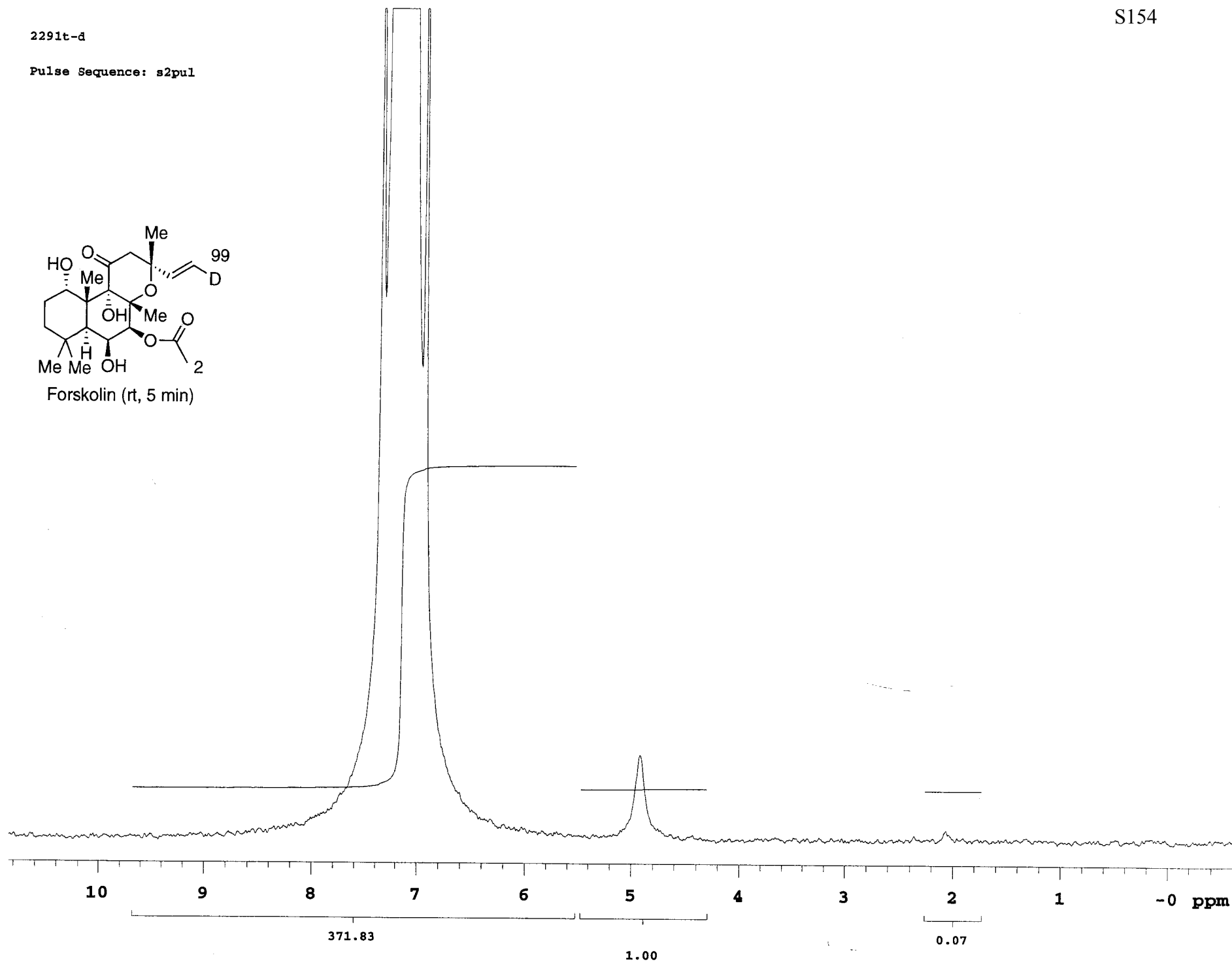


2291t-d

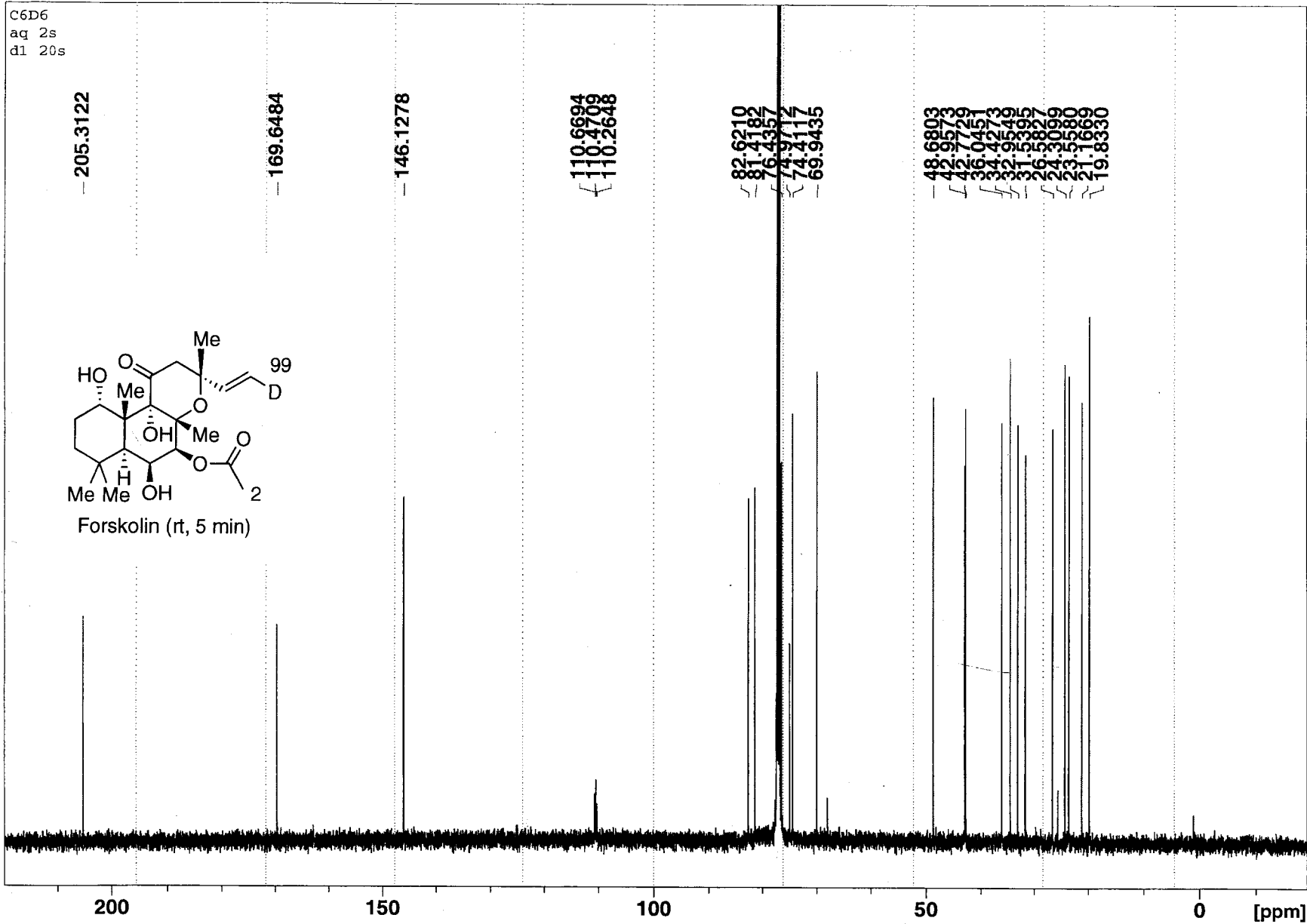
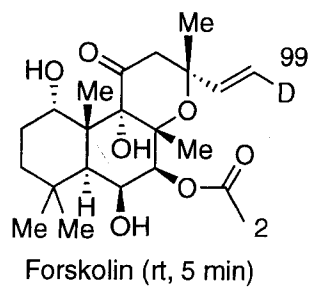
Pulse Sequence: s2pul



Forskolin (rt, 5 min)

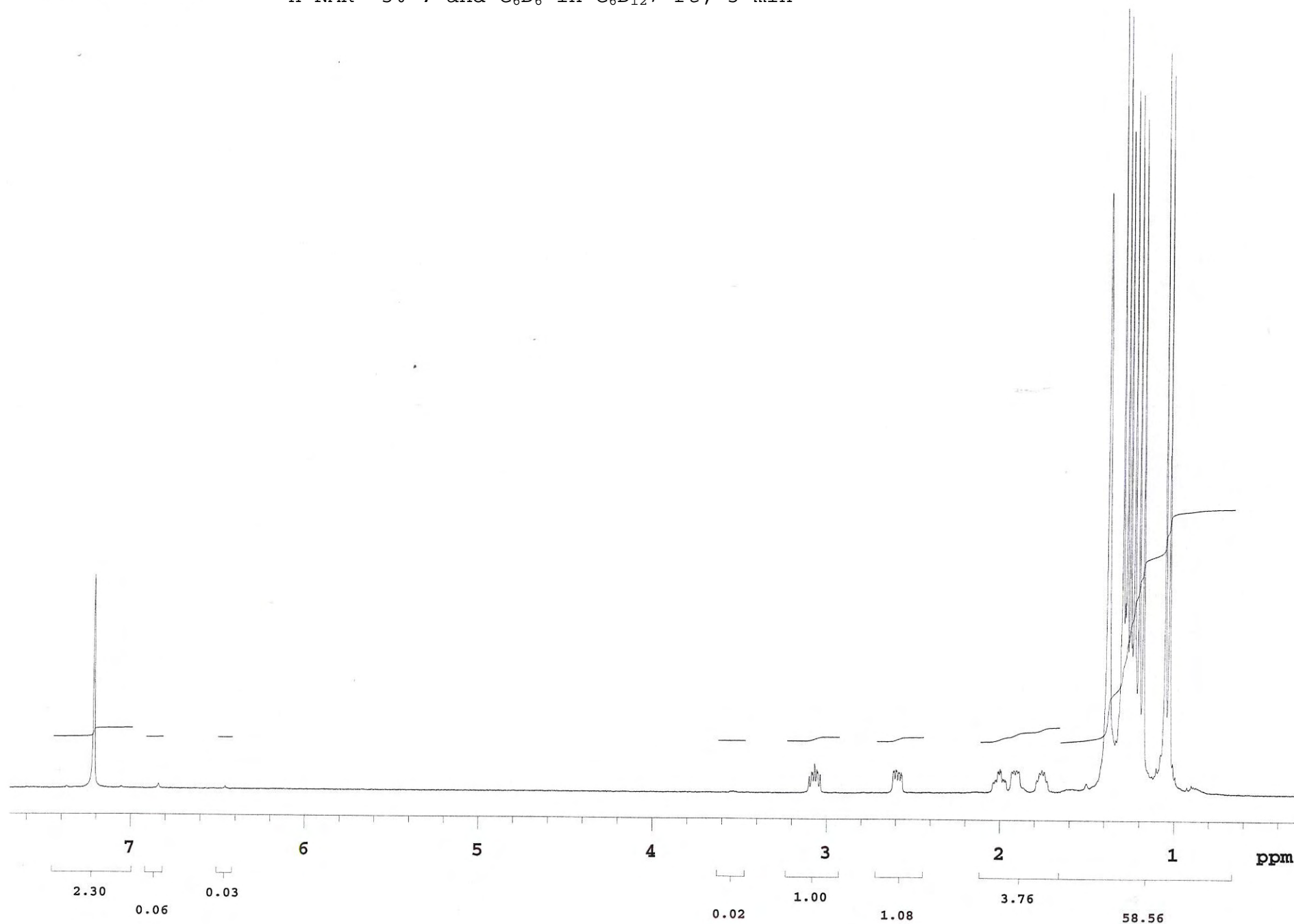


2291r-CDCl3-c 20 1 /opt/topspin-1.3 jzhou

C6D6
aq 2s
d1 20s

5131-5min-c6d6-c6d12

Pulse Sequence: s2pul

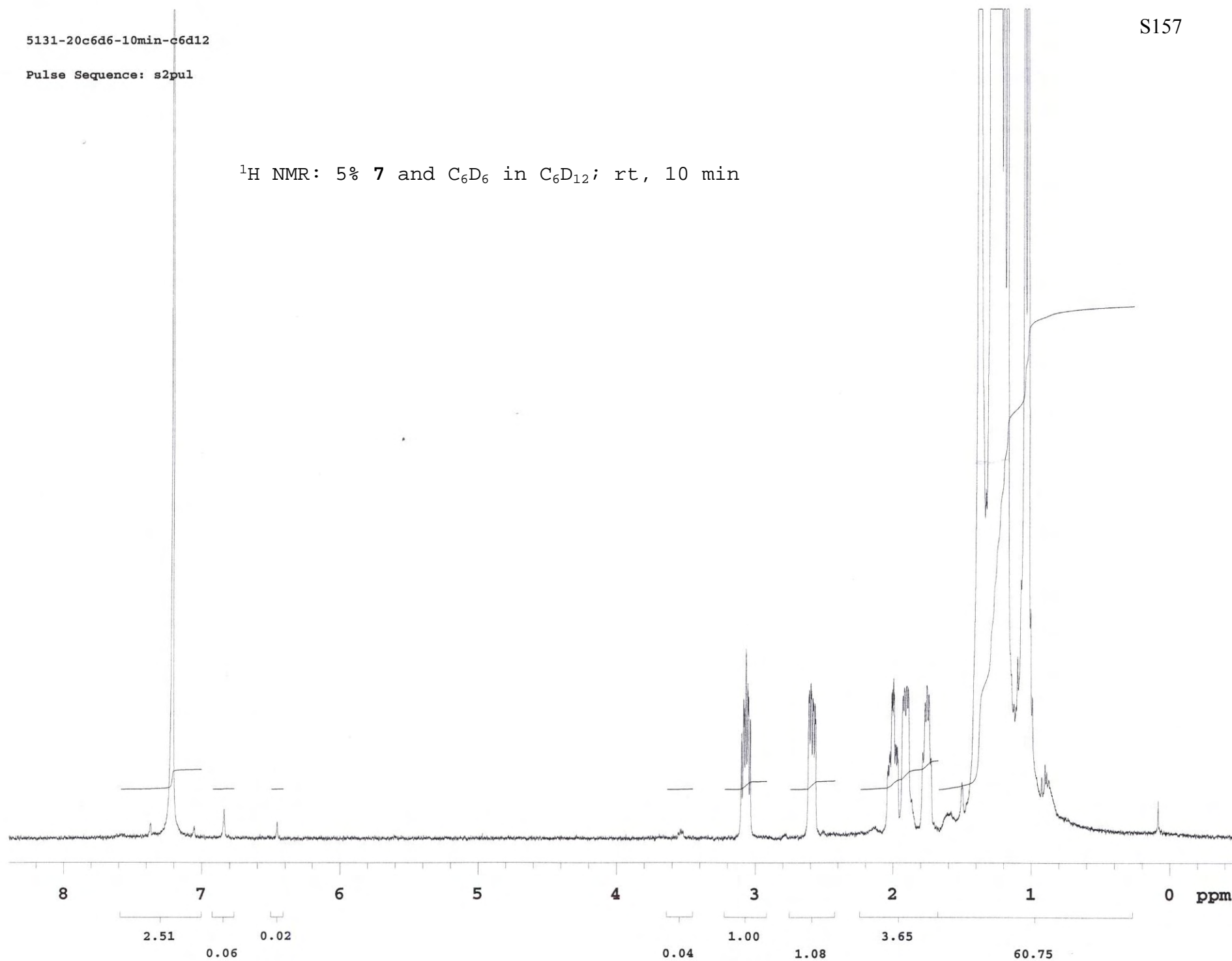
 ^1H NMR: 5% **7** and C_6D_6 in C_6D_{12} ; rt, 5 min

5131-20c6d6-10min-c6d12

Pulse Sequence: s2pul

S157

^1H NMR: 5% **7** and C_6D_6 in C_6D_{12} ; rt, 10 min

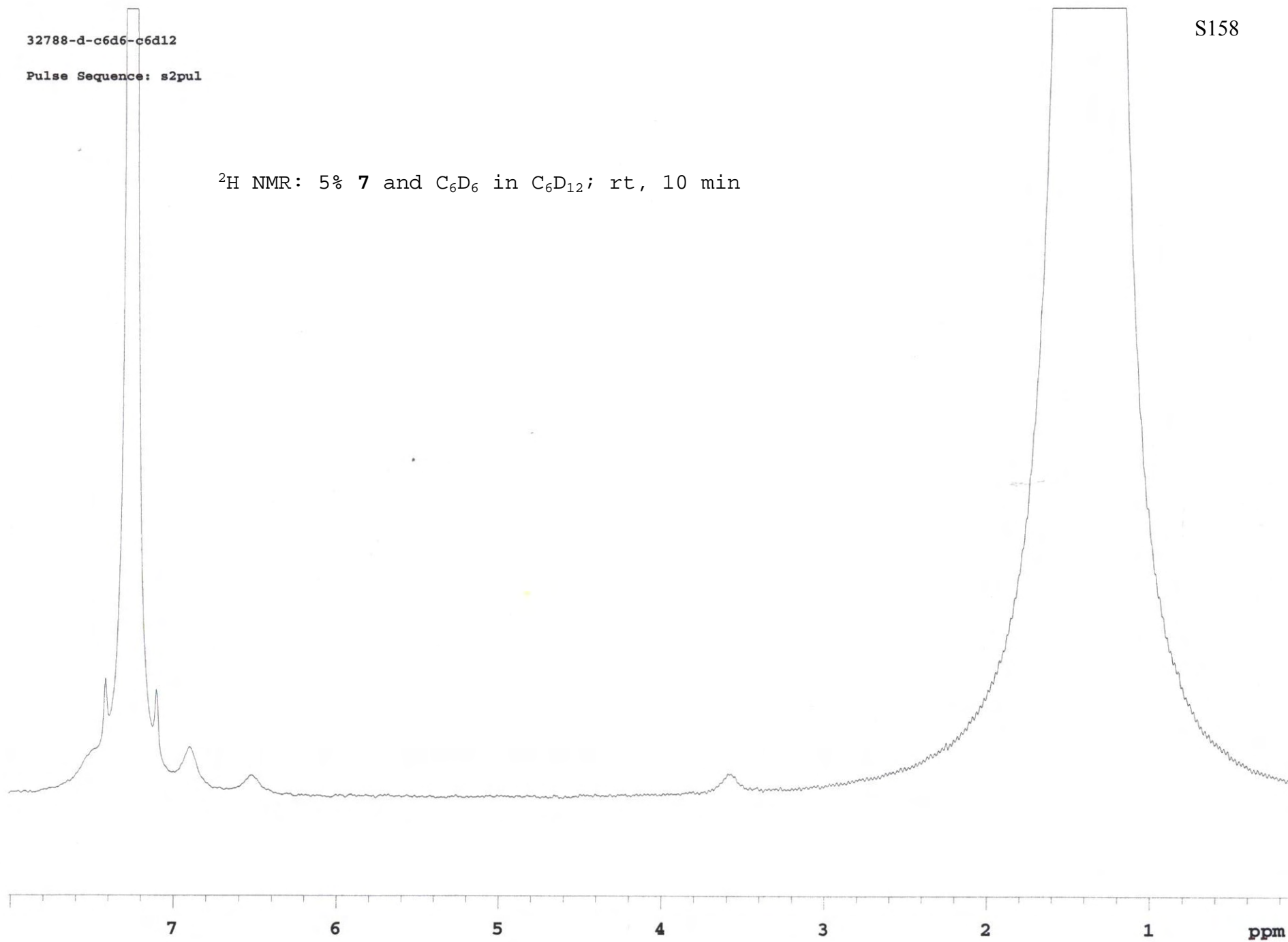


32788-d-c6d6-c6d12

Pulse Sequence: s2pul

S158

^2H NMR: 5% **7** and C_6D_6 in C_6D_{12} ; rt, 10 min

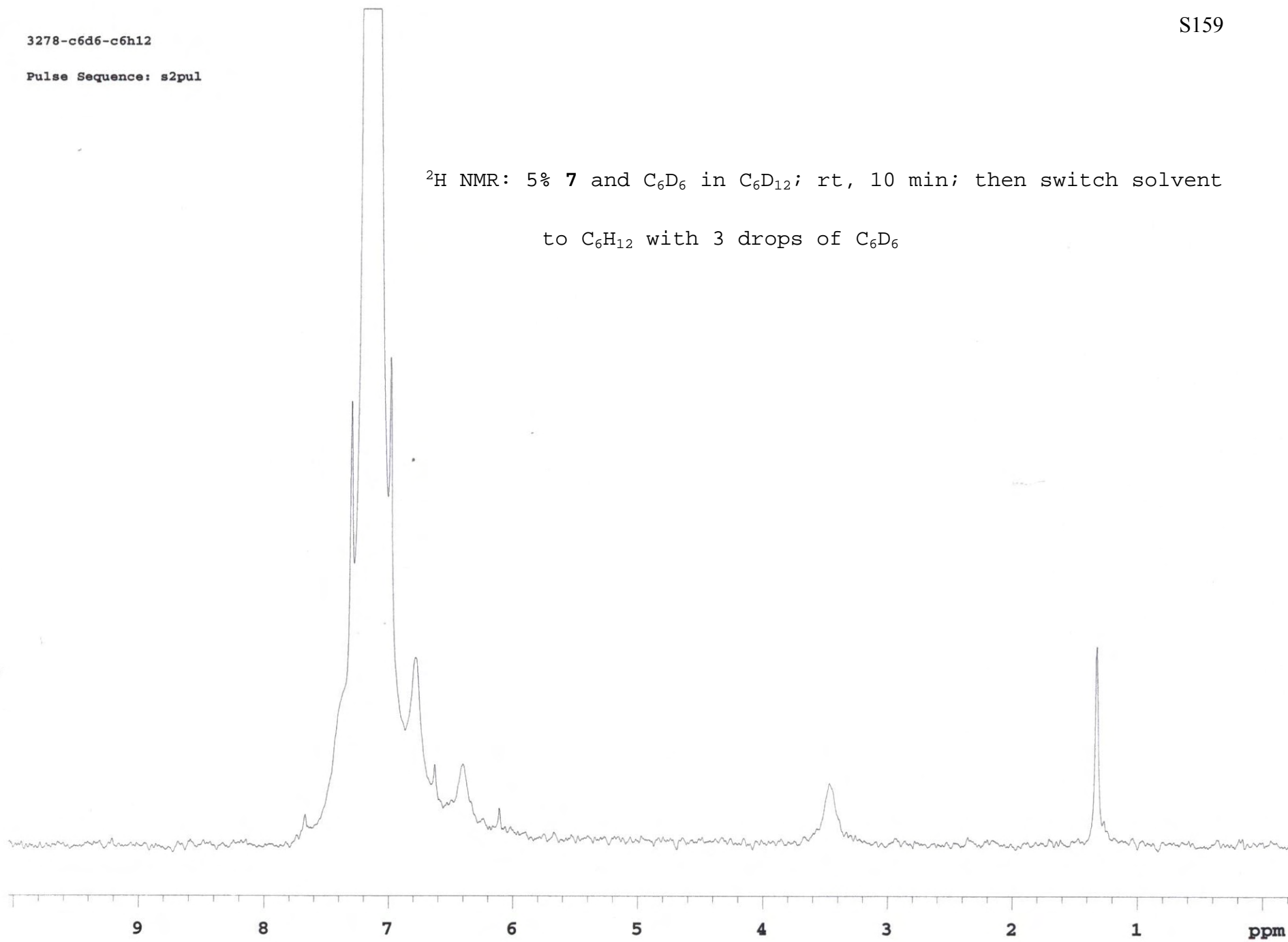


3278-c6d6-c6h12

S159

Pulse Sequence: s2pul

^2H NMR: 5% **7** and C_6D_6 in C_6D_{12} ; rt, 10 min; then switch solvent
to C_6H_{12} with 3 drops of C_6D_6

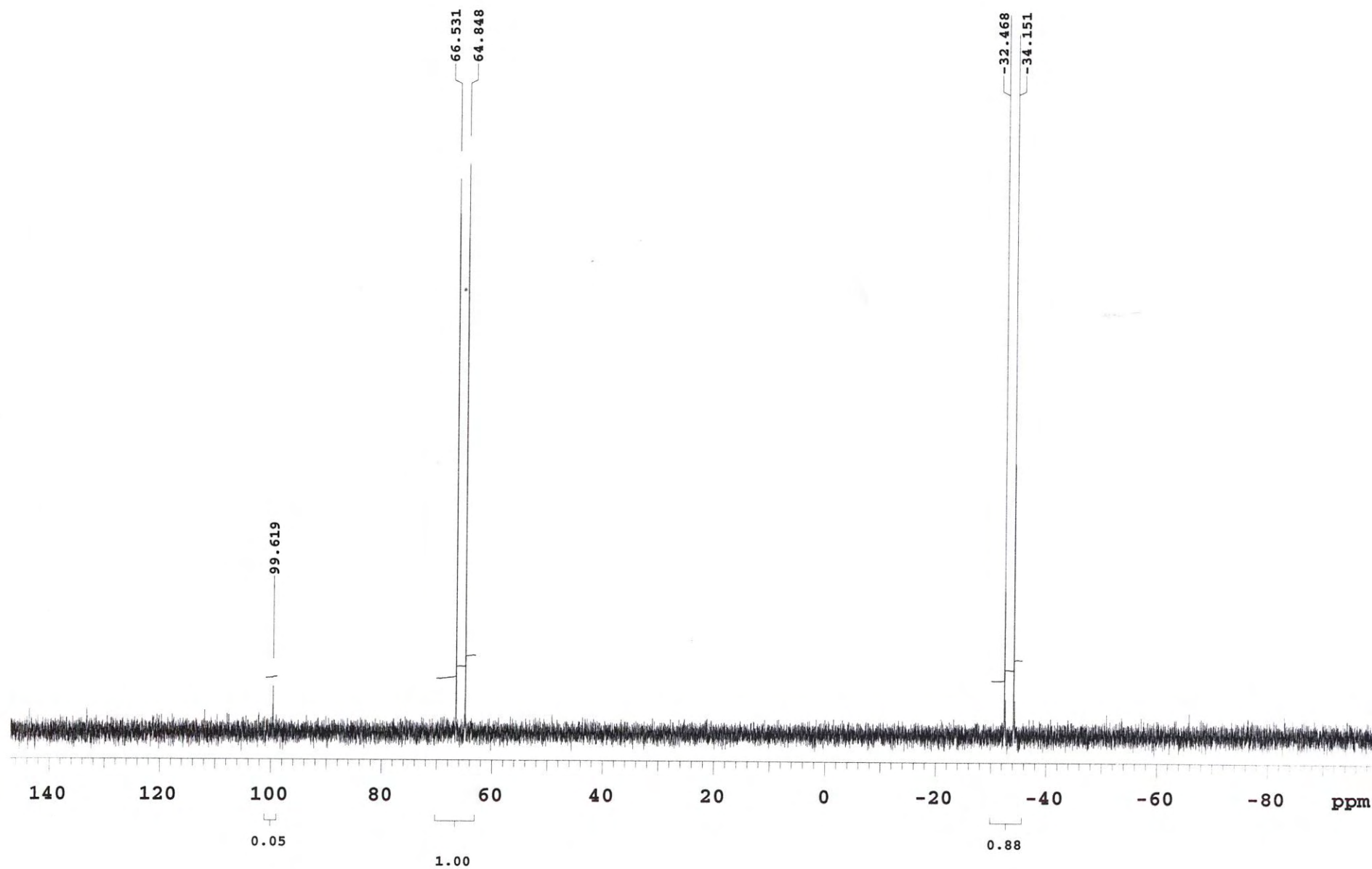


3278-c6d6-30min-c6d12

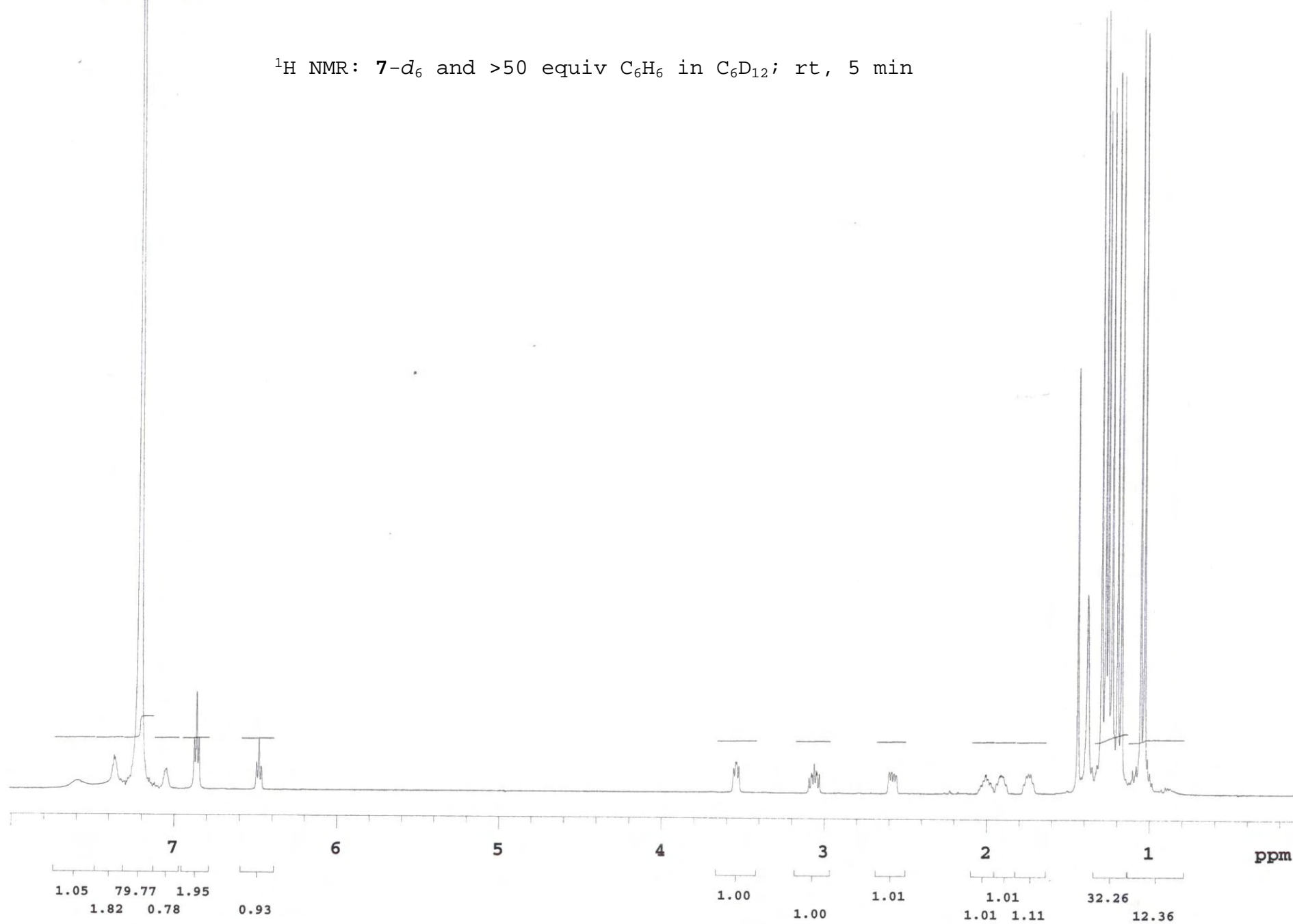
S160

Pulse Sequence: s2pul

^{31}P NMR: 5% **7** and C_6D_6 in C_6D_{12} ; rt, 10 min



Pulse Sequence: s2pul

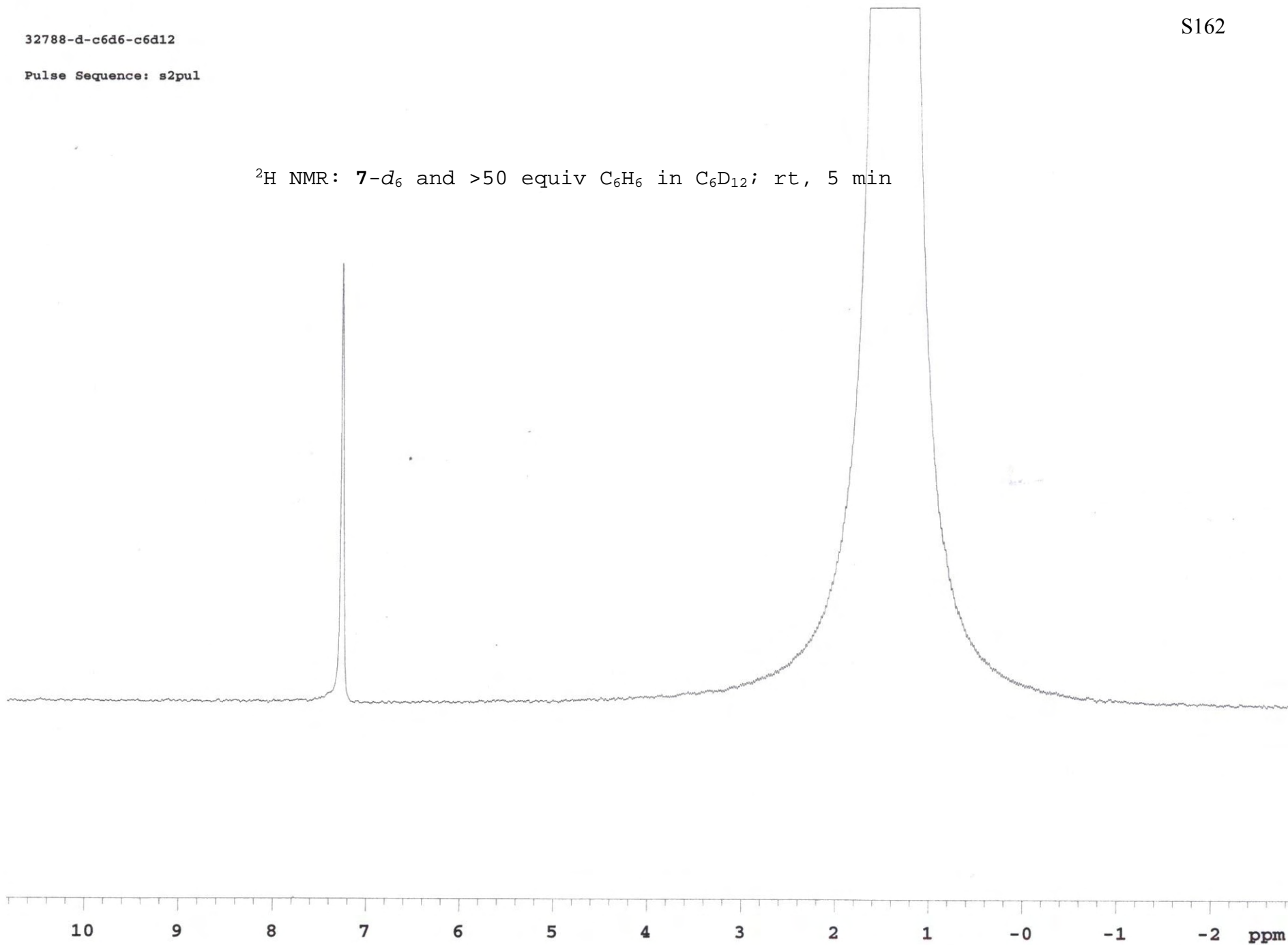
 ^1H NMR: 7- d_6 and >50 equiv C_6H_6 in C_6D_{12} ; rt, 5 min

32788-d-c6d6-c6d12

S162

Pulse Sequence: s2pul

^2H NMR: $7\text{-}d_6$ and >50 equiv C_6H_6 in C_6D_{12} ; rt, 5 min

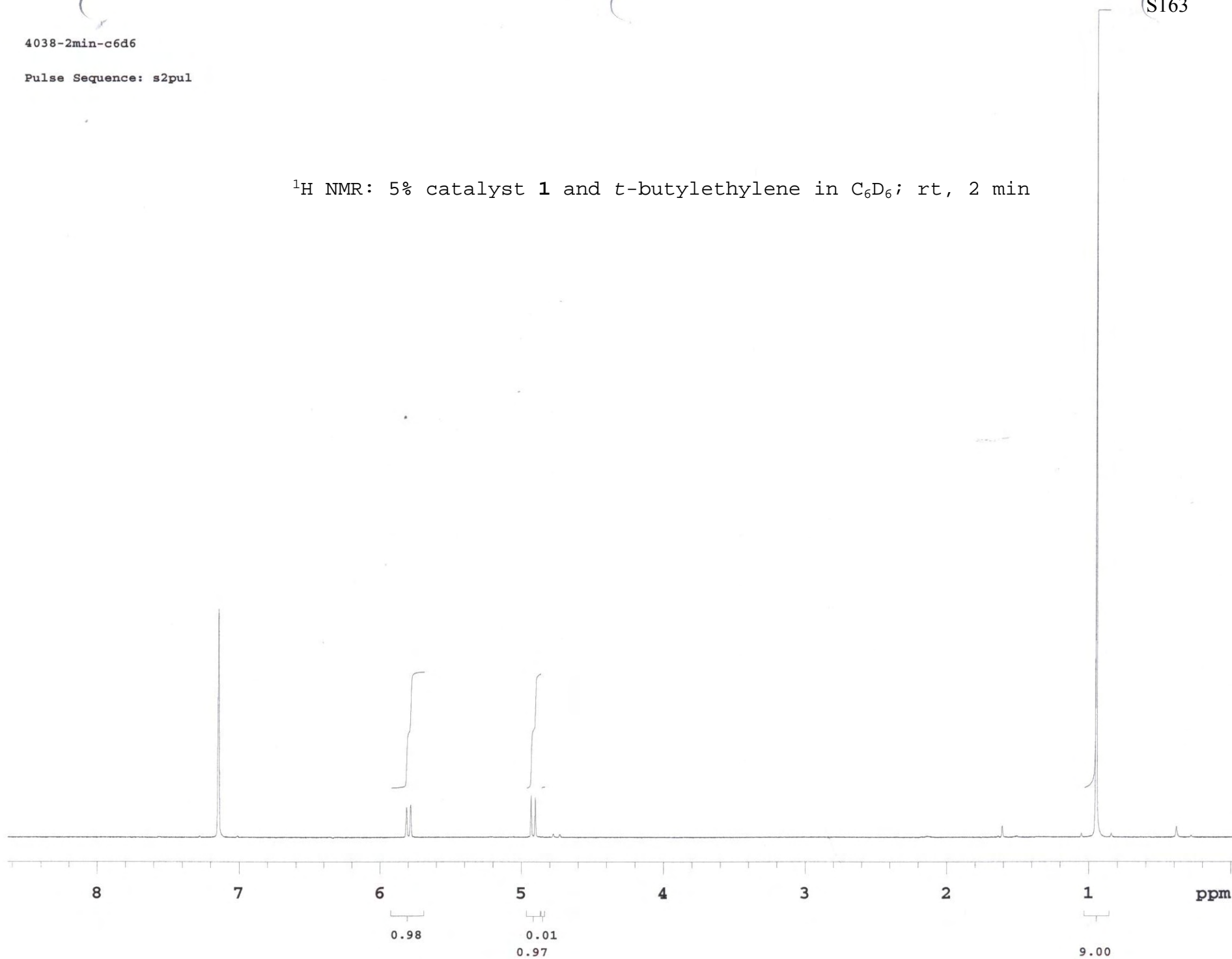


4038-2min-c6d6

Pulse Sequence: s2pul

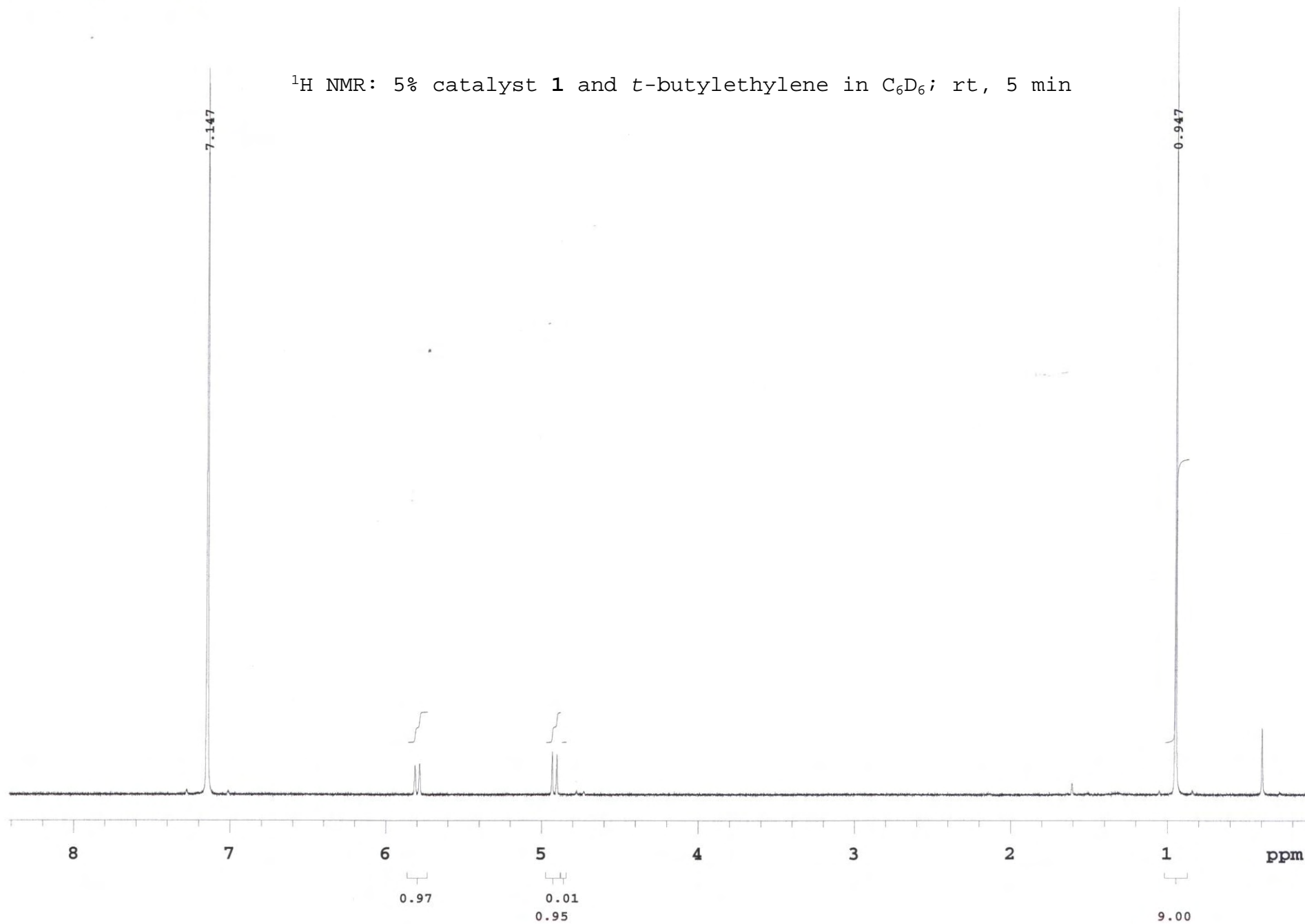
S163

^1H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 2 min



4038-

Pulse Sequence: s2pul

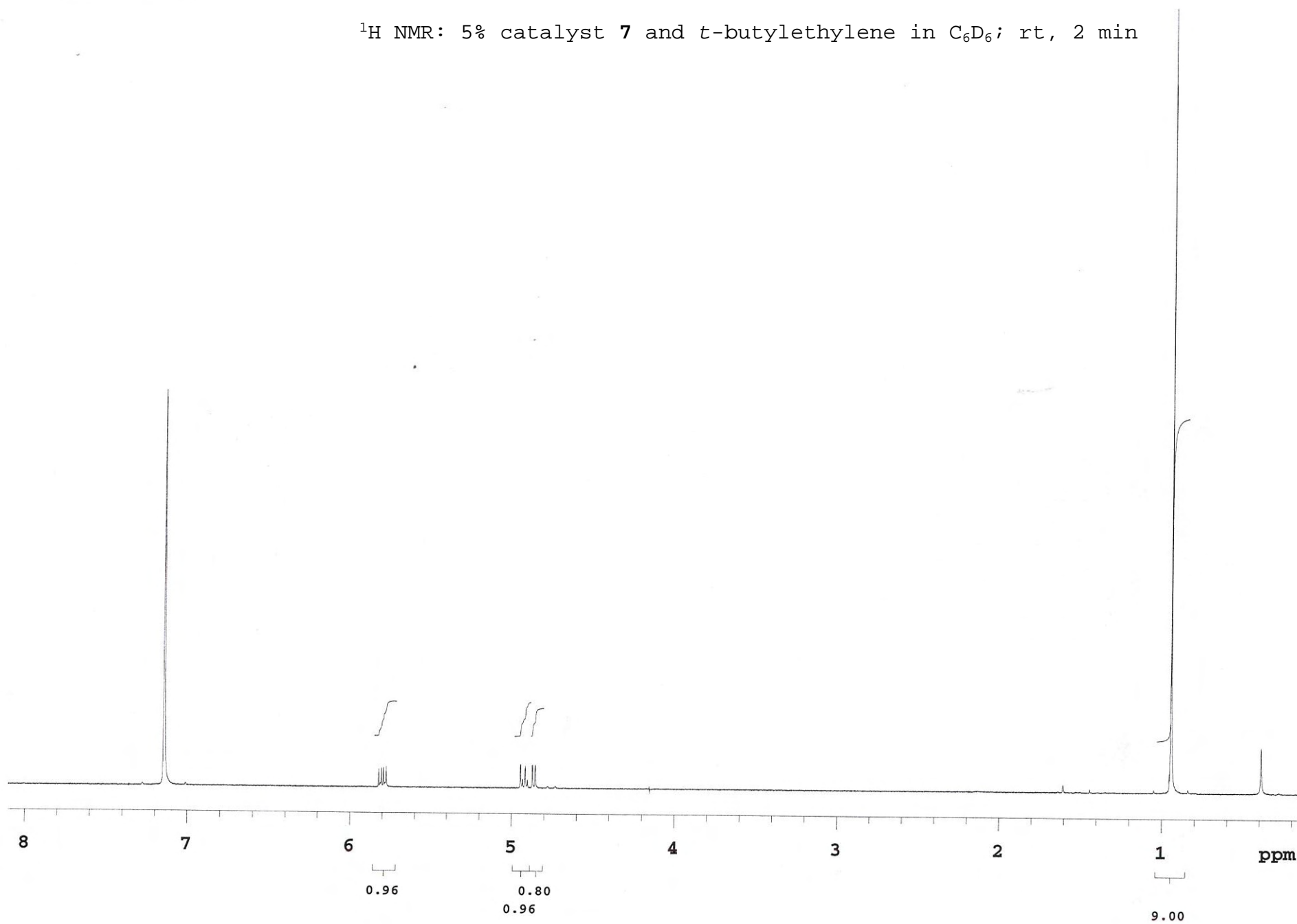
 ^1H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 5 min

4039-2min

S165

Pulse Sequence: s2pul

^1H NMR: 5% catalyst **7** and *t*-butylethylene in C_6D_6 ; rt, 2 min

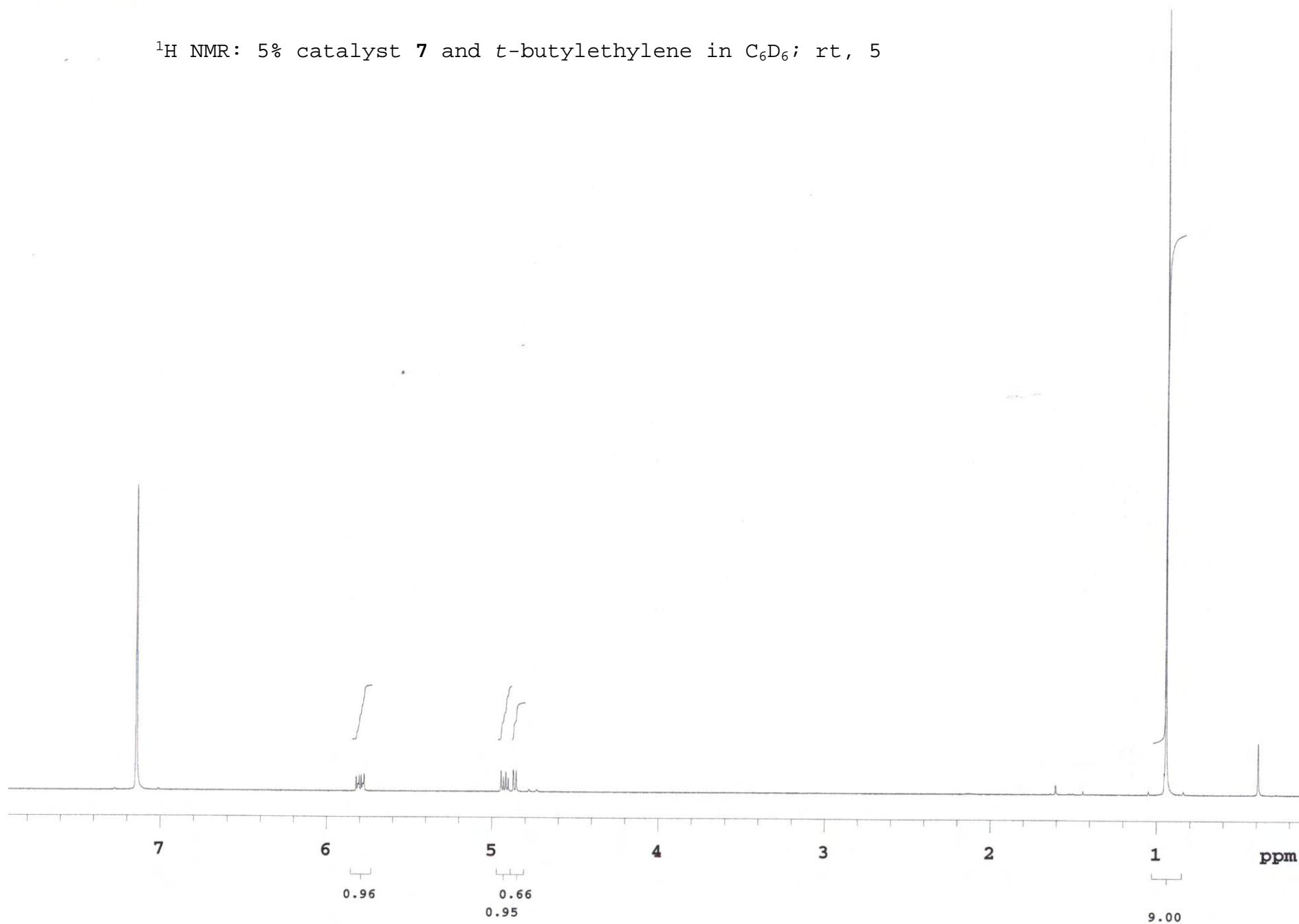


4029-5min

S166

Pulse Sequence: s2pul

^1H NMR: 5% catalyst **7** and *t*-butylethylene in C_6D_6 ; rt, 5

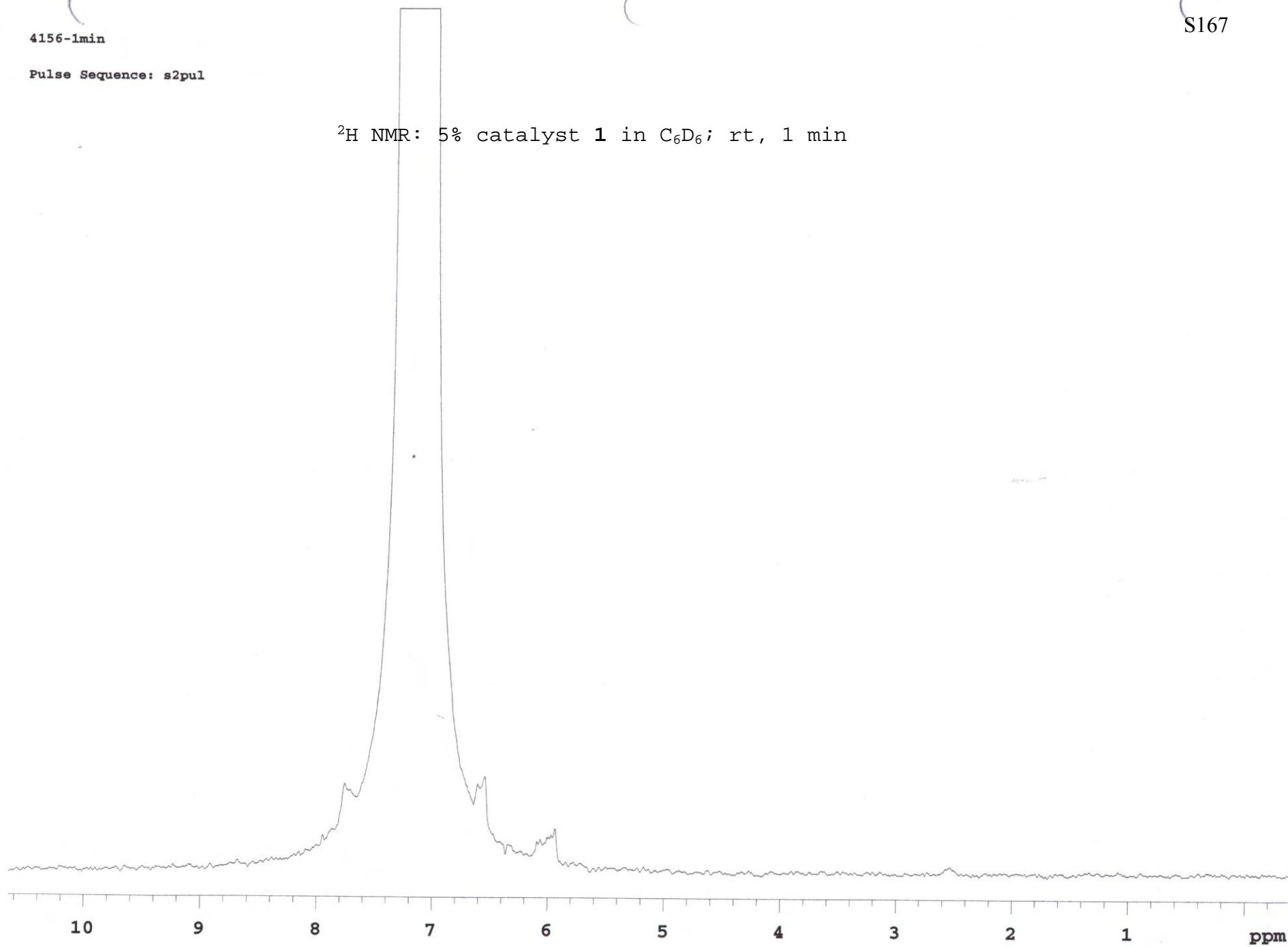


4156-1min

Pulse Sequence: s2pul

S167

^2H NMR: 5% catalyst **1** in C_6D_6 ; rt, 1 min

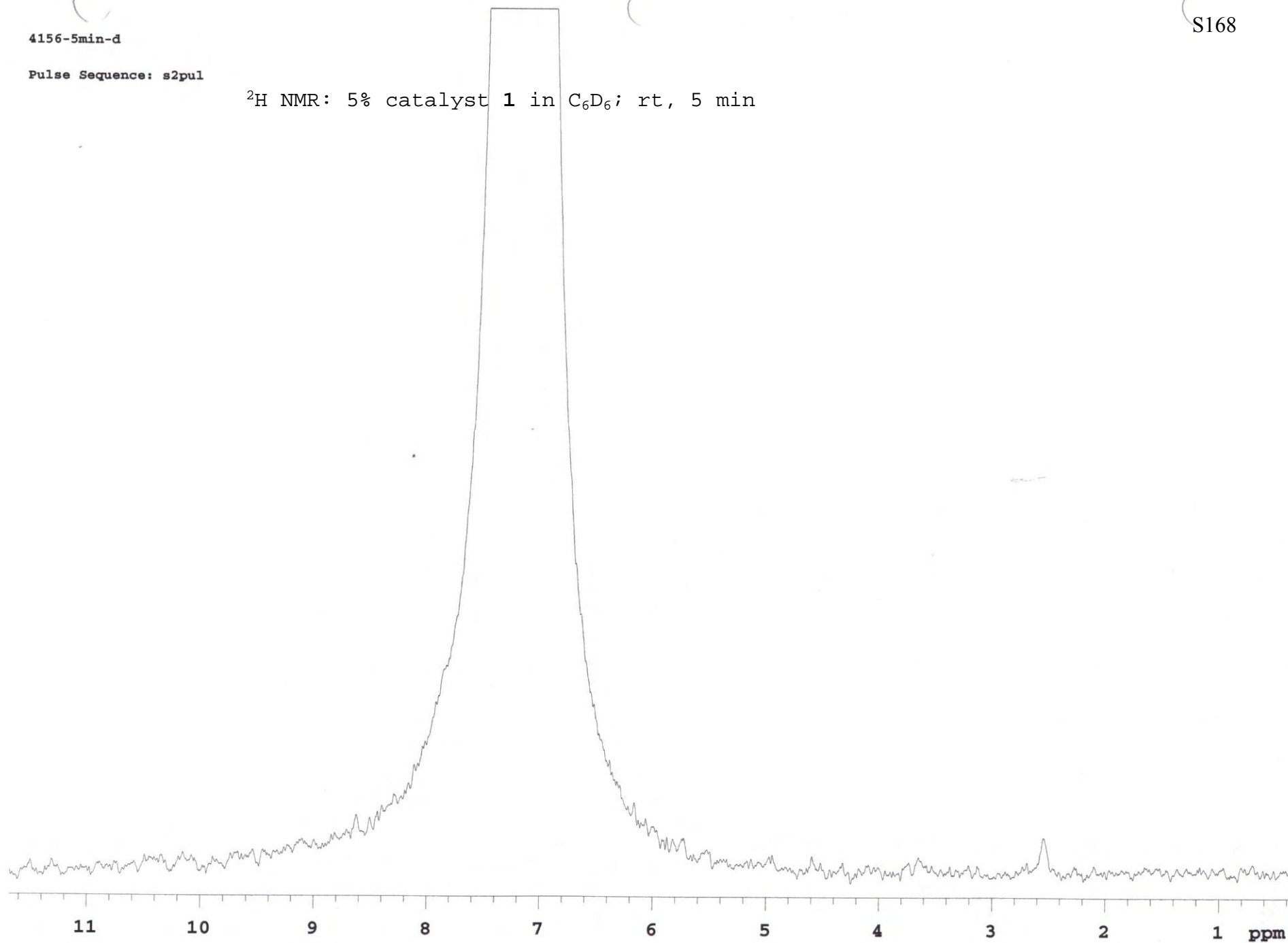


4156-5min-d

S168

Pulse Sequence: s2pul

^2H NMR: 5% catalyst **1** in C_6D_6 ; rt, 5 min

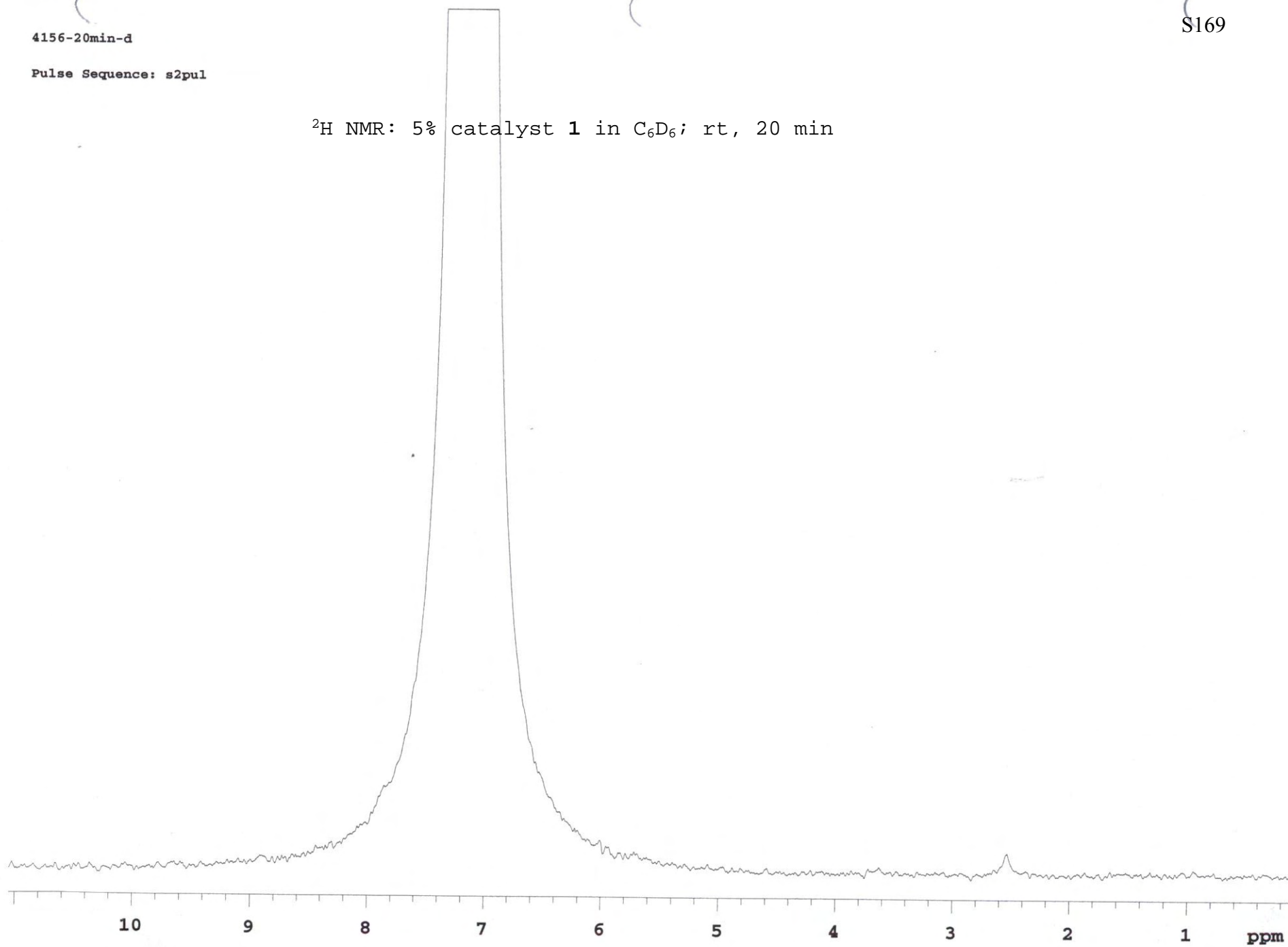


4156-20min-d

Pulse Sequence: s2pul

S169

^2H NMR: 5% catalyst **1** in C_6D_6 ; rt, 20 min

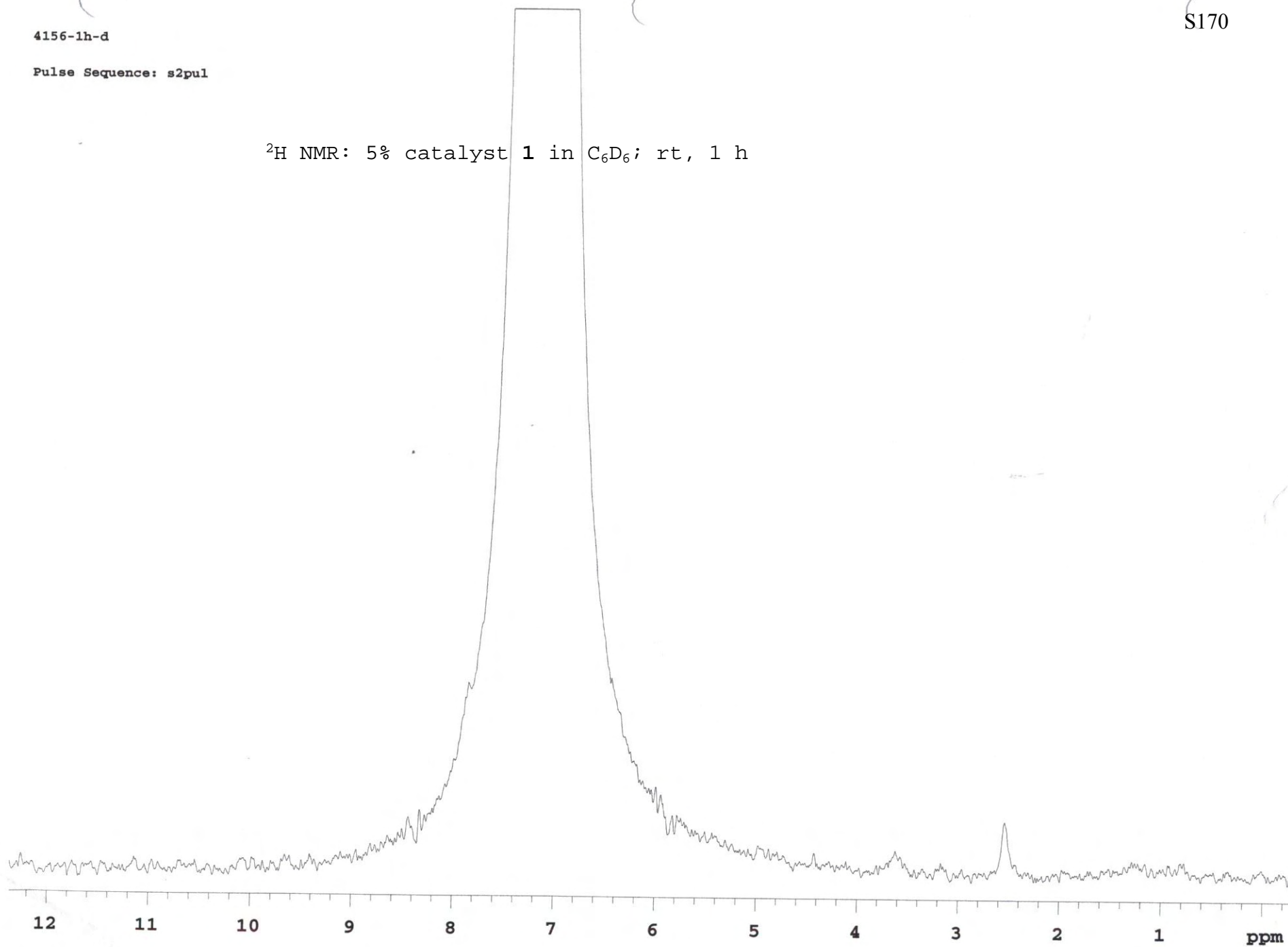


4156-1h-d

Pulse Sequence: s2pul

S170

^2H NMR: 5% catalyst **1** in C_6D_6 ; rt, 1 h

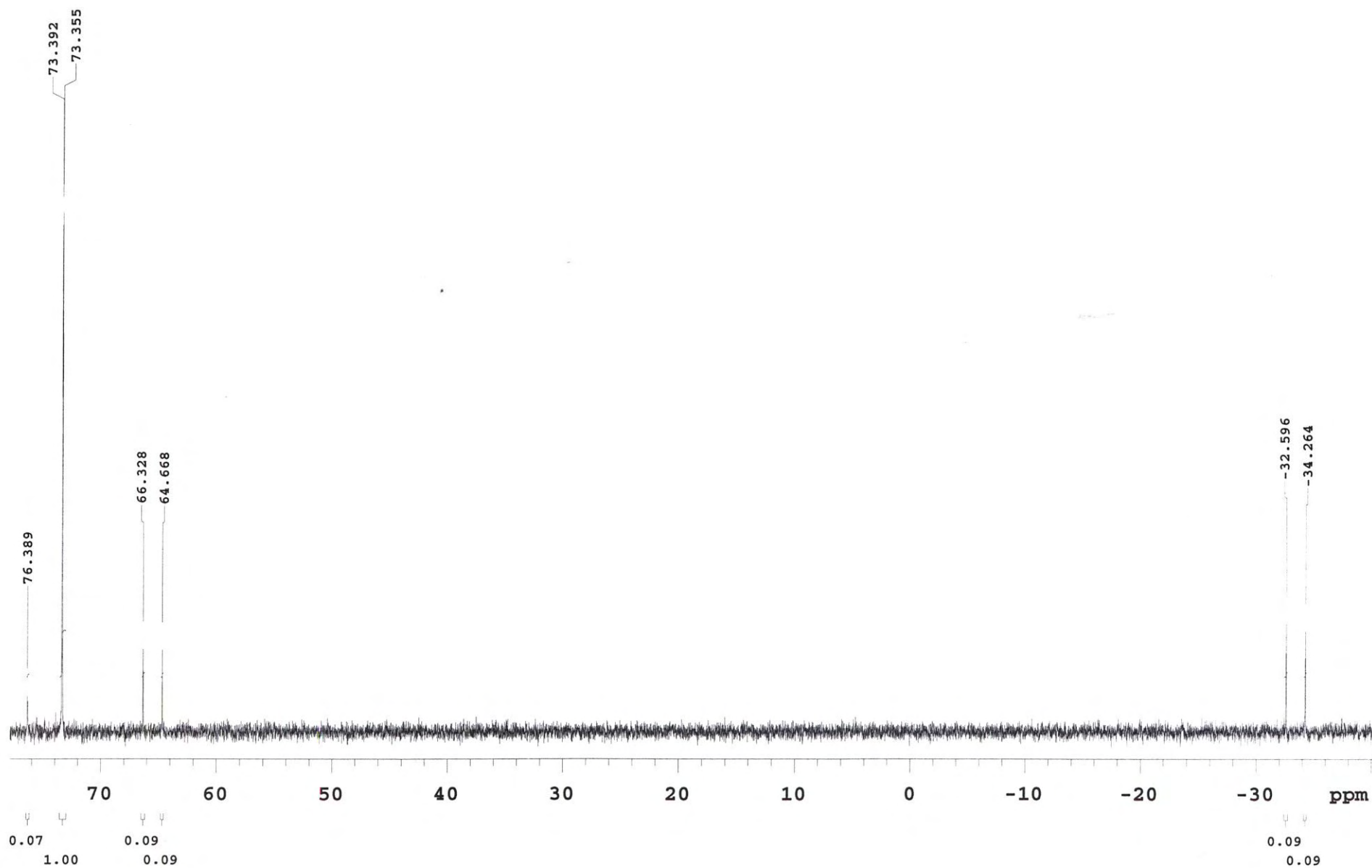


4156-5min

S171

Pulse Sequence: s2pul

^{31}P NMR: 5% catalyst 1 in C_6D_6 ; rt, 5 min

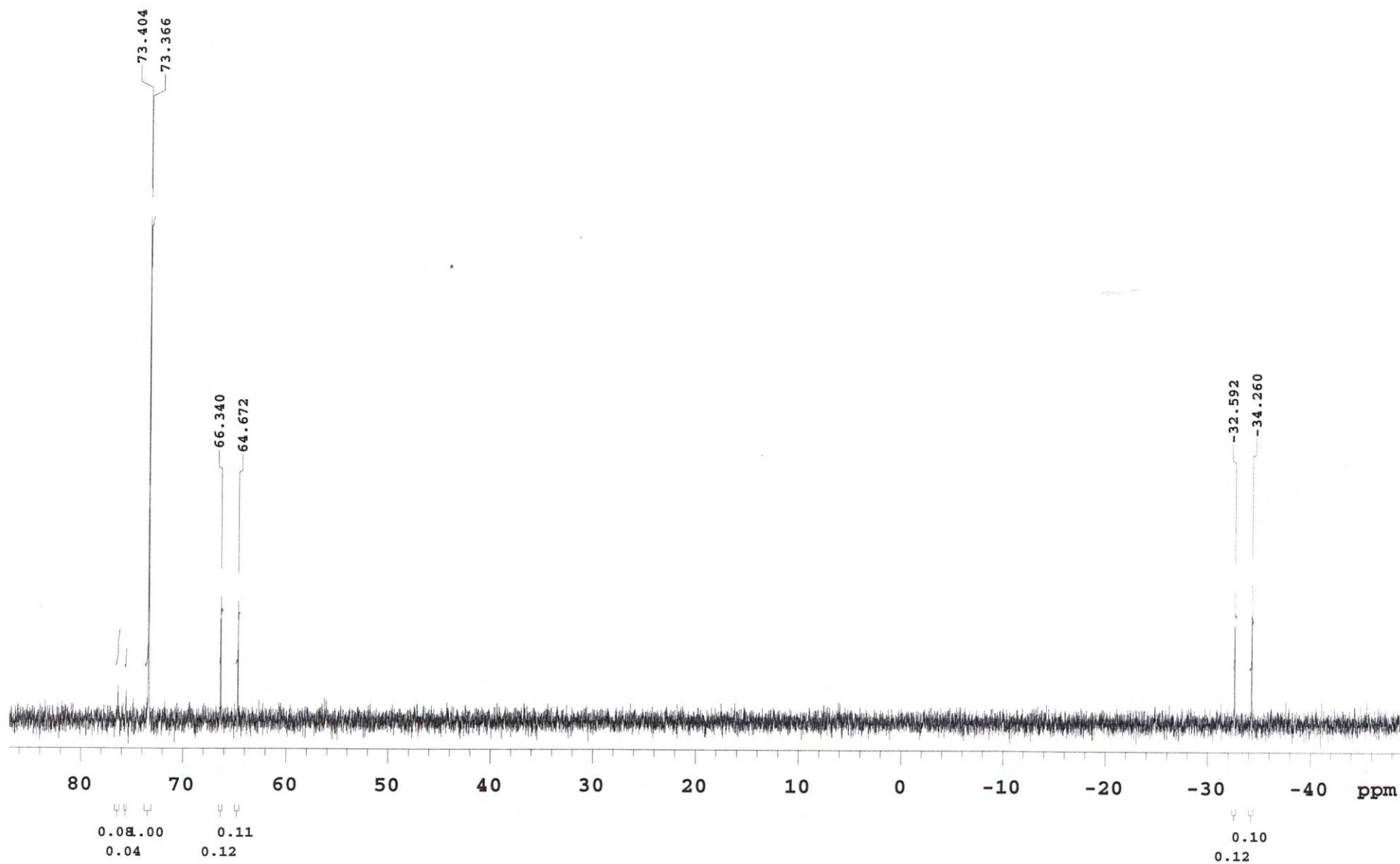


4156-1h

S172

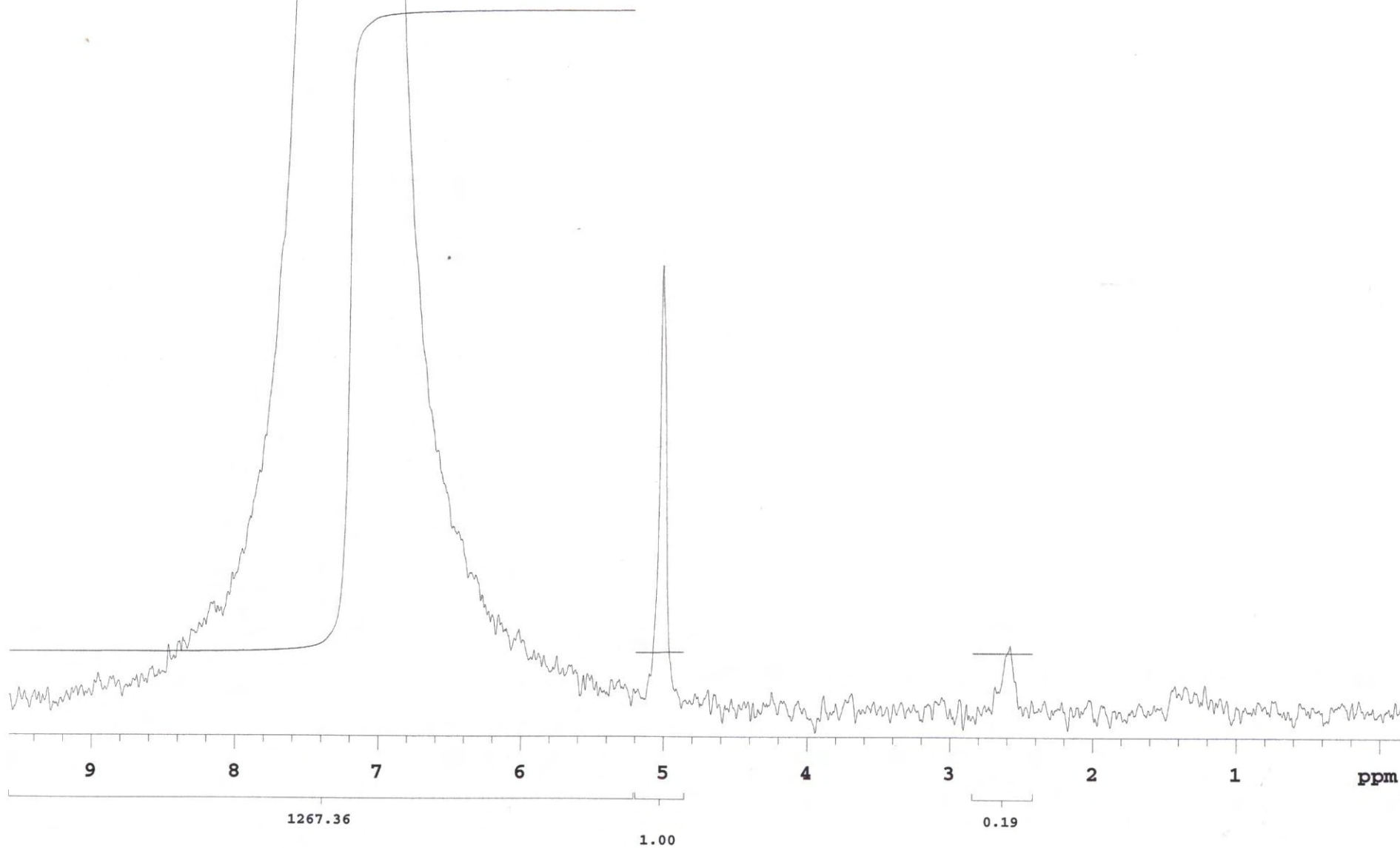
Pulse Sequence: s2pul

^{31}P NMR: 5% catalyst **1** in C_6D_6 ; rt, 1 h



4154-1min

Pulse Sequence: s2pul

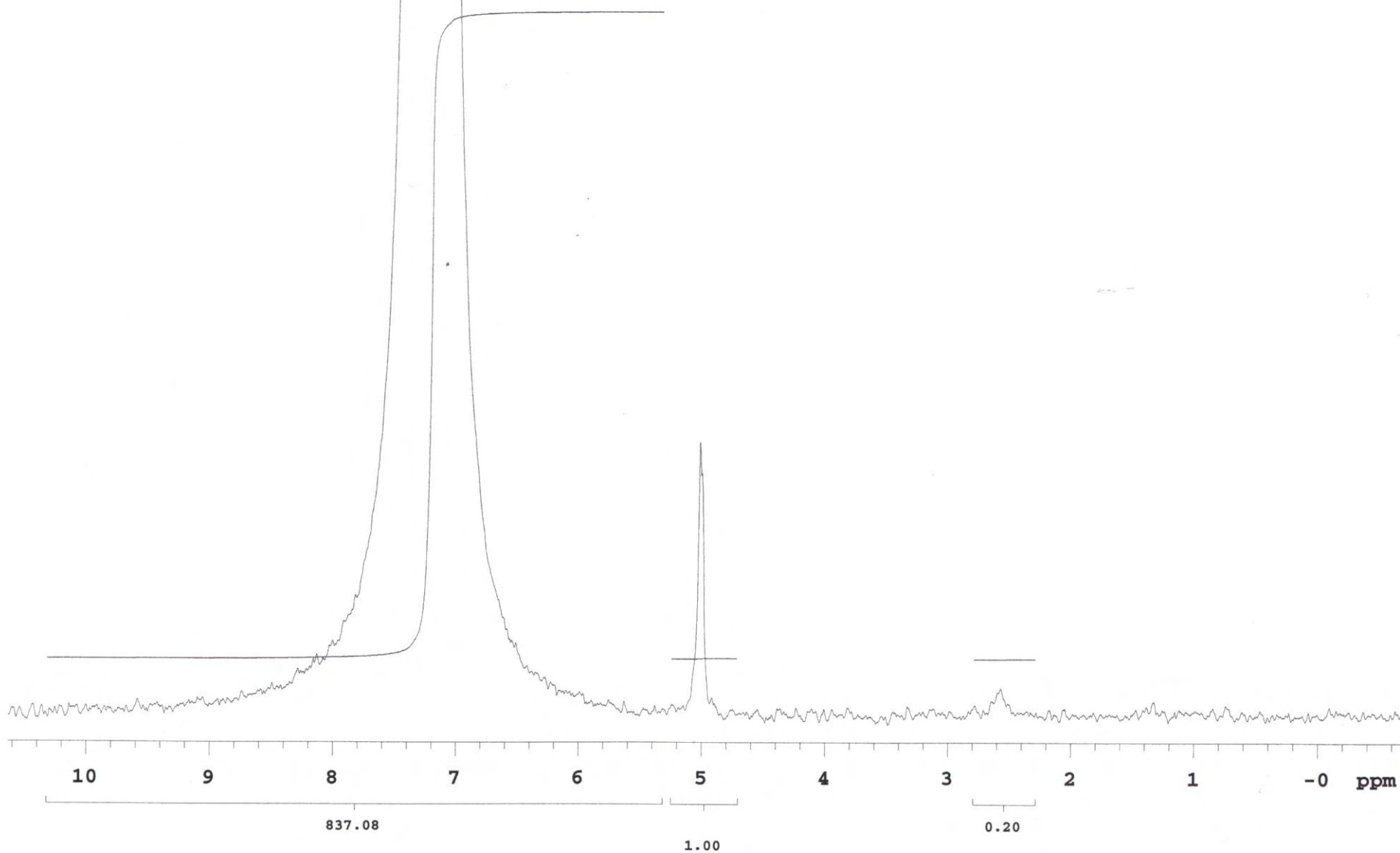
 ^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 1 min

4154-2min

S174

Pulse Sequence: s2pul

^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 2 min

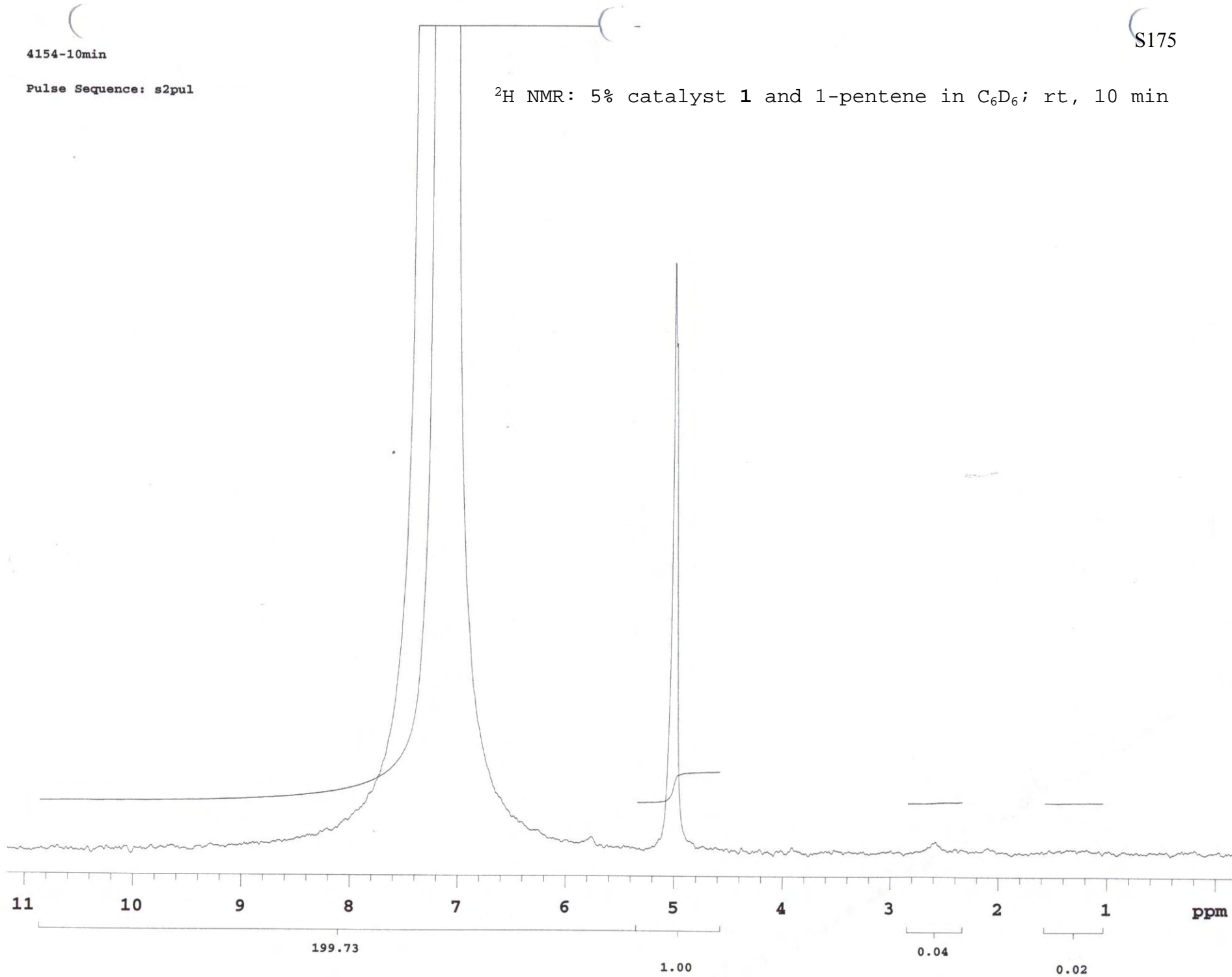


4154-10min

Pulse Sequence: s2pul

S175

^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 10 min

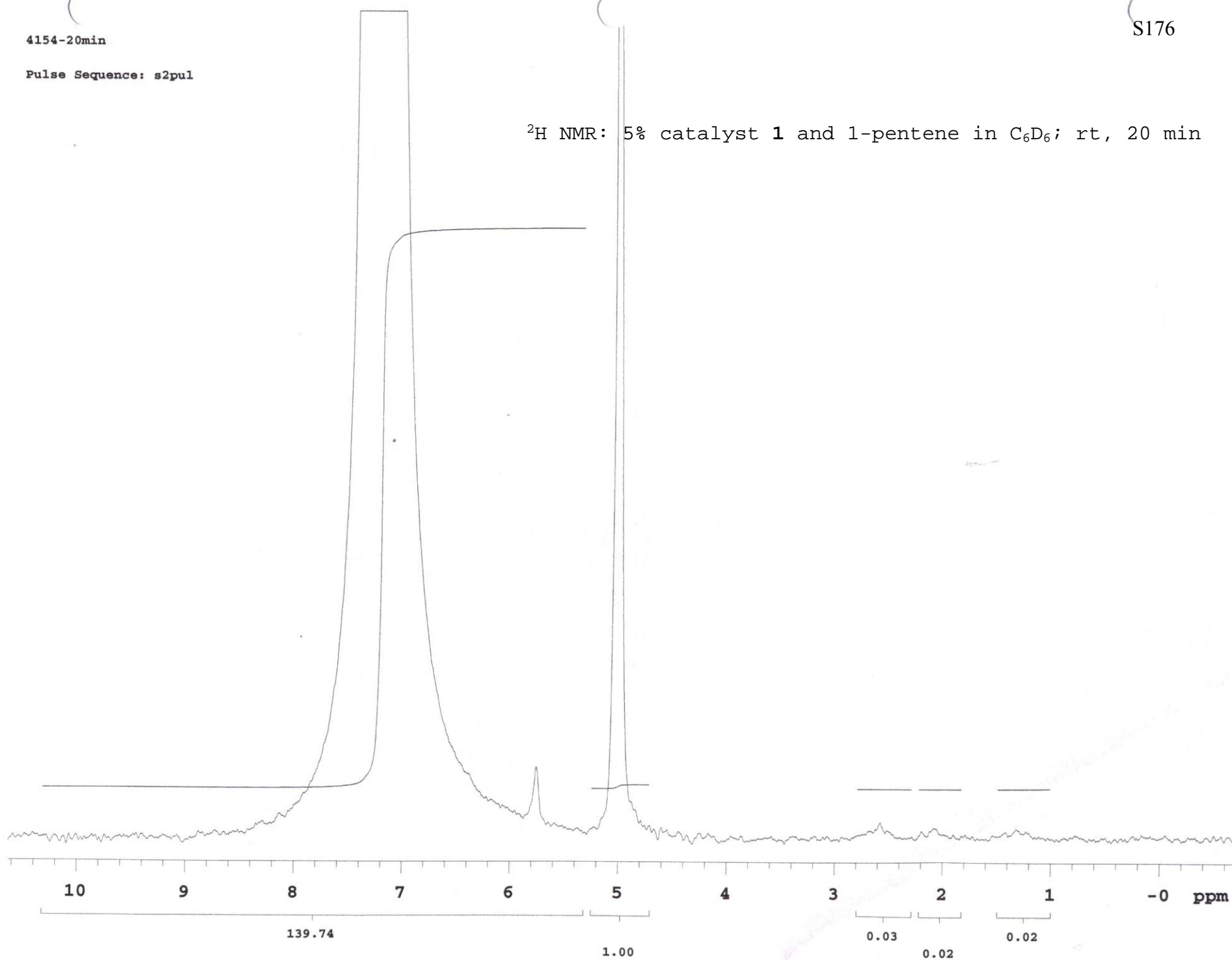


4154-20min

Pulse Sequence: s2pul

S176

^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 20 min

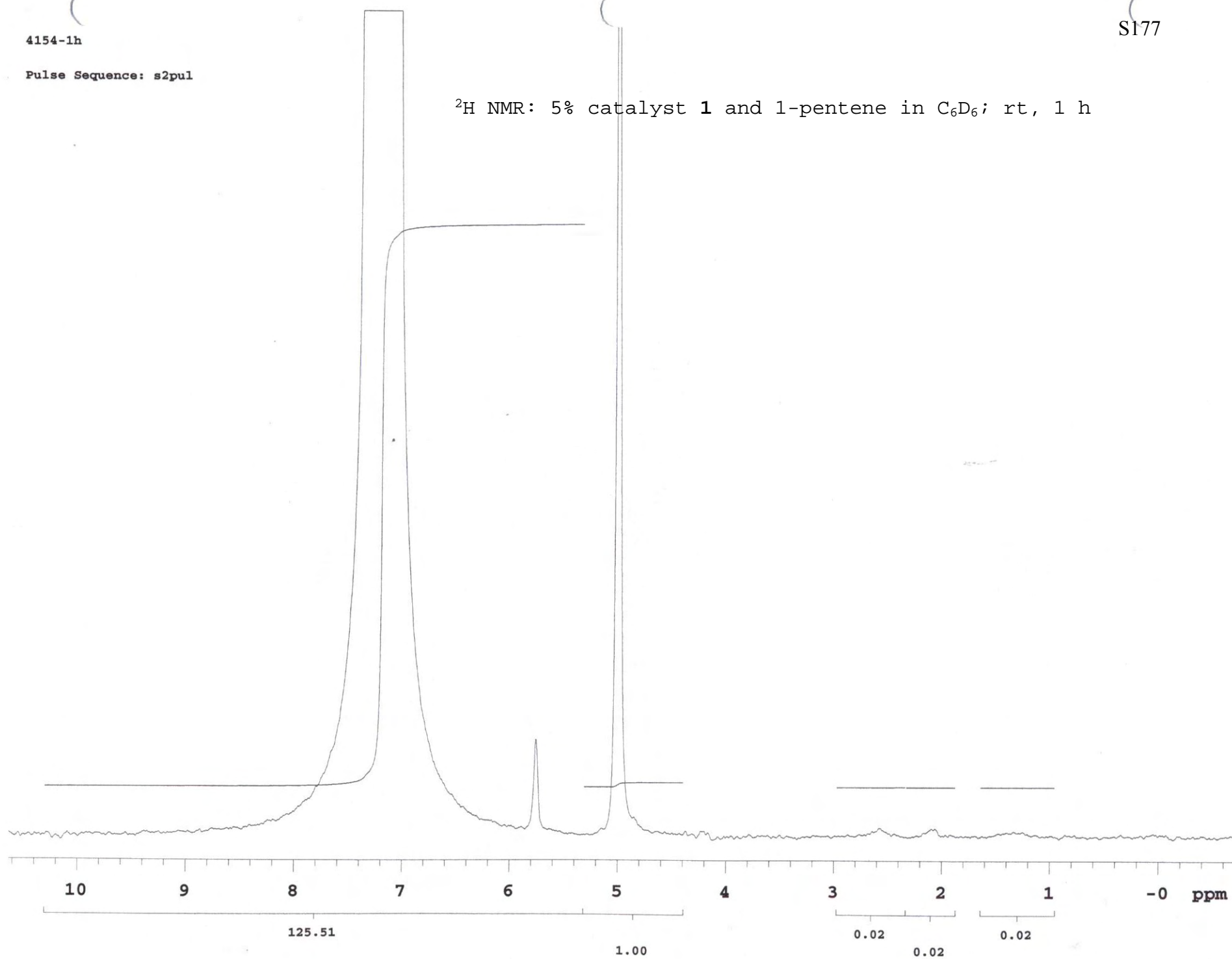


4154-1h

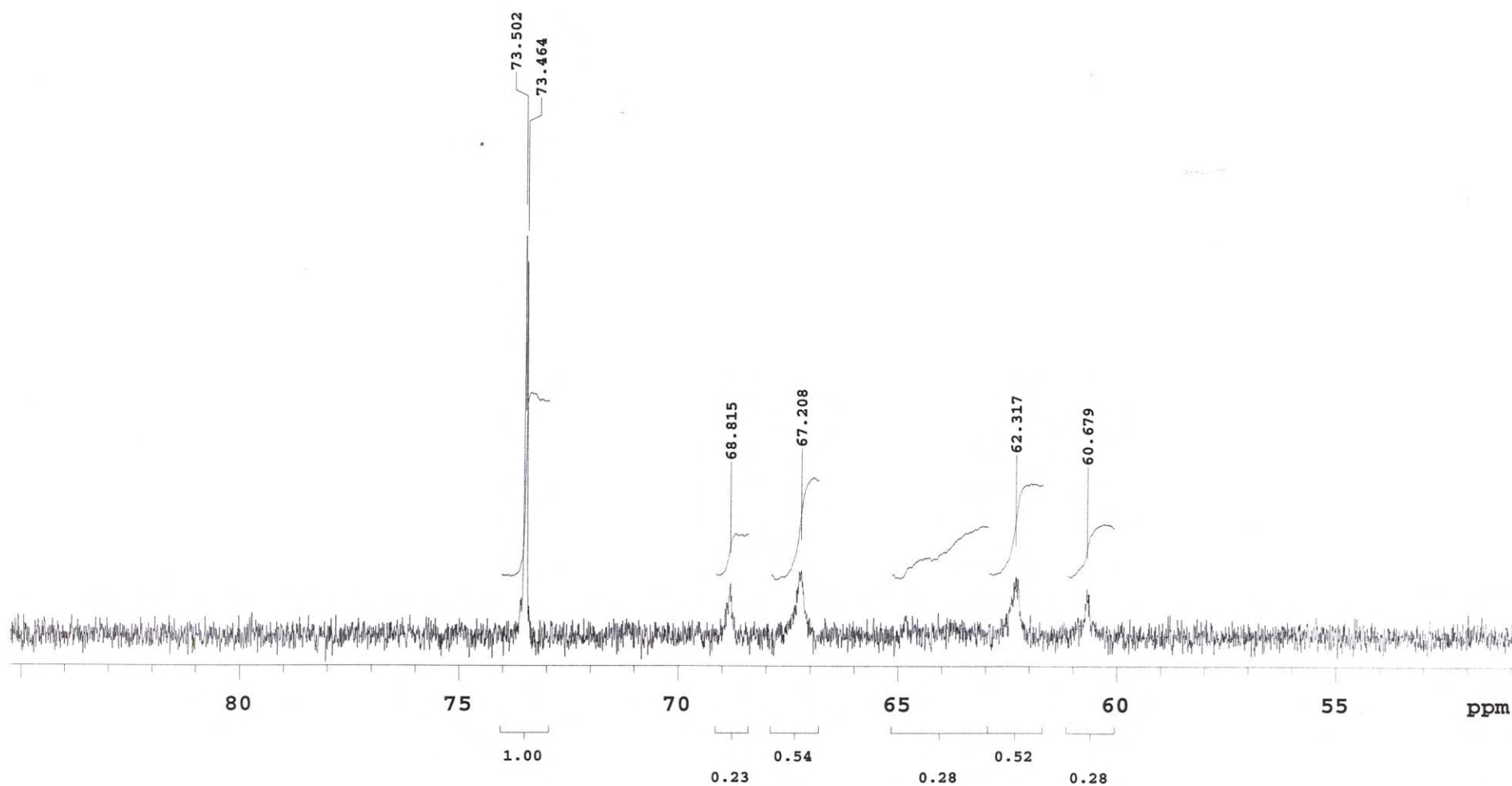
Pulse Sequence: s2pul

S177

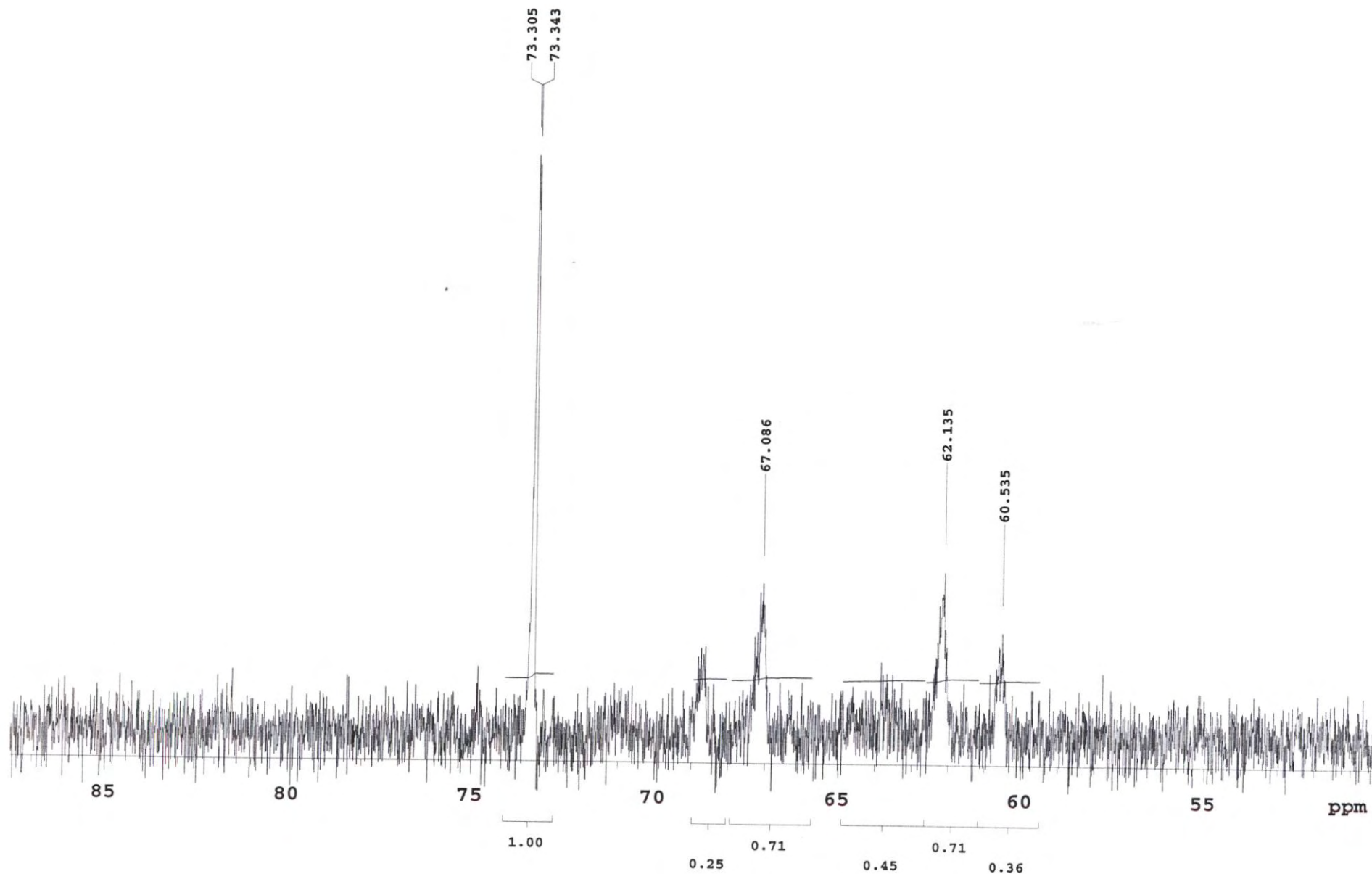
^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 1 h



Pulse Sequence: s2pul

 ^{31}P NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 20 min

Pulse Sequence: s2pul

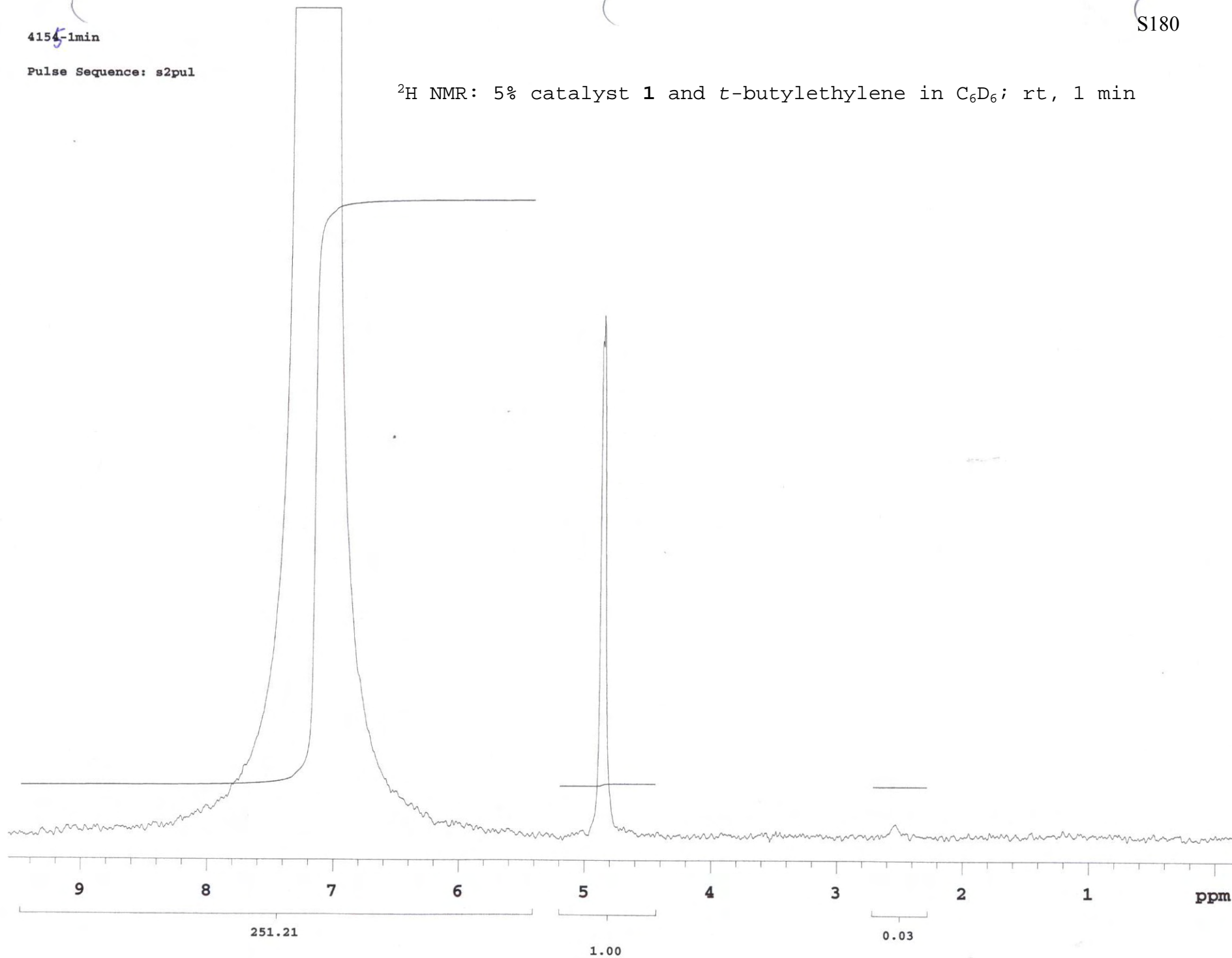
 ^{31}P NMR: 5% catalyst **1** and 1-pentene in C_6D_6 ; rt, 1 h

4154-1min

S180

Pulse Sequence: s2pul

^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 1 min

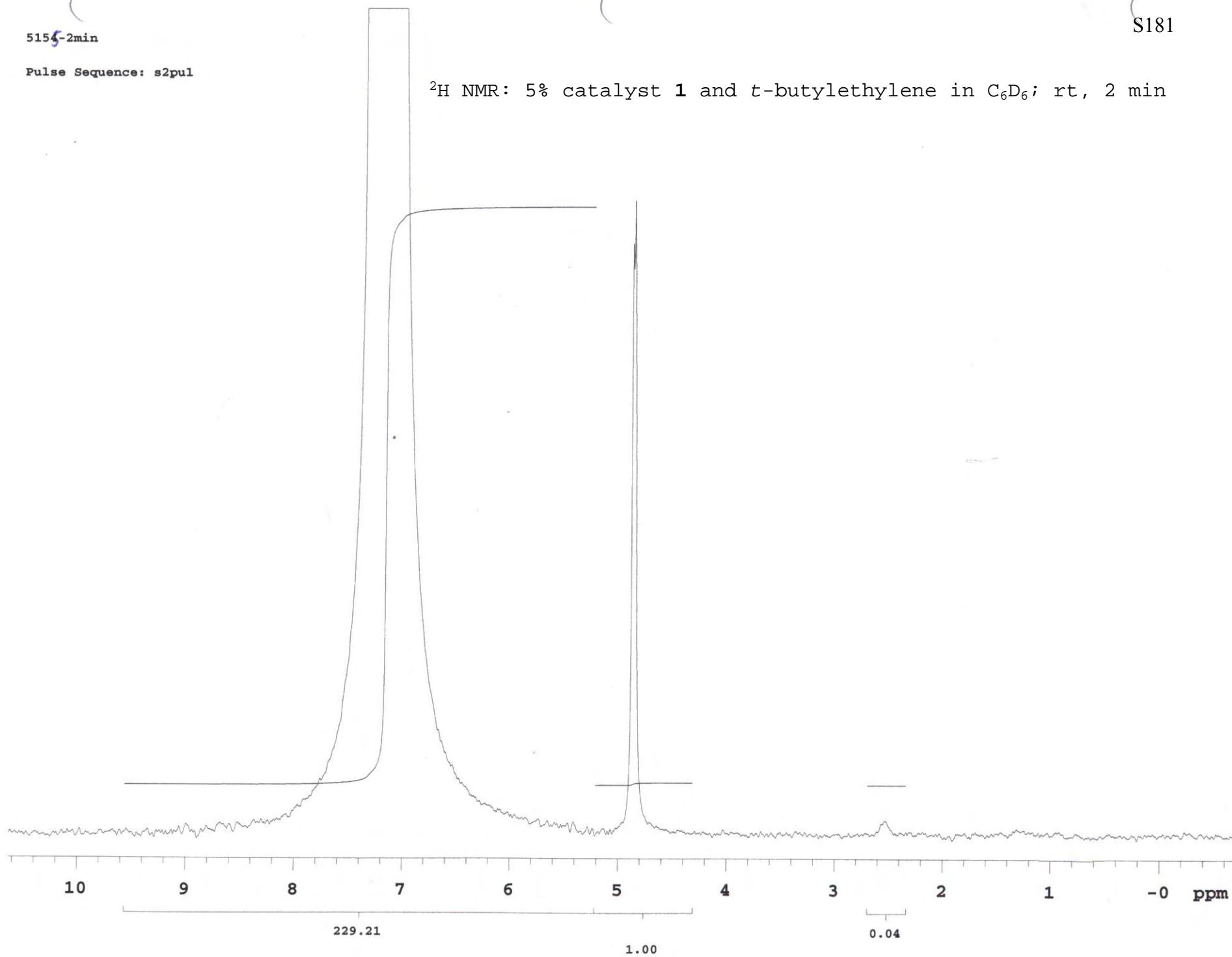


5154-2min

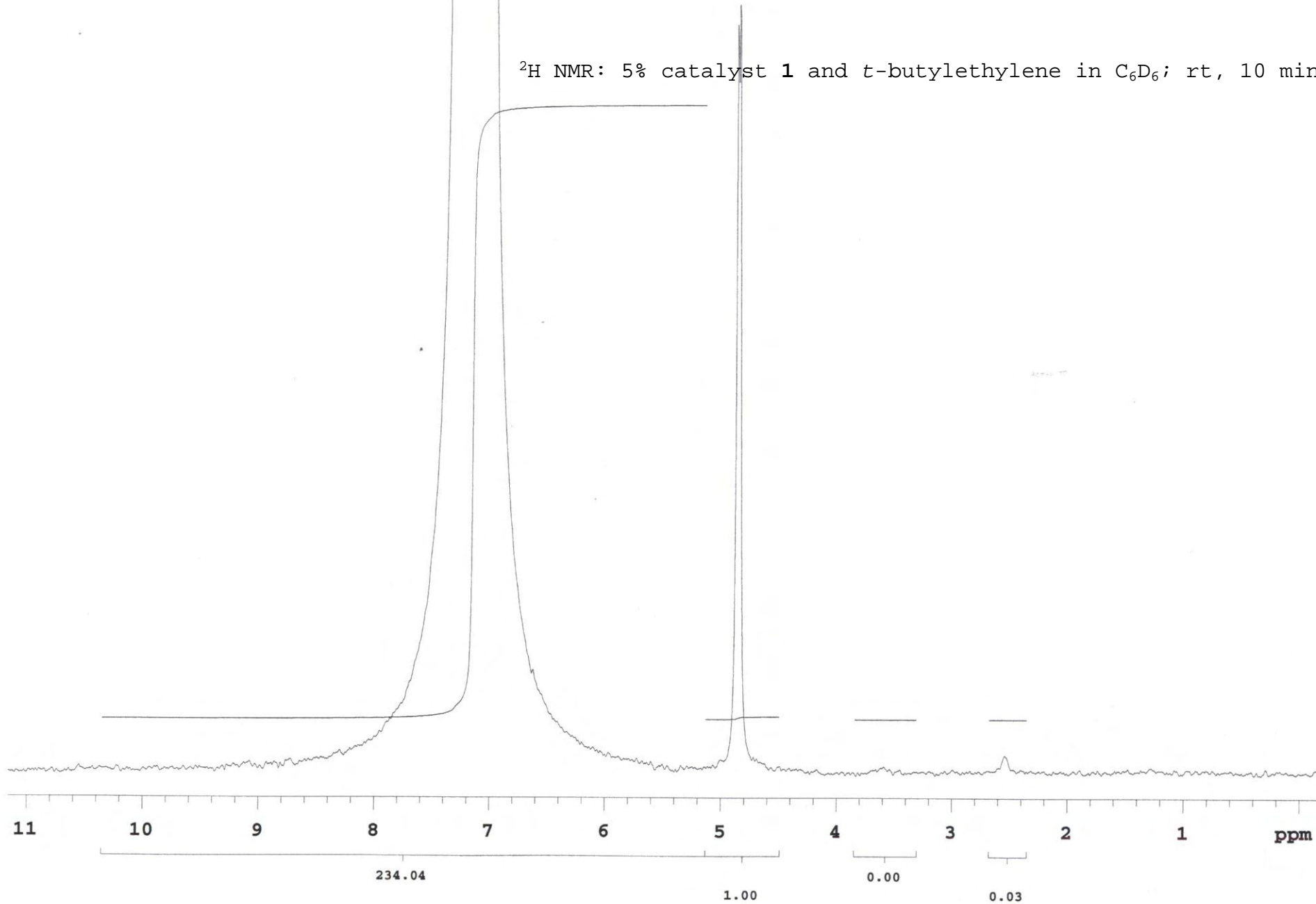
S181

Pulse Sequence: s2pul

^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 2 min



^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 10 min

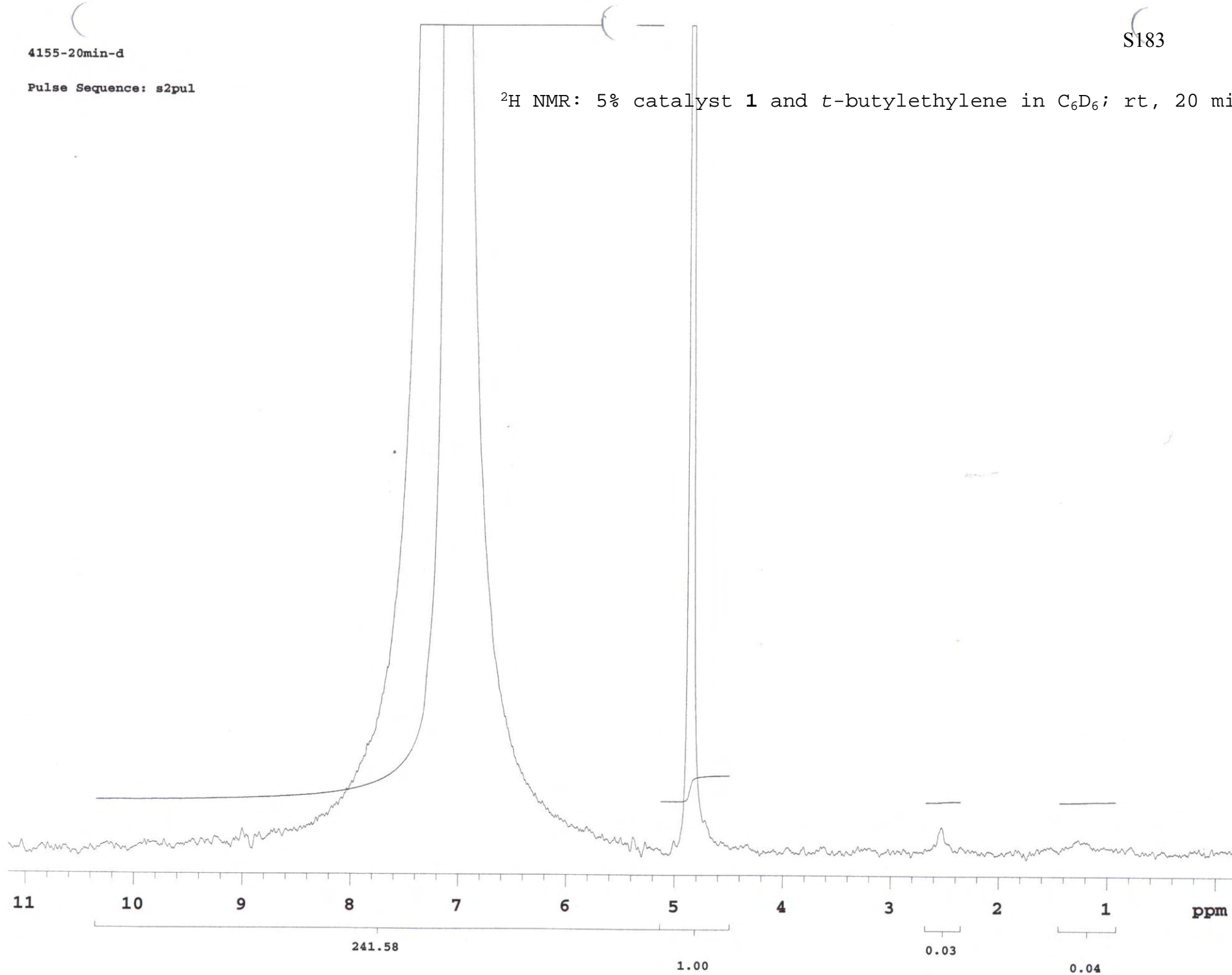


4155-20min-d

Pulse Sequence: s2pul

S183

^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 20 min

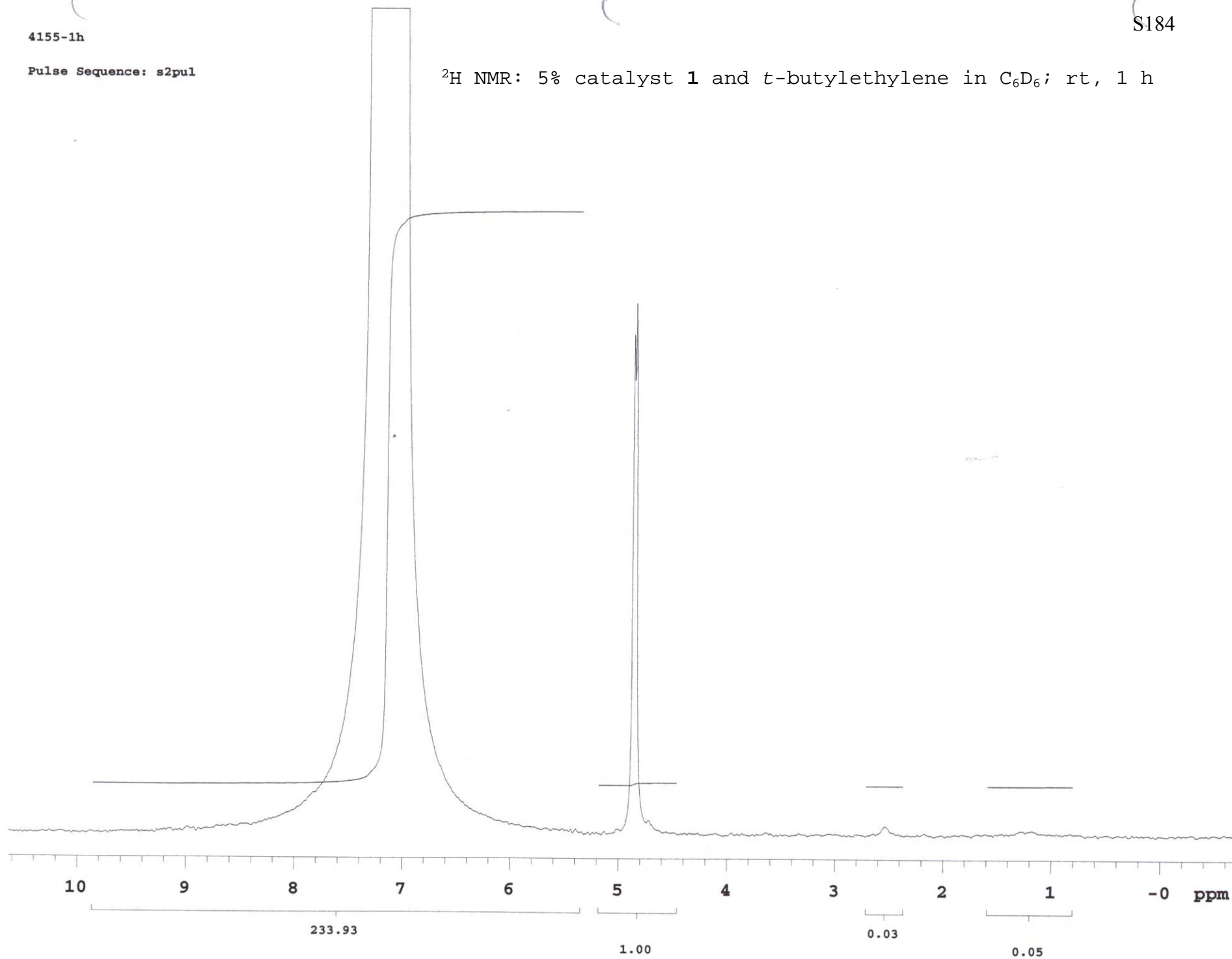


4155-1h

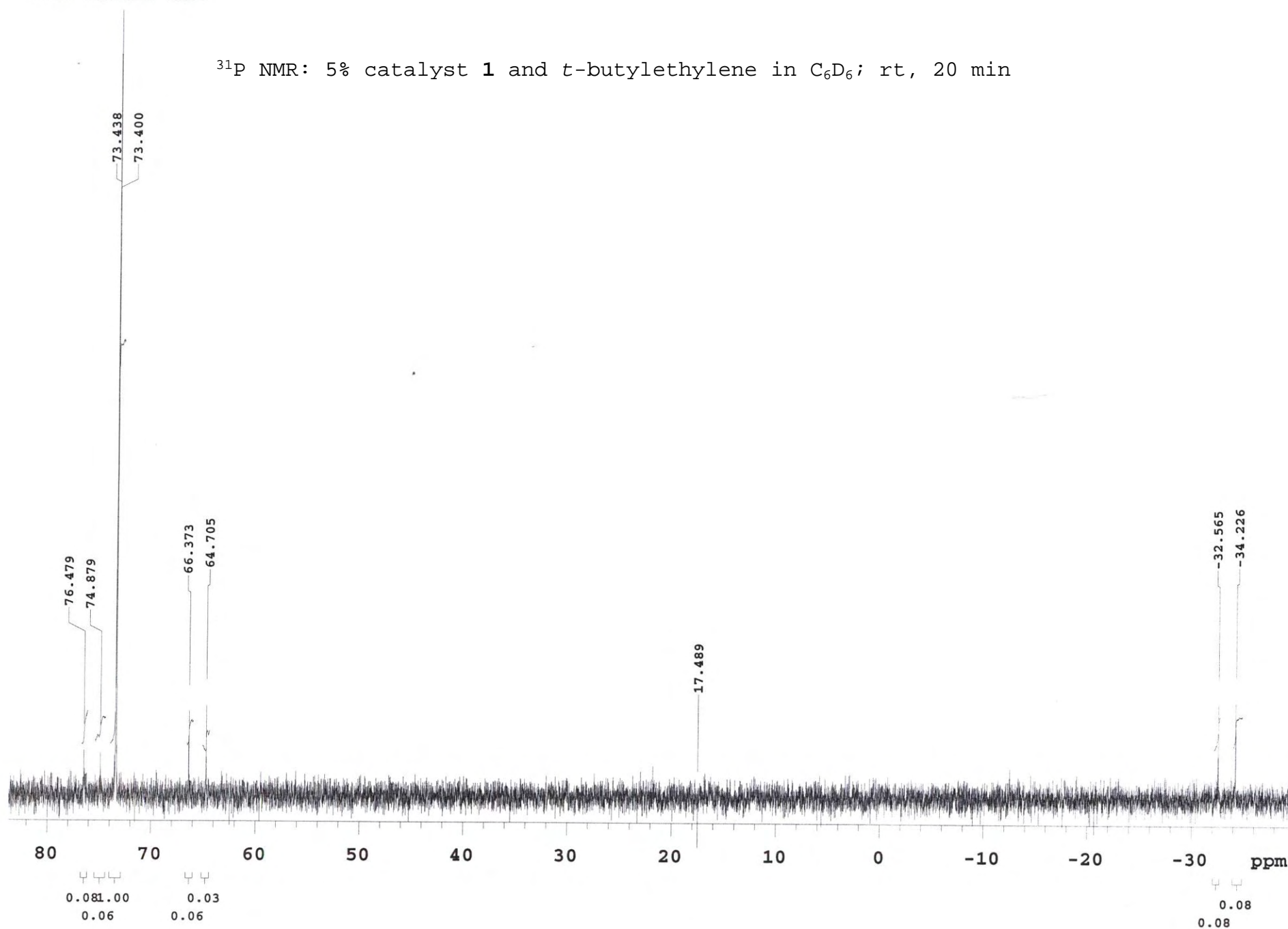
S184

Pulse Sequence: s2pul

^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 1 h



Pulse Sequence: s2pul

 ^{31}P NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 20 min

Pulse Sequence: s2pul

 ^{31}P NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6 ; rt, 1 h