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Supporting Information

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

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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 ºC for at least 4 hours. THF, Et_2O, toluene, benzene and pentane were collected from a solvent purification system containing a 1 m column of activated alumina under argon. Quantitative ^{1}H 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 (C_6D_6: δ7.15). ^{13}C NMR spectra were obtained at 125.8 MHz on a 500 MHz instrument, and chemical shifts were recorded relative to the solvent resonance (C_6D_6: δ128.0). Both ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{31}P NMR spectra were obtained at 202.2 MHz, and chemical shifts are reported in parts per million downfield of 85% H_3PO_4.

The percentage of H/D exchange in a sample was based on a decrease in the integral of the ^{1}H NMR signals, as compared to the integral of the corresponding signals in the starting material. The ^{1}H 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 ^{2}H 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^{t}BPP)Ir(H)(NH_2) **1**[3], **2**,[4] **4**,[5] **5**,[6] and (D^{t}BPP)RhHCl[7] were synthesized according to reported procedures. Dry C_6D_6 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^{t}BPP)Rh(NH_3) 3

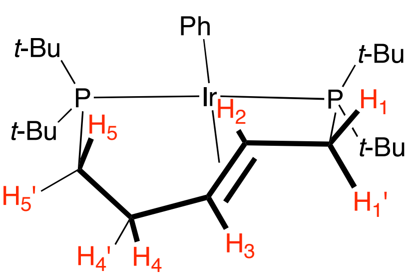
In an argon-filled dry box, solid KHMDS (44 mg, 0.22 mmol) was added to a suspension of (D^{t}BPP)RhHCl (100 mg, 0.20 mmol) in dry pentane (3 mL) in a 20 mL vial fitted with a cap containing a Teflon-lined septum. The stirred yellow suspension was then purged with excess, dry ammonia gas. After stirring 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). ^{1}H NMR (500 MHz, C_6D_{12}) _ 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); ^{13}C NMR (500 MHz, C_6D_{12}) _ 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); ^{32}P NMR (500 MHz, C_6D_{12}) _ 81.3 (d, J = 184.6 Hz). Anal. Calcd for $C_{21}H_{48}NP_2Rh$: 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), C_6D_6 (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 C_6D_6 washings to remove iridium complexes. The filtrate was pure by ^{1}H and ^{13}C 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. ^{1}H, ^{2}H and ^{13}C 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)$_2$PCH$_2$CH$_2$CH=CHCH$_2$P(*t*-Bu$_2$)]IrPh 7



In an argon-filled dry box, (D^{t}BPP)IrH$_4$ **2** (56 mg, 0.10 mmol) was stirred with 2-norbornene (47 mg, 0.50 mmol) in 2.0 mL of dry C_6H_6 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 C_6D_{12} in the absence of trace C_6H_6. The proton and carbon signals were assigned with the aid of a combination of DEPT-135, COSY, C-H HMQC and selective ^{31}P-decoupled ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_{12}; additional C_6*H*$_6$ peak at _ 7.25) _ 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 C*Me*$_3$ at _ 1.28), 1.28 (d, *J*= 11.8 Hz, 9H, **C*Me*$_3$**), 1.25 (d, *J*= 12.6 Hz, 9H, **C*Me*$_3$**), 1.19 (d, *J*= 12.4 Hz, 9H, **C*Me*$_3$**), 1.13-1.00 (m, **H5**, overlapping with C*Me*$_3$ at _ 1.04), 1.04 (d, *J*= 12.0 Hz, 9H, **C*Me*$_3$**); ^{13}C NMR (500 MHz, C_6D_{12}; additional *C*$_6$H$_6$ peak at _ 128.7) _ 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, ***C*Me$_3$**), 35.6 (d, *J*= 20.5 Hz, ***C*Me$_3$**), 34.4 (d, *J*= 14.7 Hz, ***C*Me$_3$**), 34.1 (s, ***C*Me$_3$**), 33.1 (d, *J*= 25.4 Hz, **C1**), 30.8 (d, *J*= 3.9 Hz, **C*Me*$_3$**), 30.5 (two overlapping **C*Me*$_3$** peaks), 30.3 (d, *J*= 3.7 Hz, **C2**), 30.0 (d, *J*= 3.9 Hz, **C*Me*$_3$**), 29.3 (d, *J*= 9.8 Hz, **C4**), 22.9 (d, *J*= 22.5 Hz, **C5**); ^{32}P NMR (500 MHz, C_6D_{12}) _ 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*-Bu)$_2$PCH$_2$CH$_2$CH=CHCH$_2$P(*t*-Bu$_2$)]IrPh 7 with C_6D_6

In an argon-filled dry box, [(*t*-Bu)$_2$PCH$_2$CH$_2$CH=CHCH$_2$P(*t*-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 ^{1}H NMR spectrum was acquired. The Ir-Ph and C-3 hydrogens were >95% deuterated. After an additional 5 min, a second ^{1}H NMR spectrum was acquired. An identical ^{1}H NMR spectrum was obtained, indicating that the exchange has reached equilibrium. The positions of deuteration were confirmed by ^{2}H NMR spectroscopy.

The solvents of the above deuterated sample were evaporated under vacuum, and the yellow solid residue d_6-**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 ^{1}H NMR spectrum was acquired. Greater than 95% ^{1}H 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 ^{2}H NMR spectroscopy.

Comparison of (D^{t}BPP)Ir(H)(NH$_2$) 1 and [(*t*-Bu)$_2$PCH$_2$CH$_2$CH=CHCH$_2$P(*t*-Bu$_2$)]IrPh 7 as catalysts in H/D exchange of *t*-butylethylene.

(D^{t}BPP)Ir(H)(NH$_2$) **1** (5.7 mg, 0.010 mmol) or [(*t*-Bu)$_2$PCH$_2$CH$_2$CH=CHCH$_2$P(*t*-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 ^{1}H NMR spectroscopy (see attached ^{1}H 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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Iridium-Catalyzed H/D Exchange at Vinyl Groups without Olefin Isomerization

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

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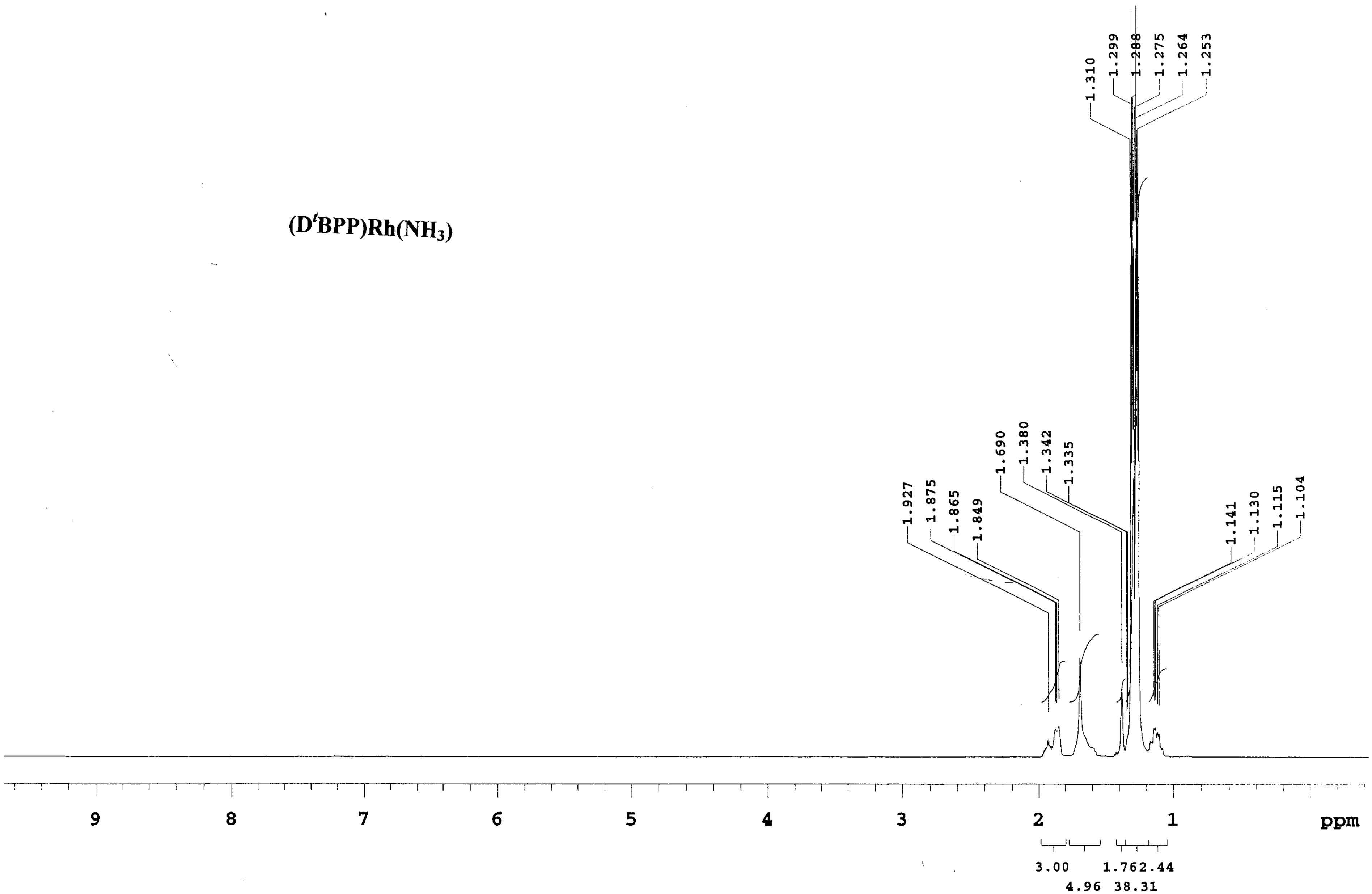
3228-h-c6d12

Pulse Sequence: s2pul

(D^{t}BPP)Rh(NH$_3$)



3238-c-c6d12

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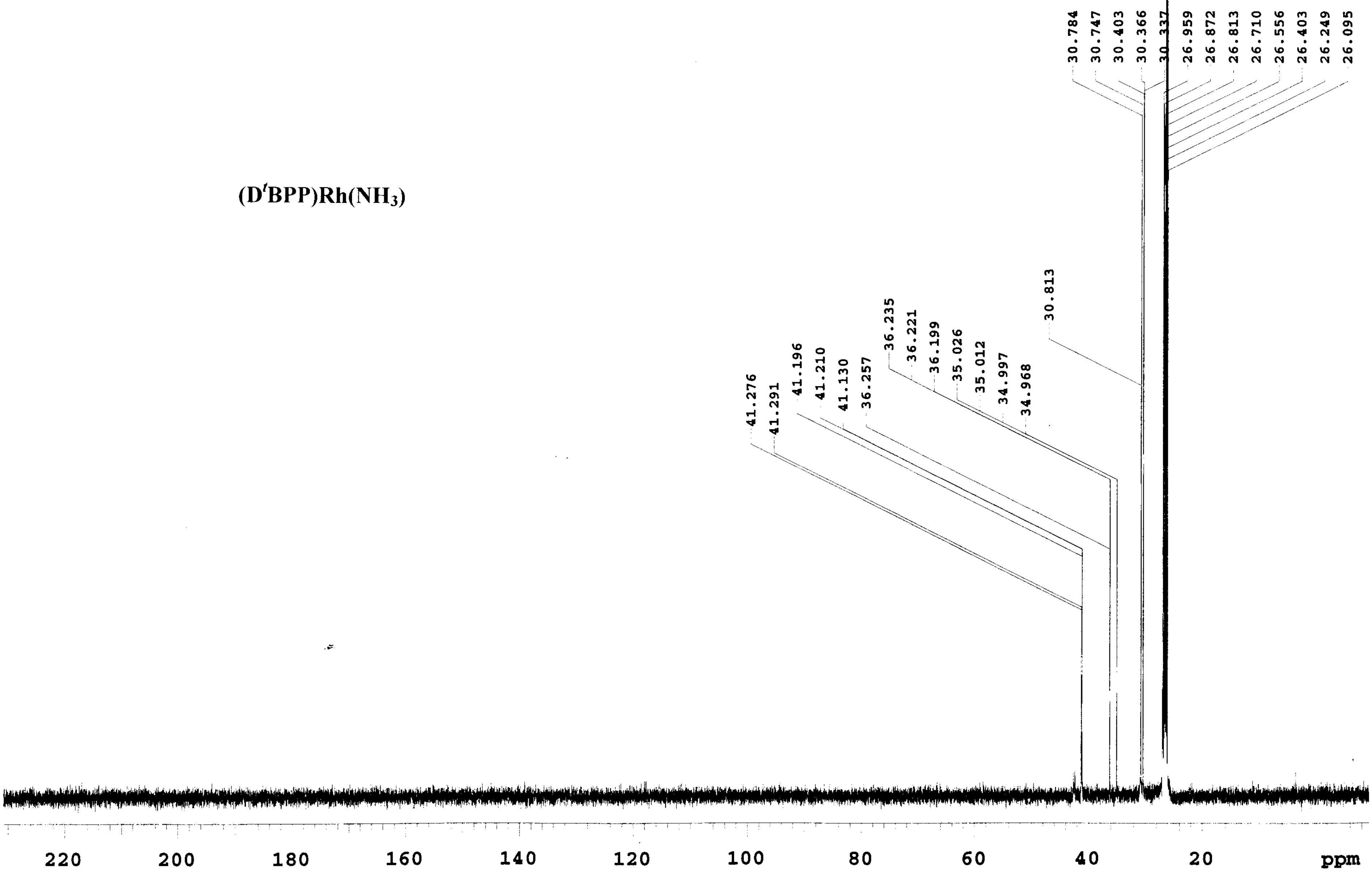

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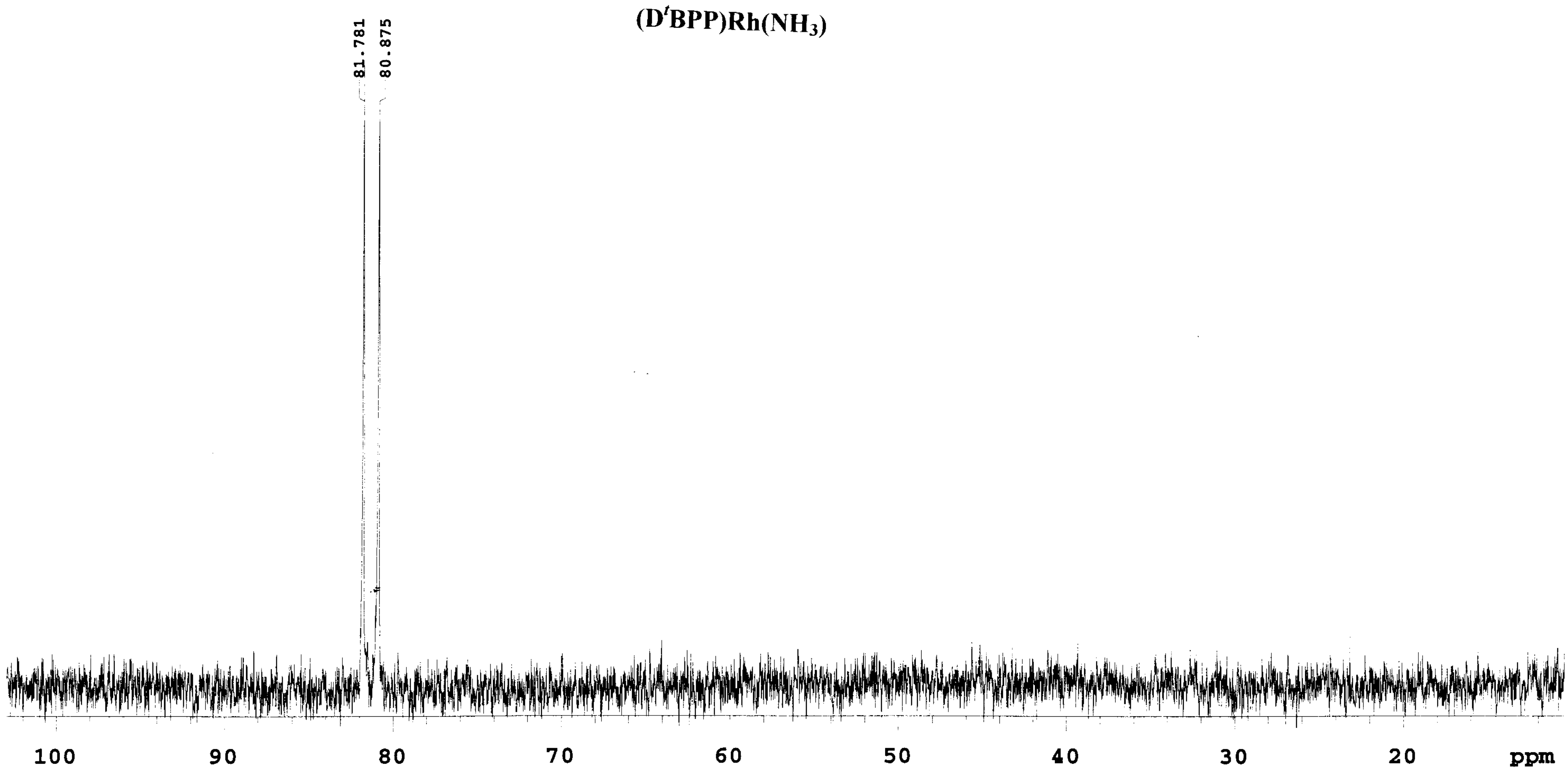

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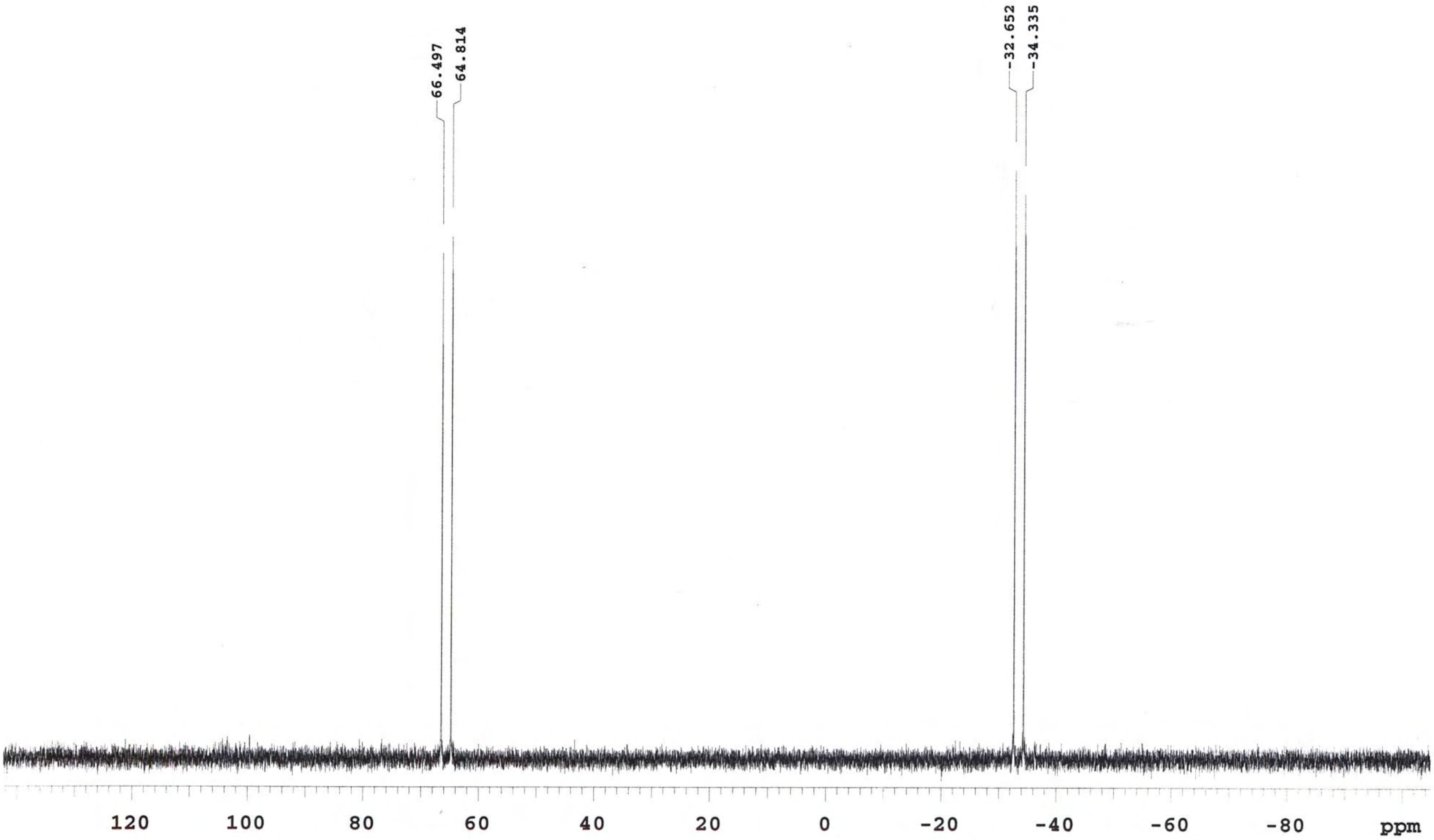
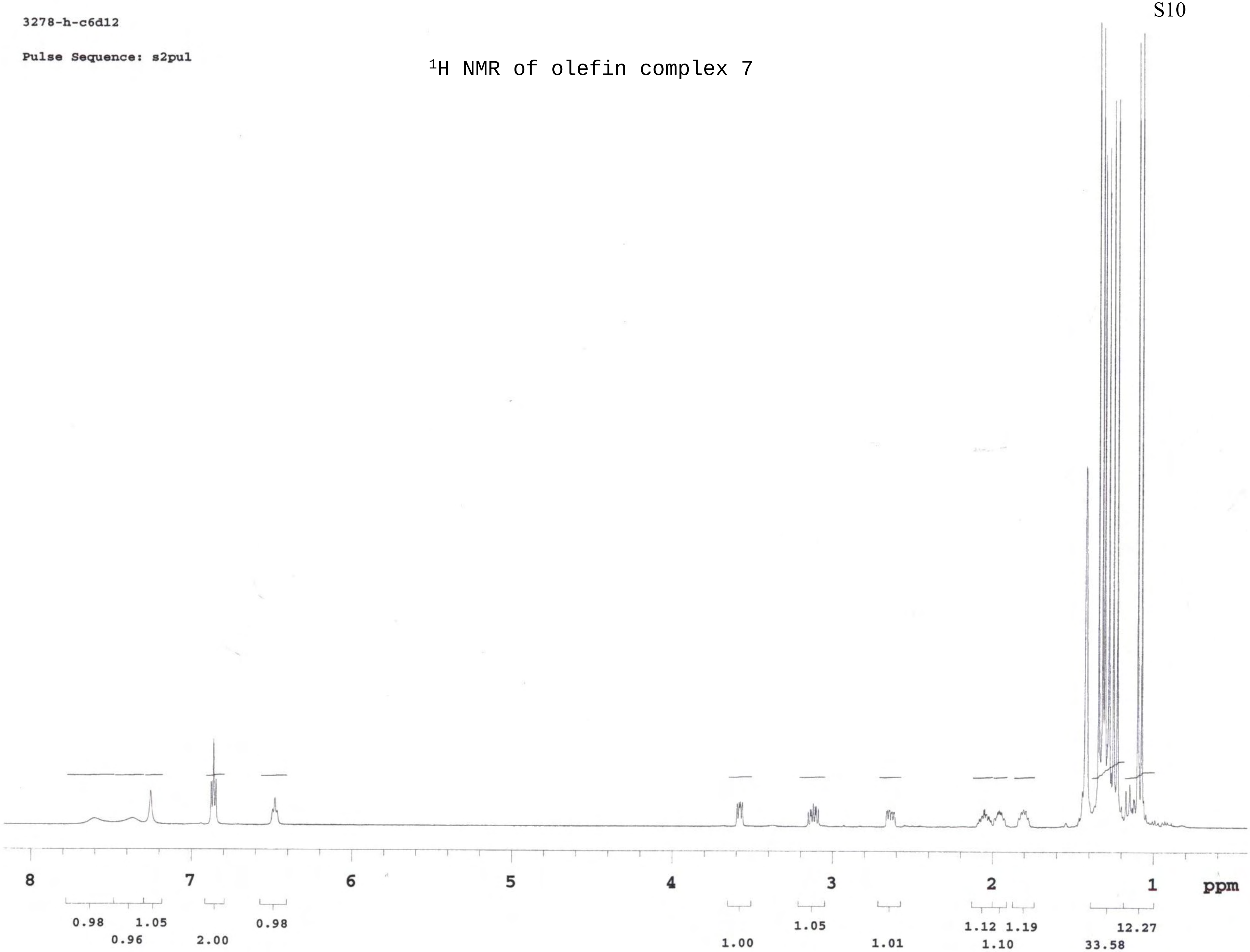
^{31}P NMR of olefin complex 7



¹H NMR of olefin complex 7



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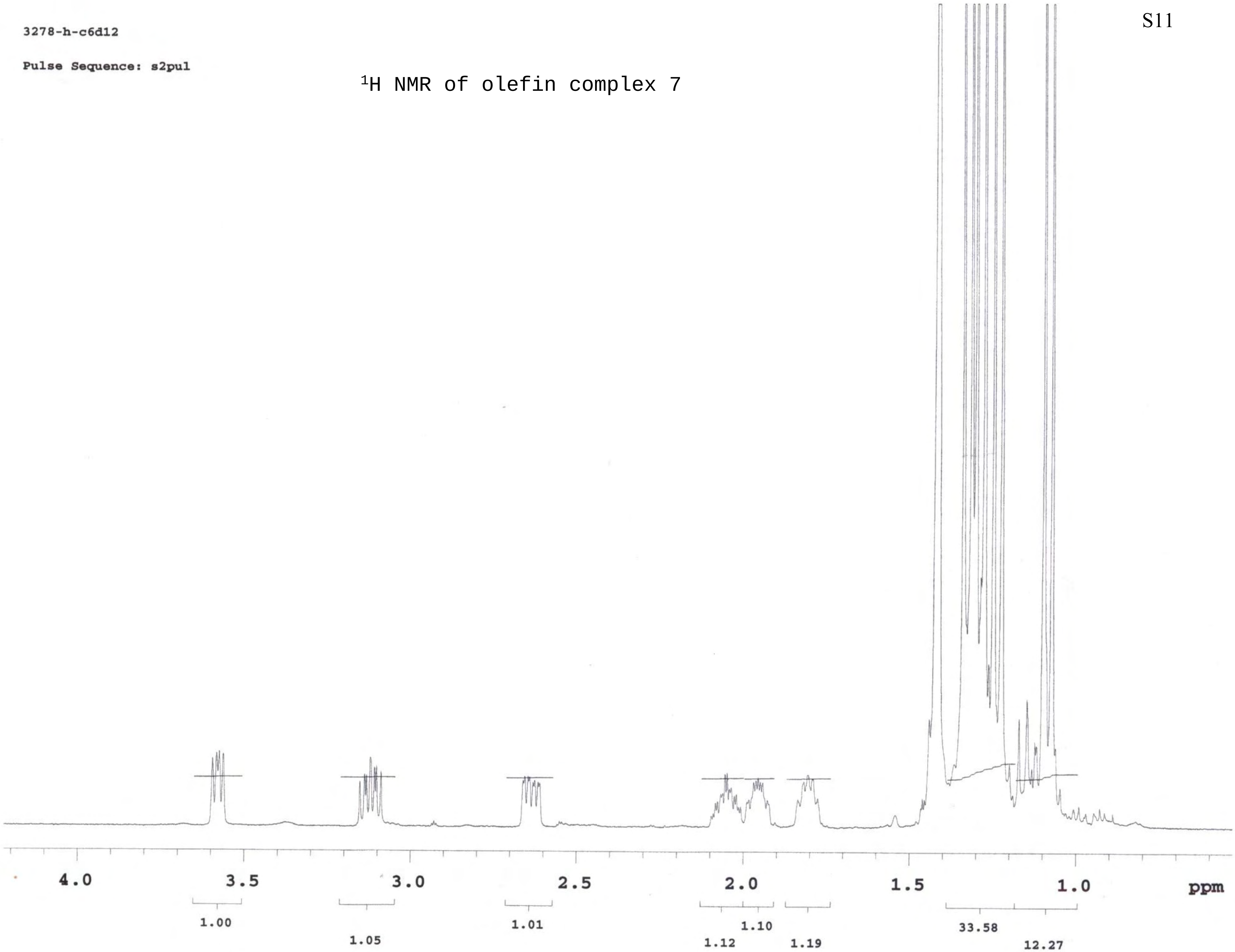

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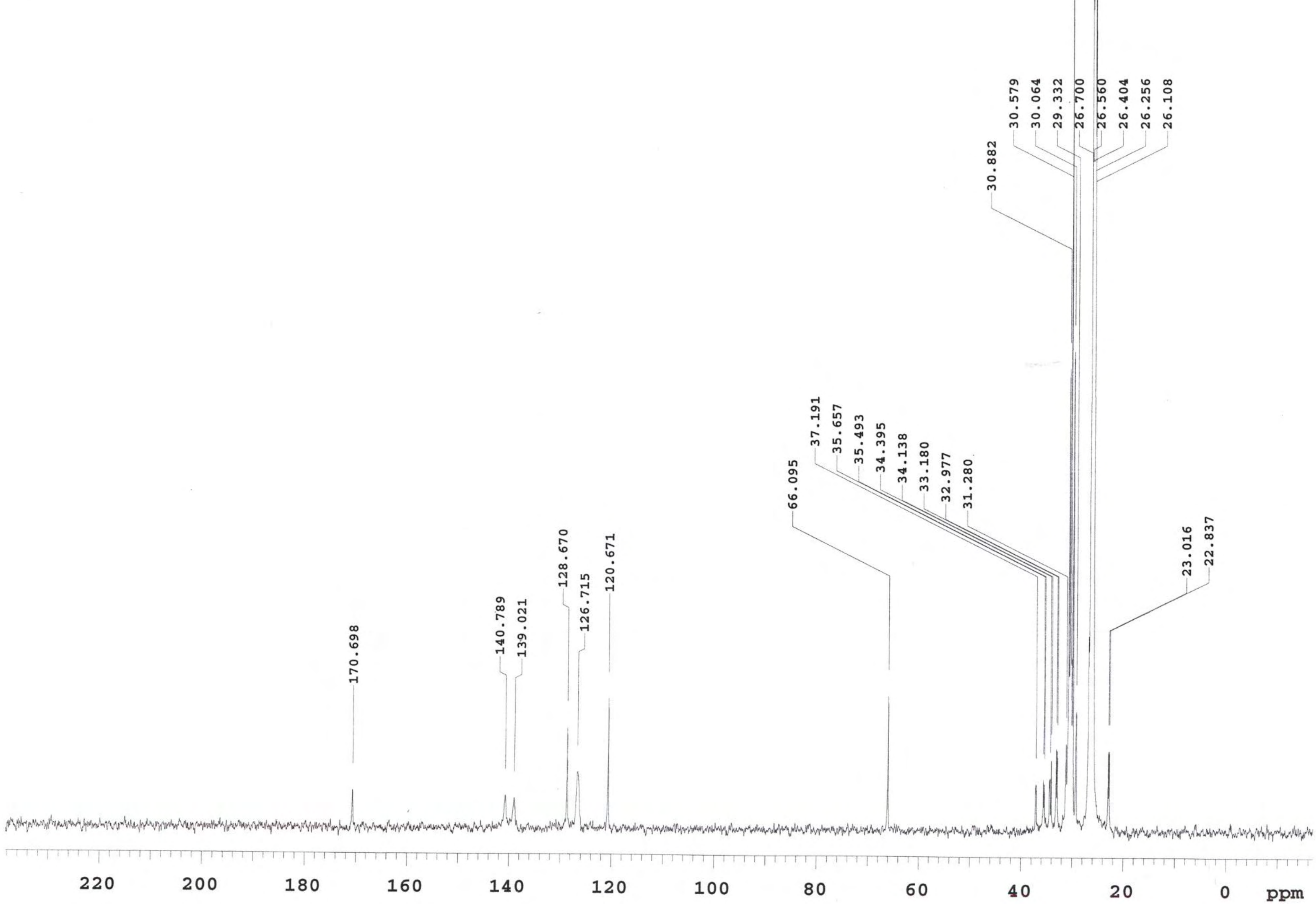

3278-c-c6d12

Pulse Sequence: s2pul

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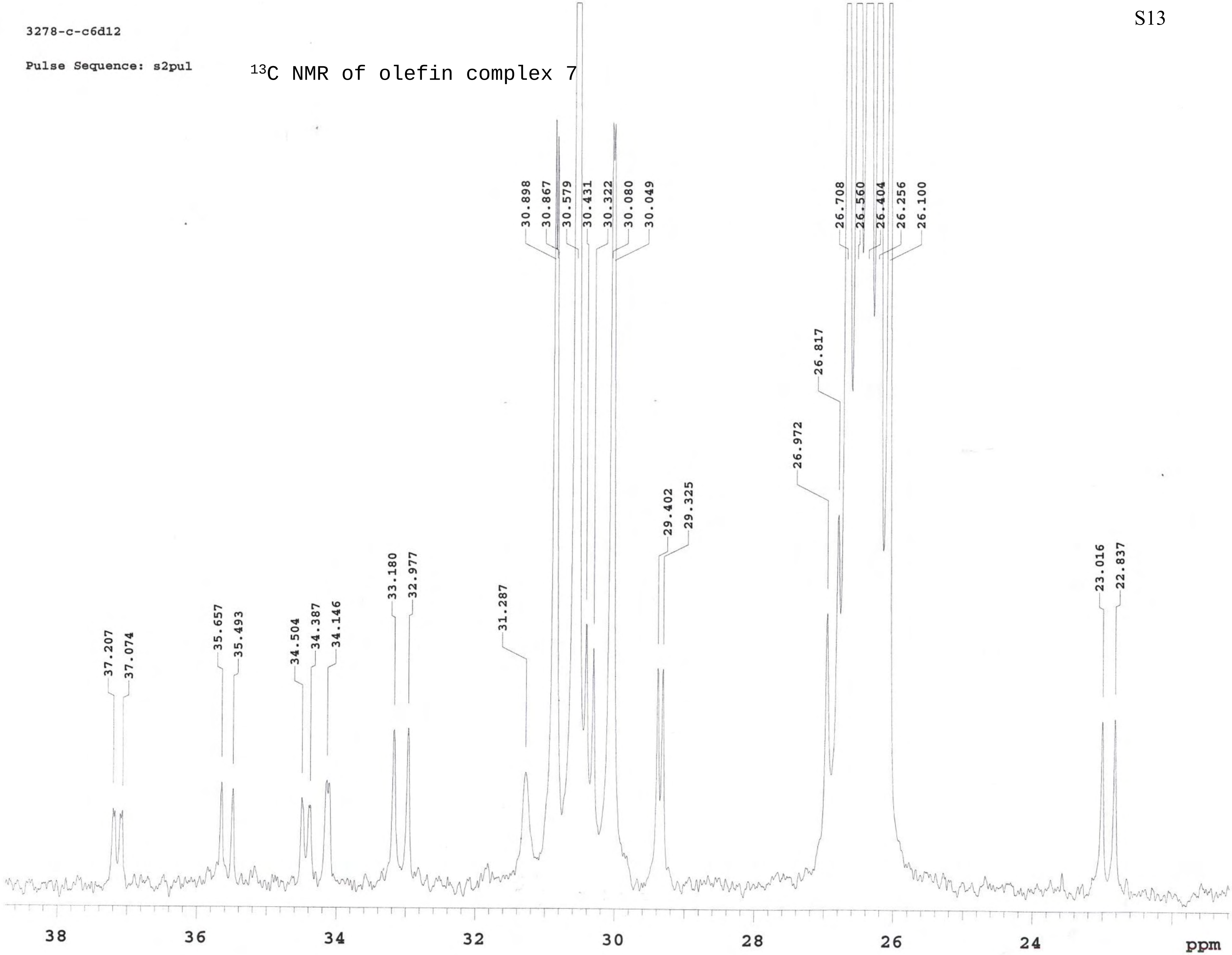

5131-dept135

Pulse Sequence: dept

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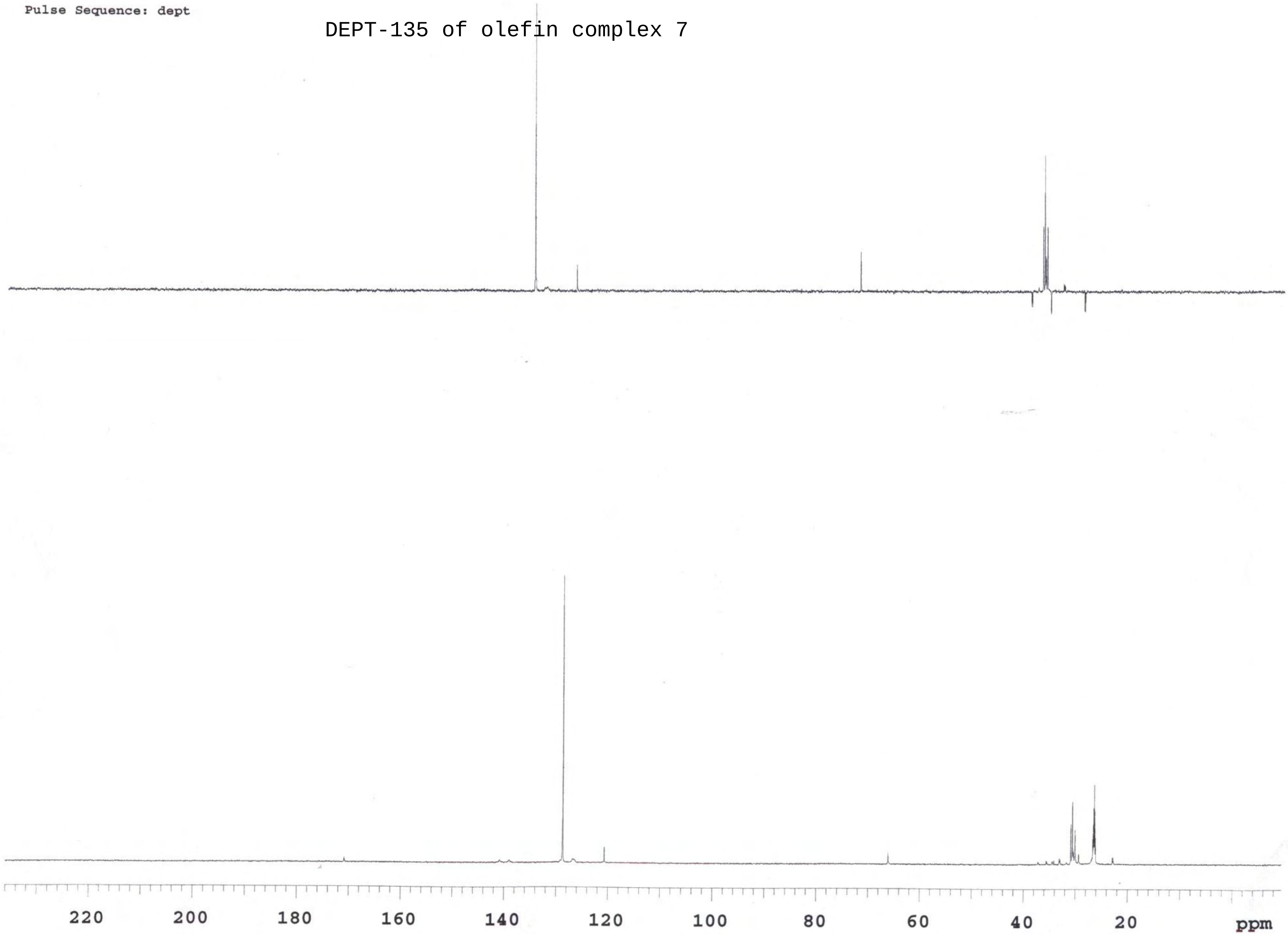
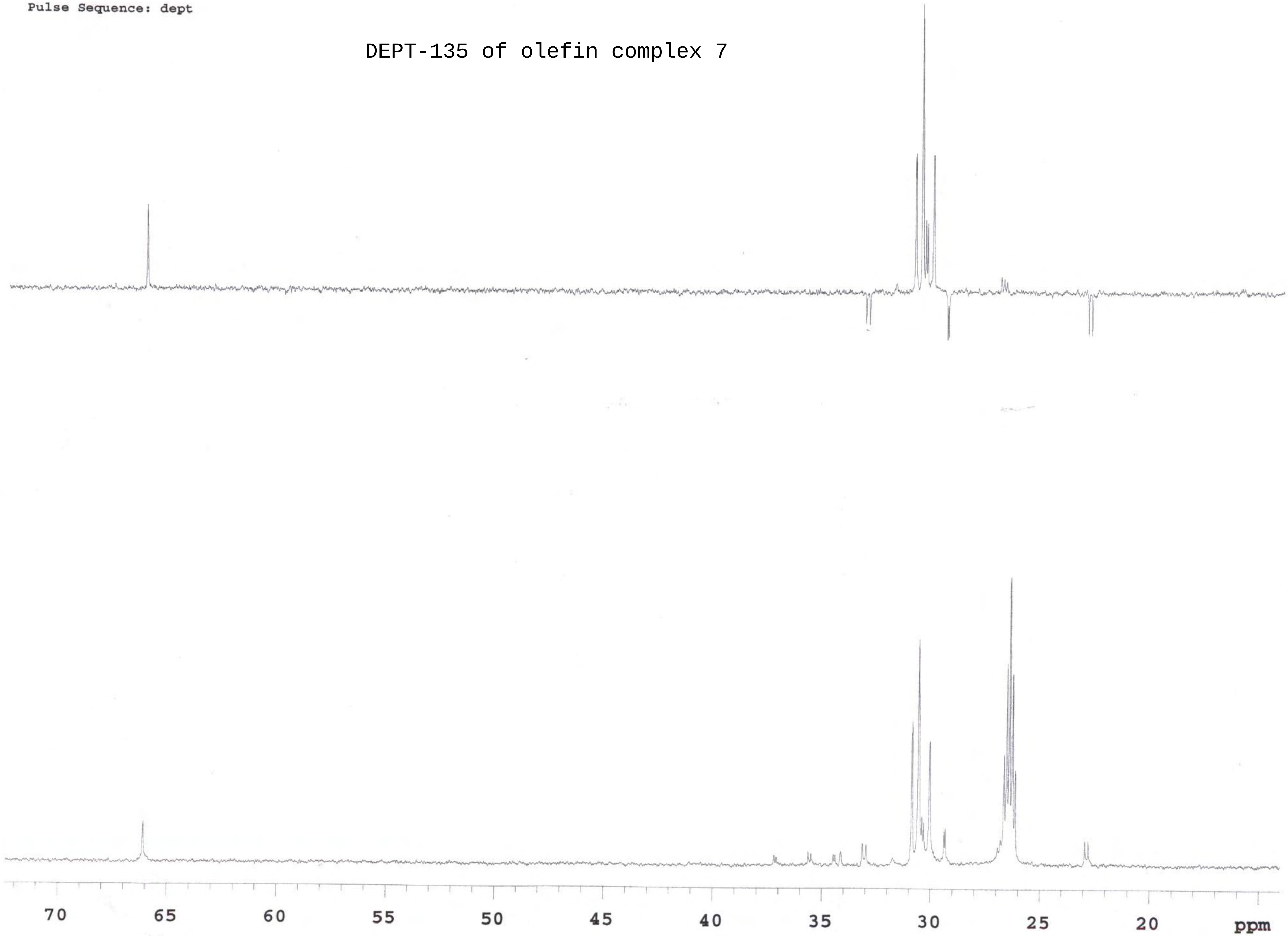


5131-dept135

Pulse Sequence: dept

DEPT-135 of olefin complex 7



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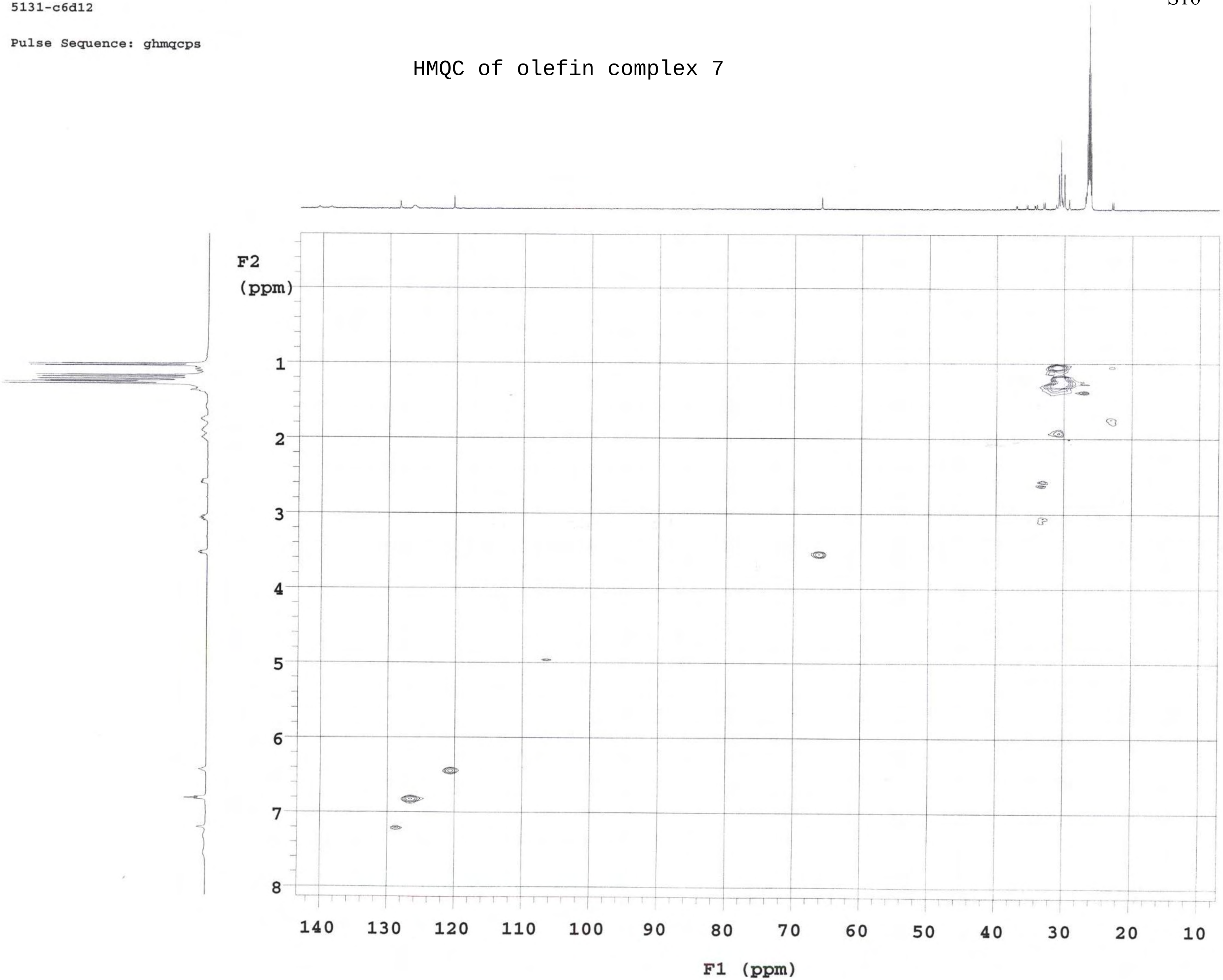

5131-c6d12

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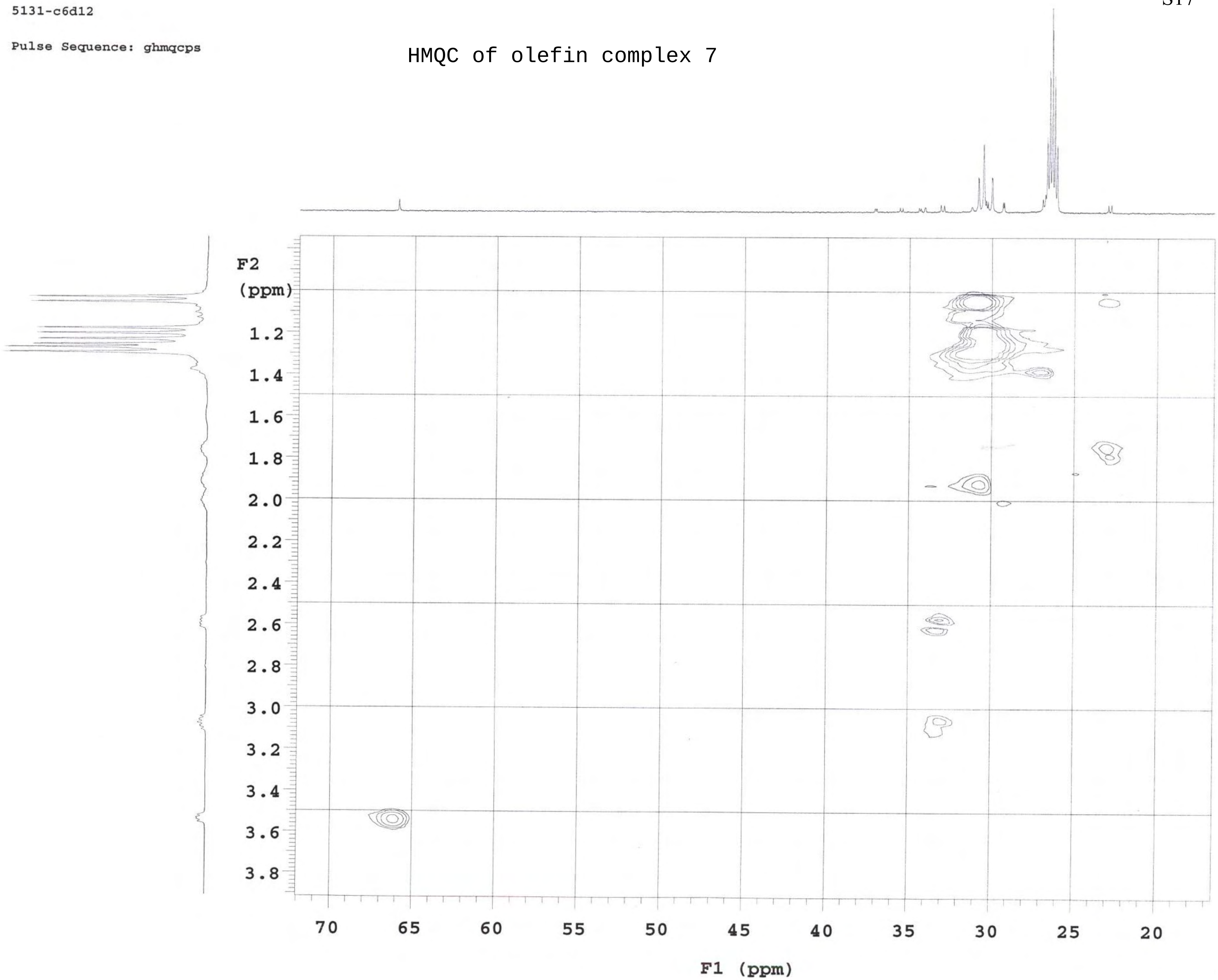

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2D Width 4070.8 Hz
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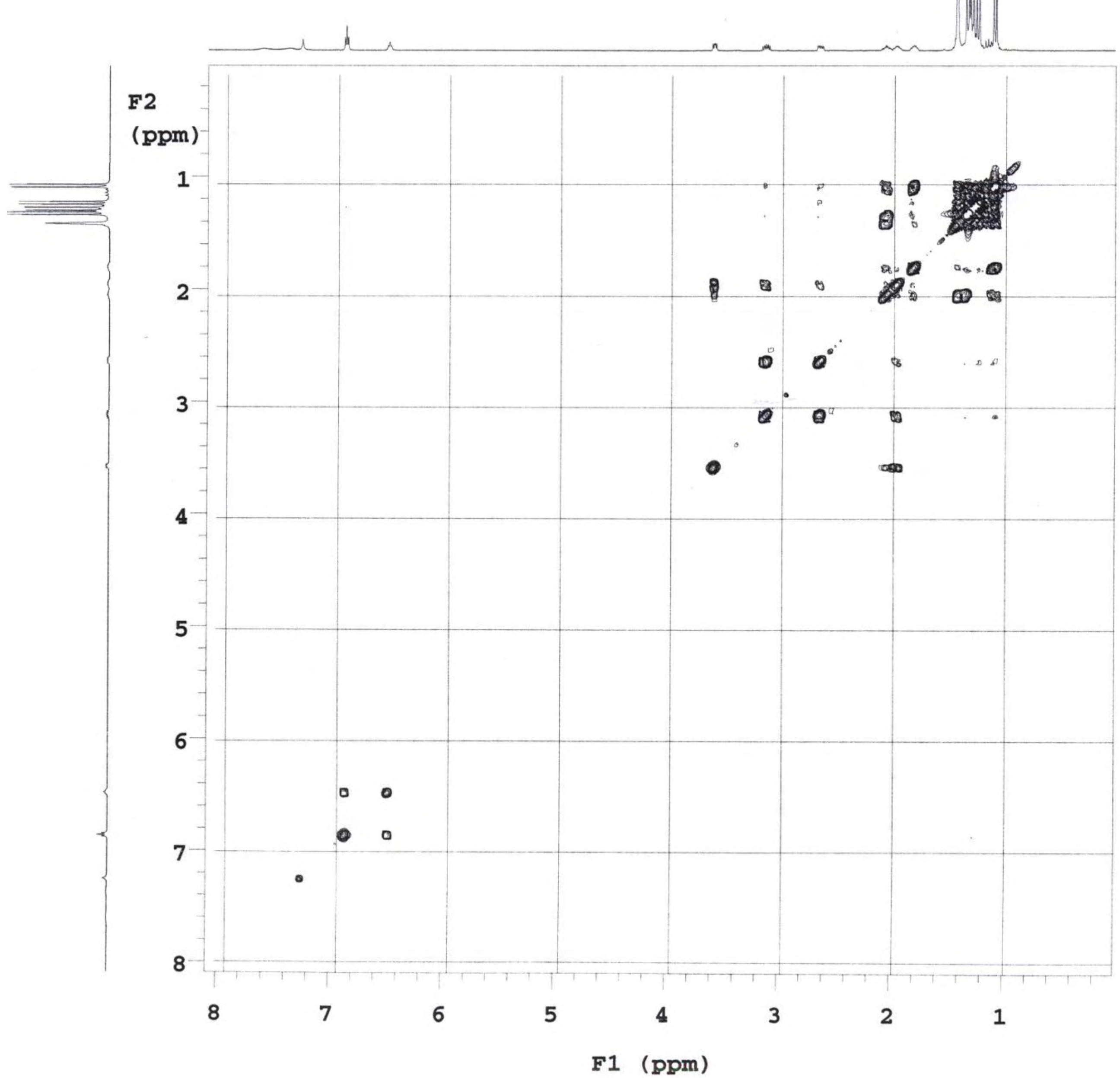
COSY of olefin complex 7



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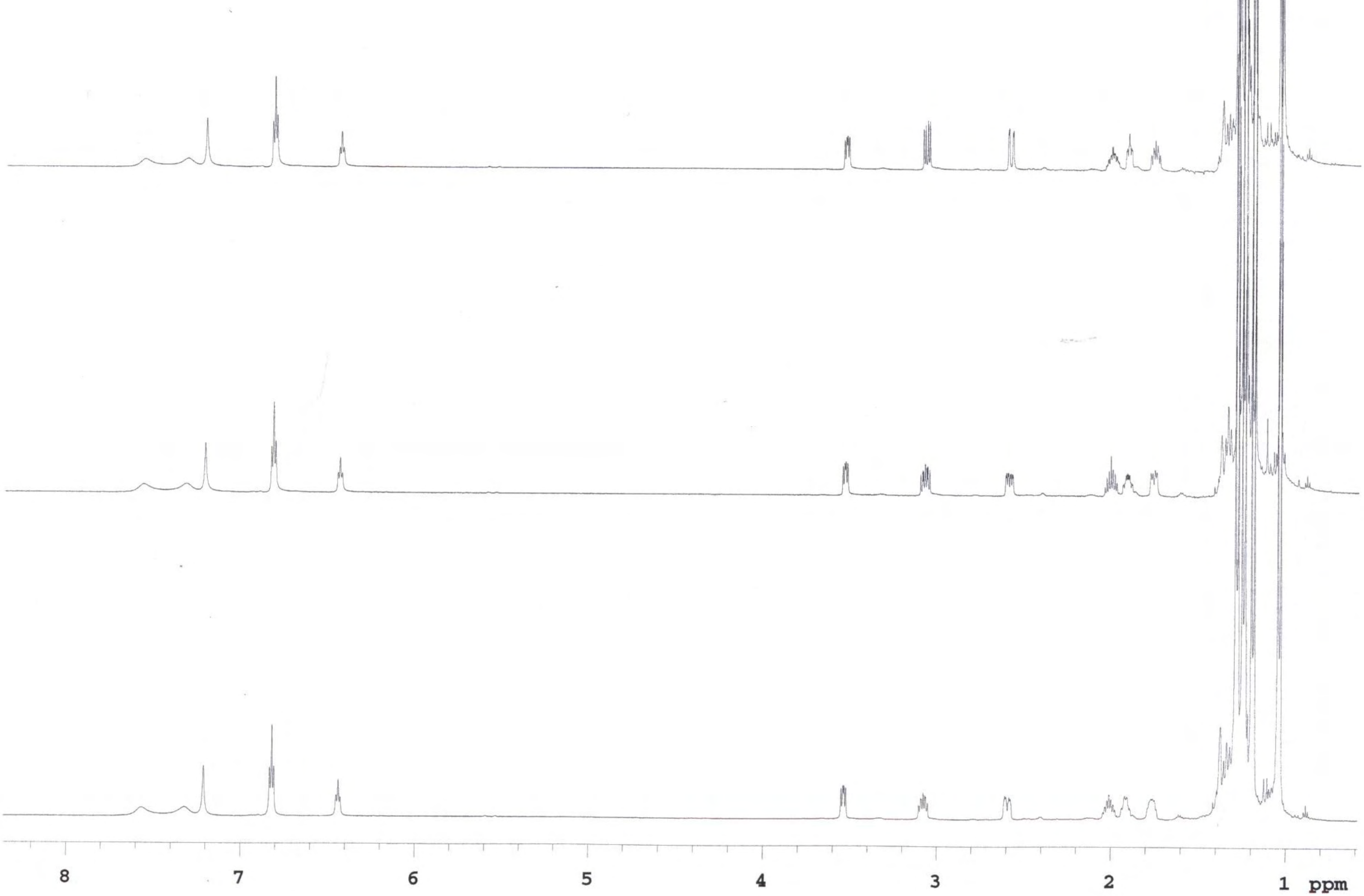
Pulse Sequence: s2pul

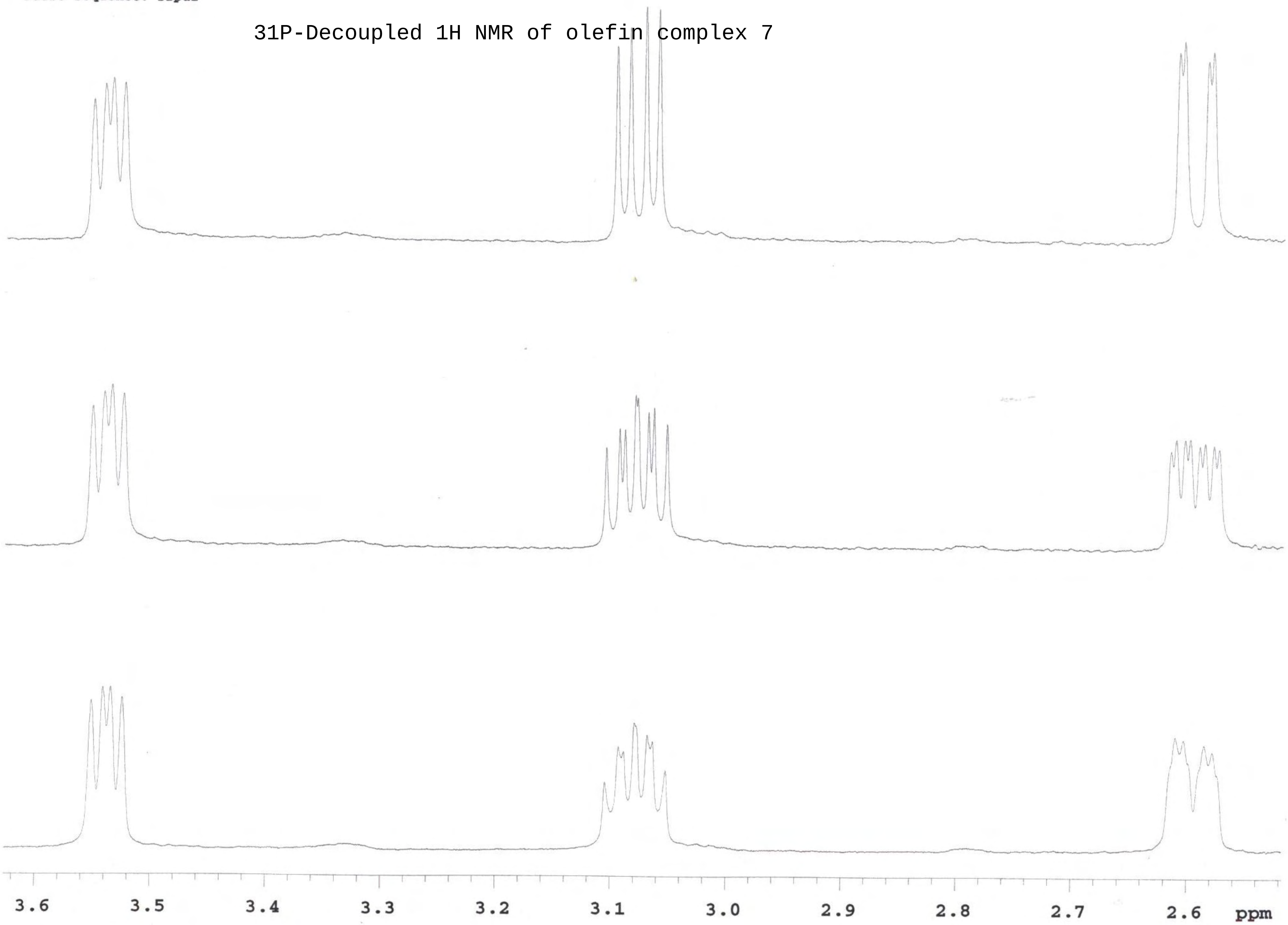
^{31}P-Decoupled ^{1}H NMR of olefin complex 7



irradiation at 0, 66, -33 ppm; bottom-up

Pulse Sequence: s2pul

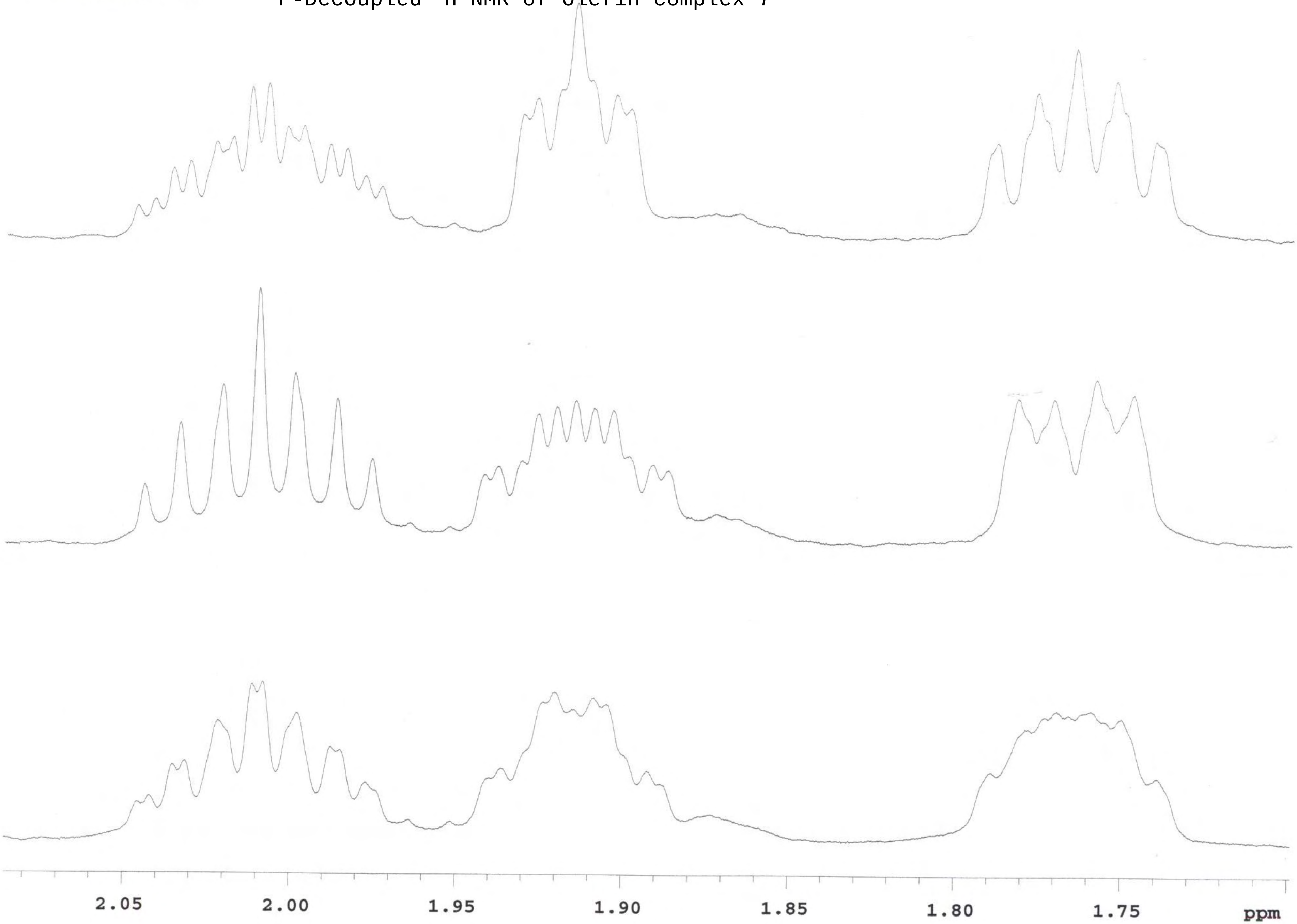
31P-Decoupled 1H NMR of olefin complex 7



irradiation at 0, 66, -33 ppm; bottom-up

Pulse Sequence: s2pul

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



irradiation at 0, 66, -33 ppm; bottom-up

Pulse Sequence: s2pul

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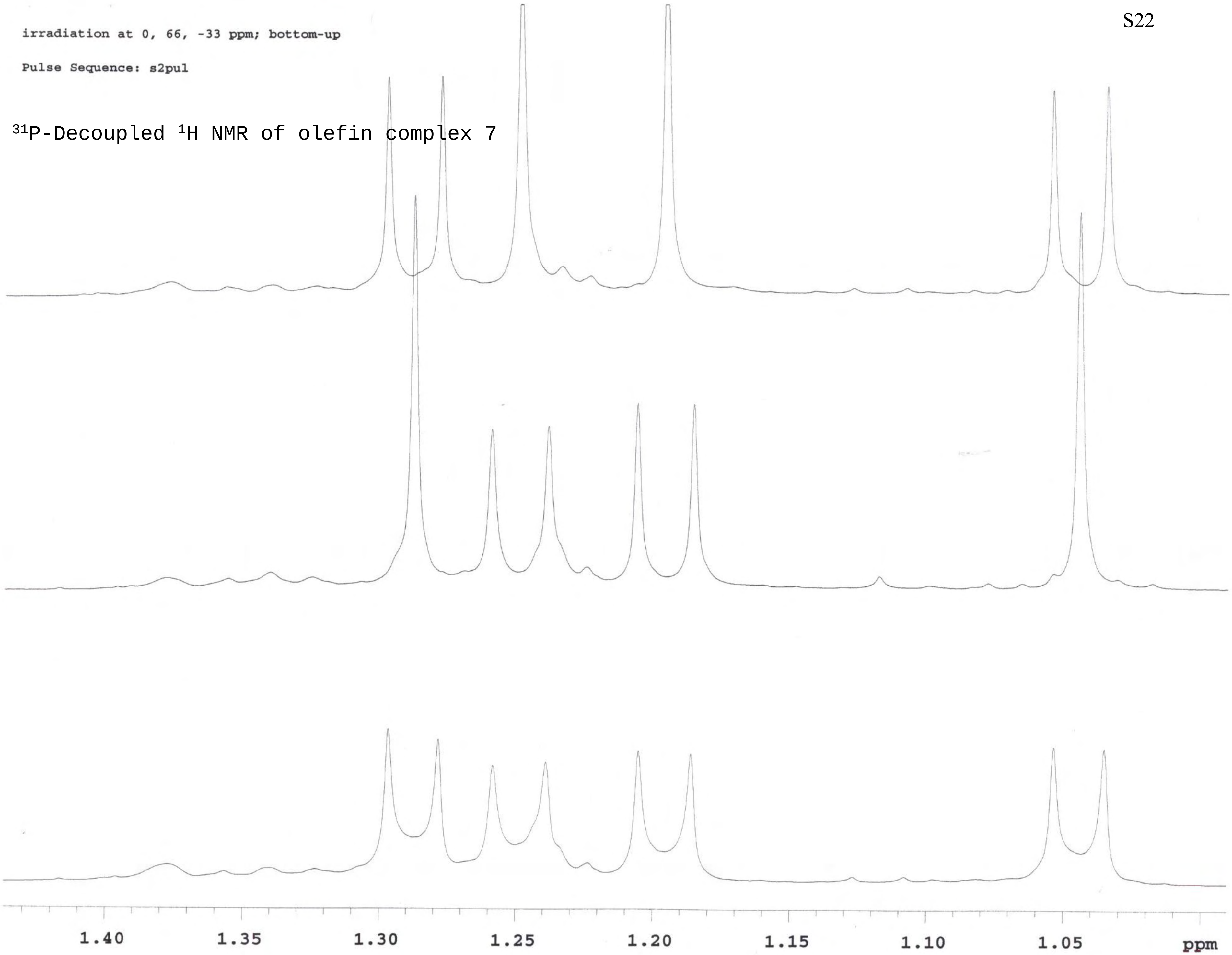
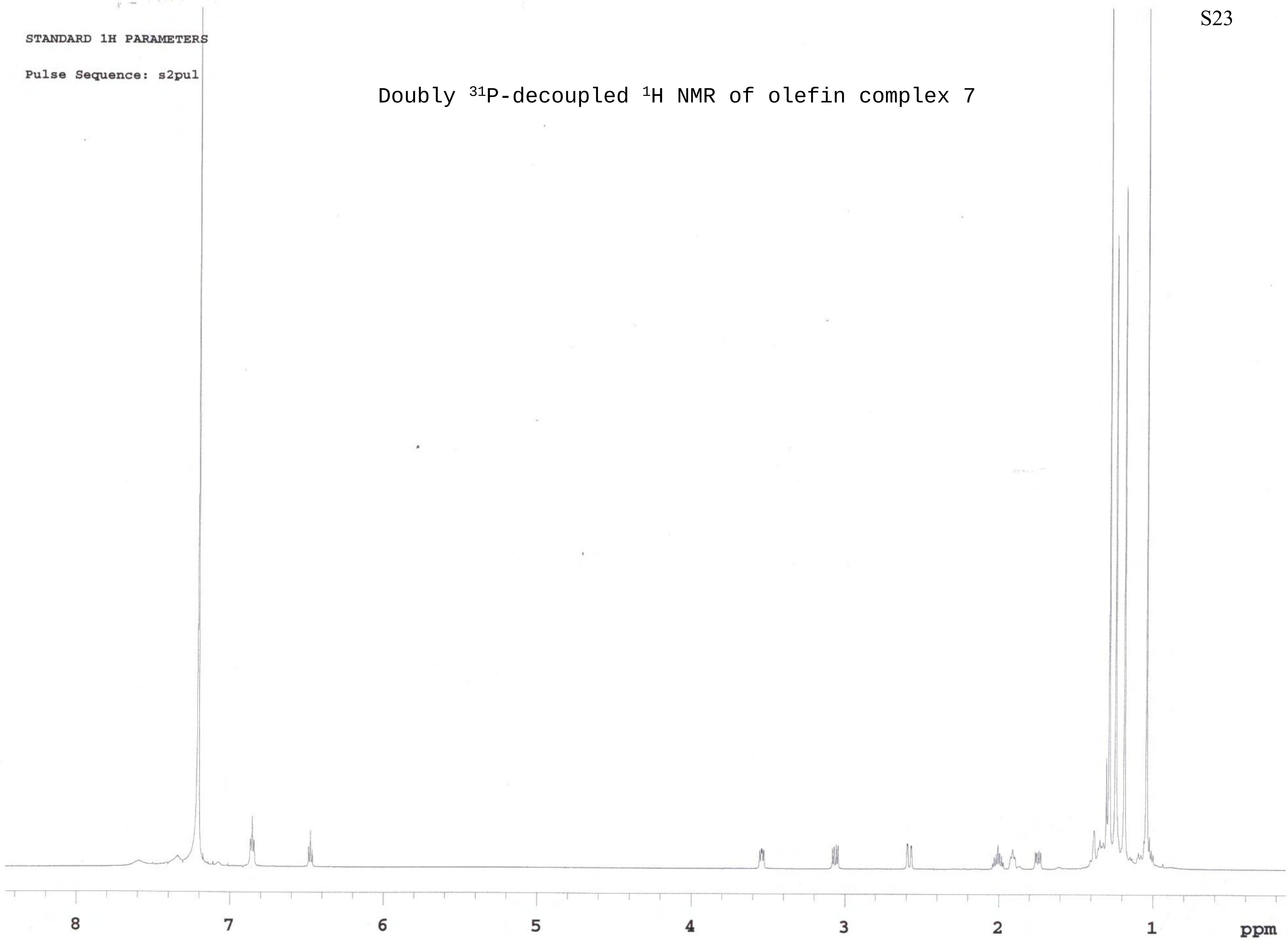


STANDARD 1H PARAMETERS

Pulse Sequence: s2pul

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



STANDARD 1H PARAMETERS

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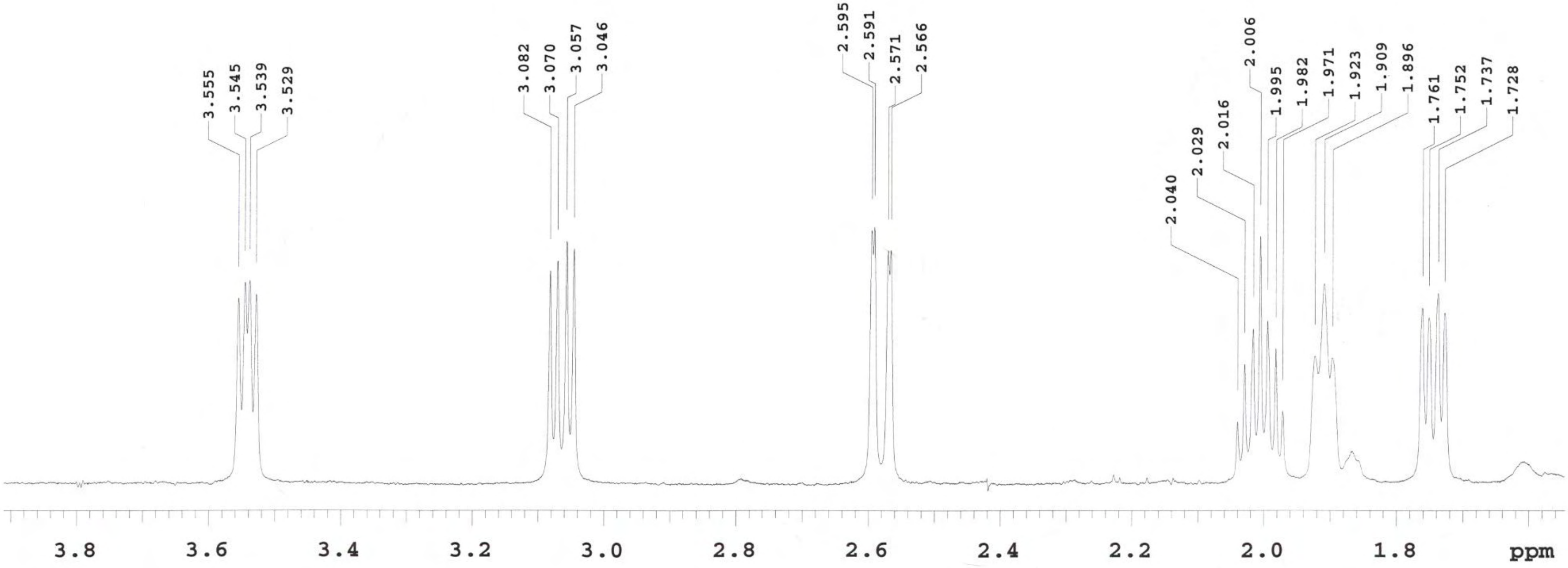

STANDARD 1H PARAMETERS

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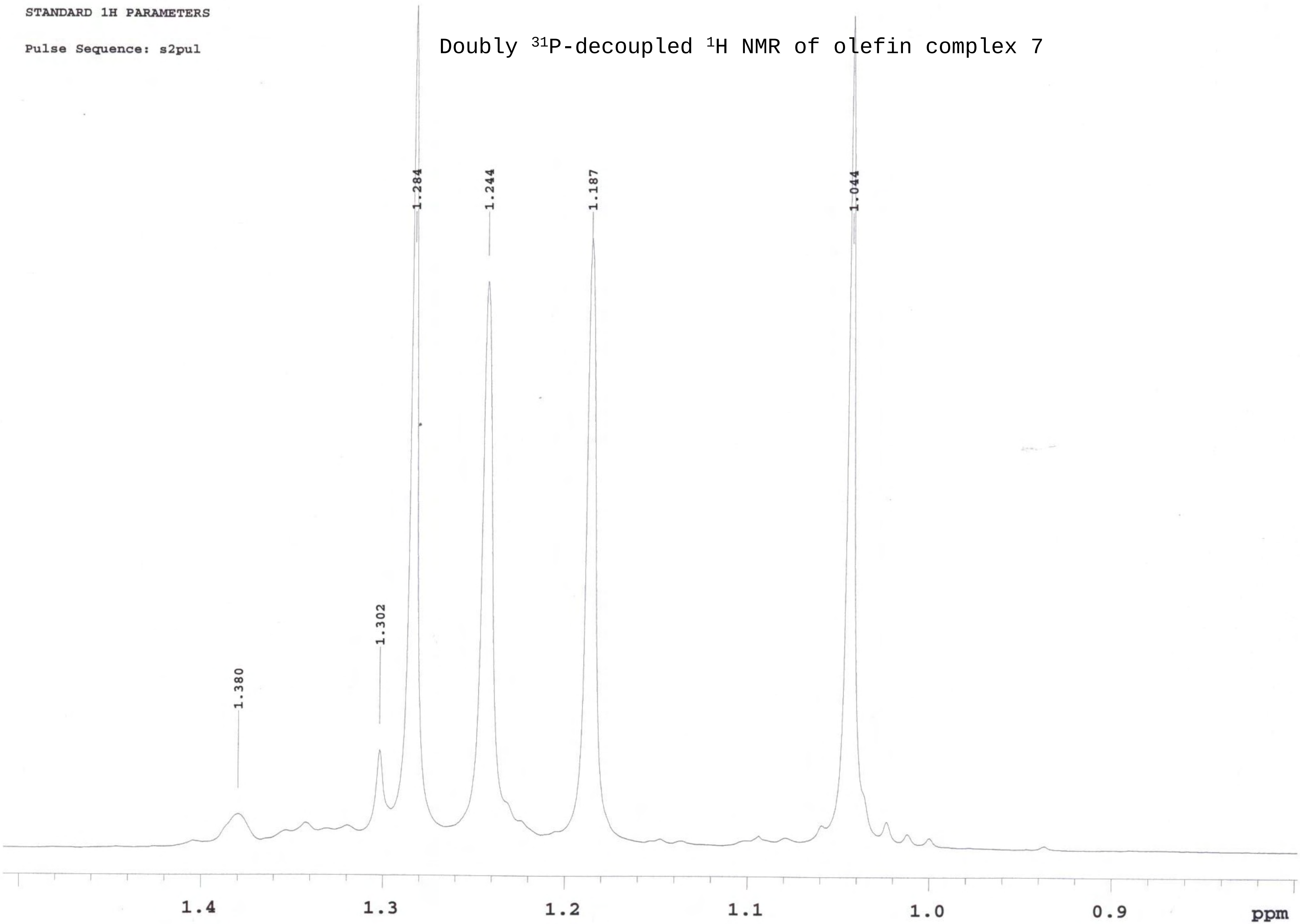
Doubly ^{31}P-decoupled ^{1}H NMR of olefin complex 7



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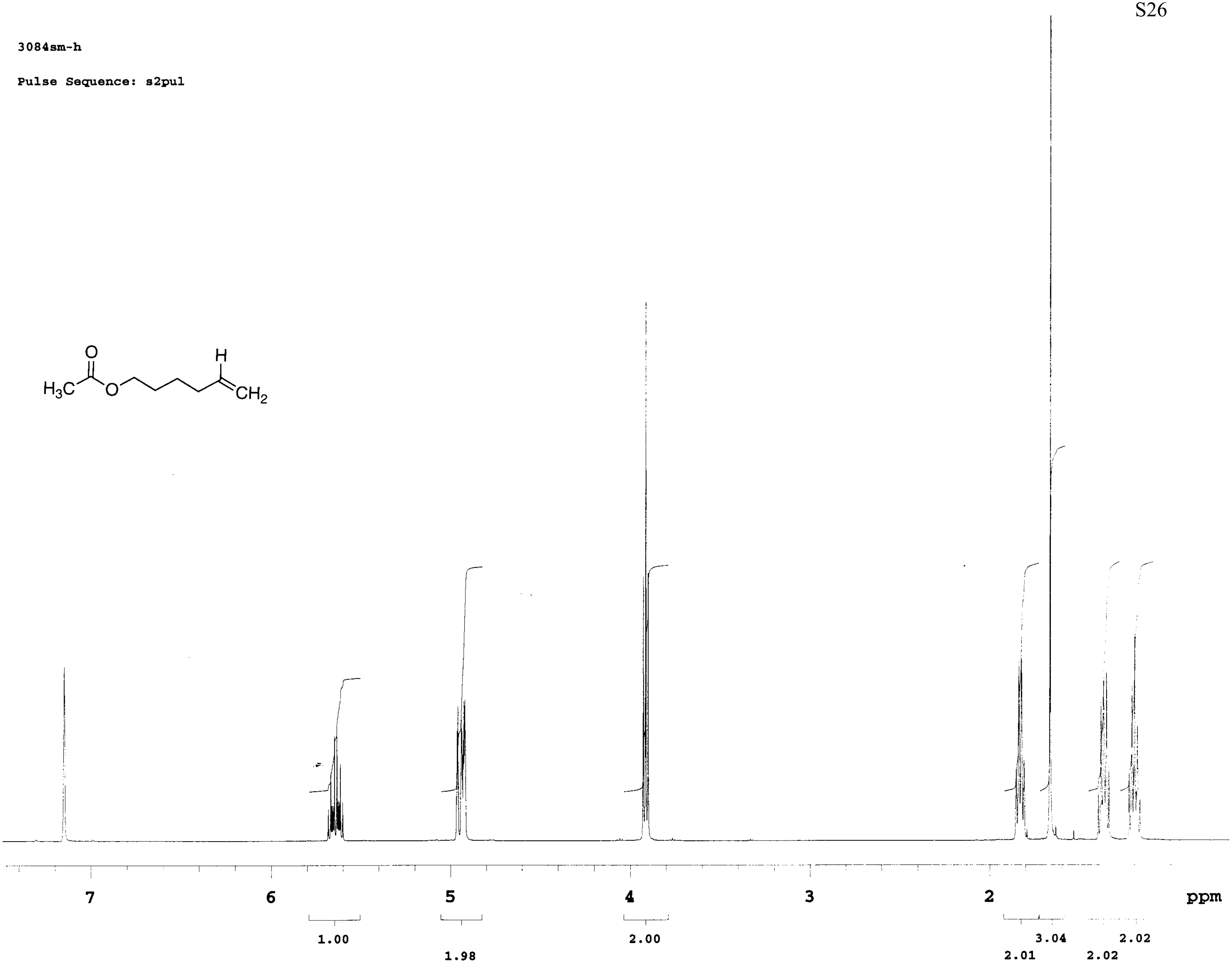

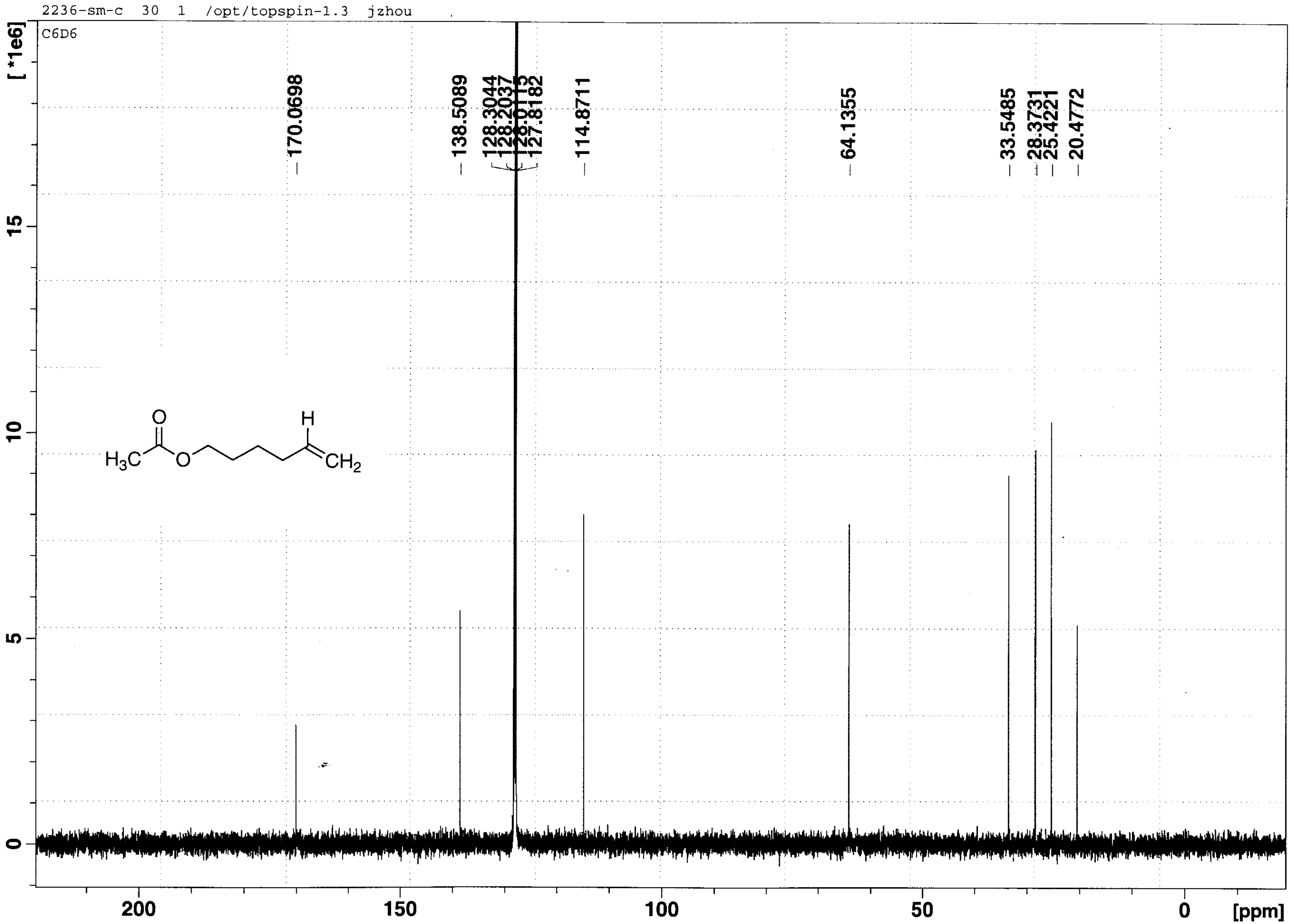
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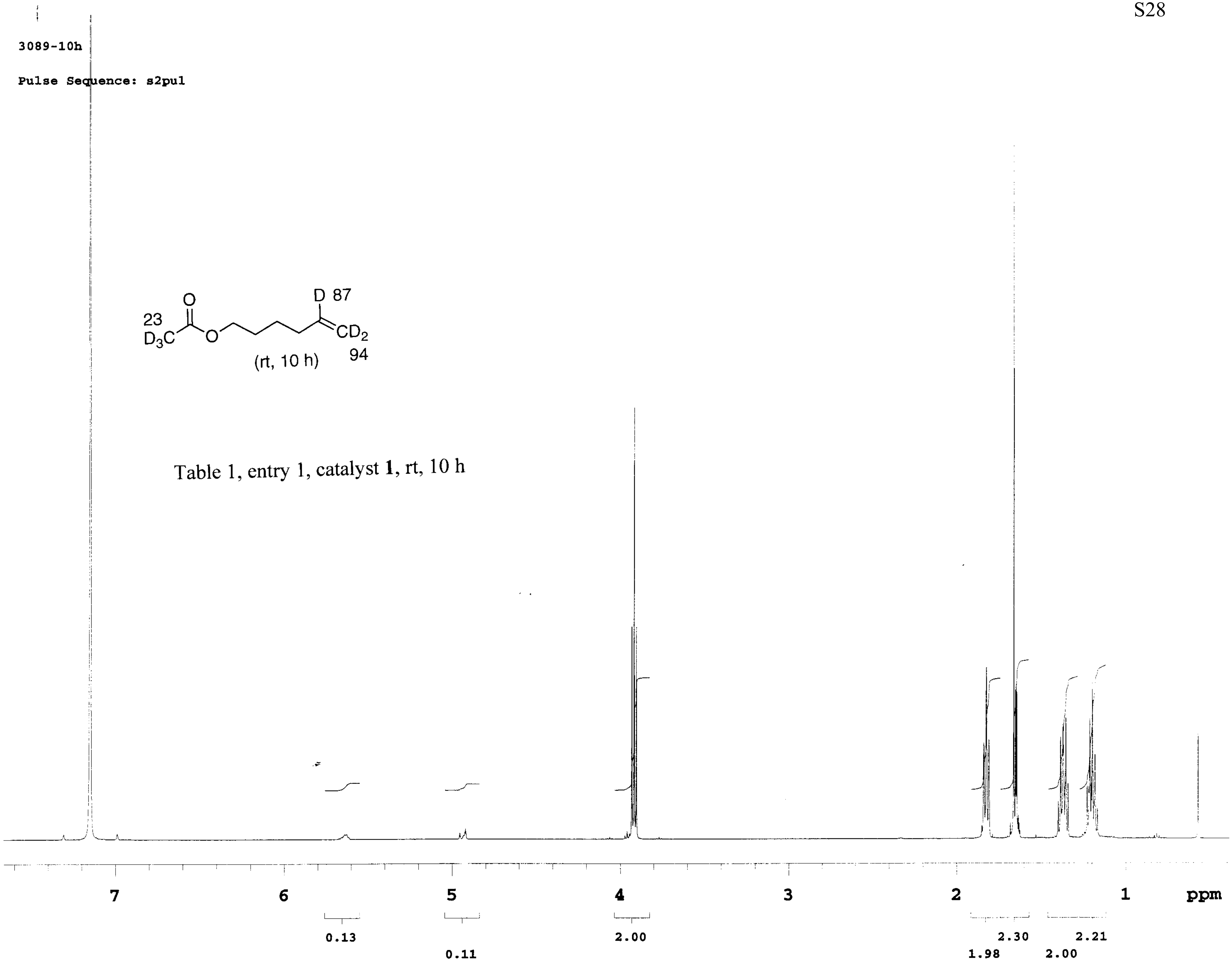

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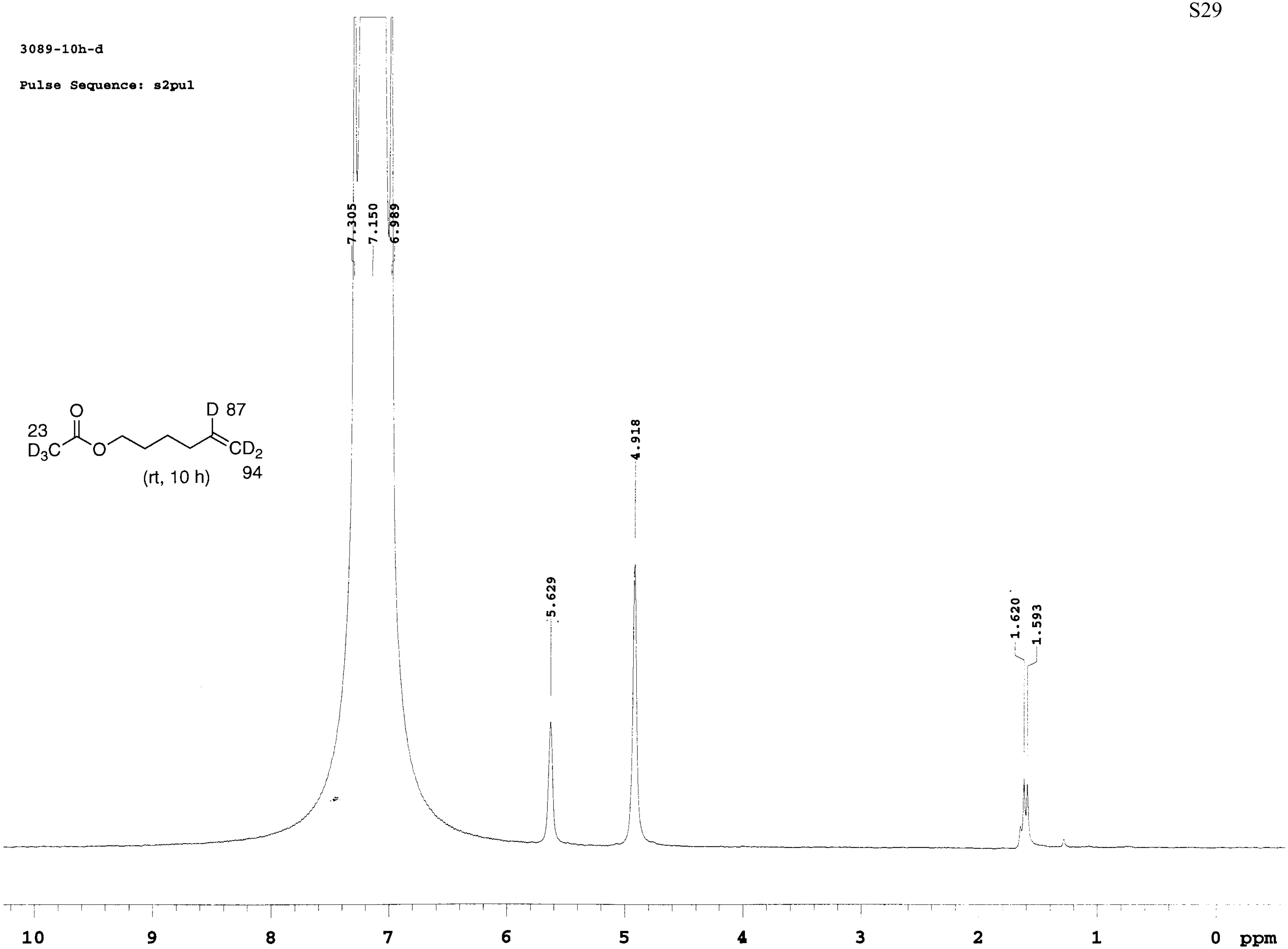
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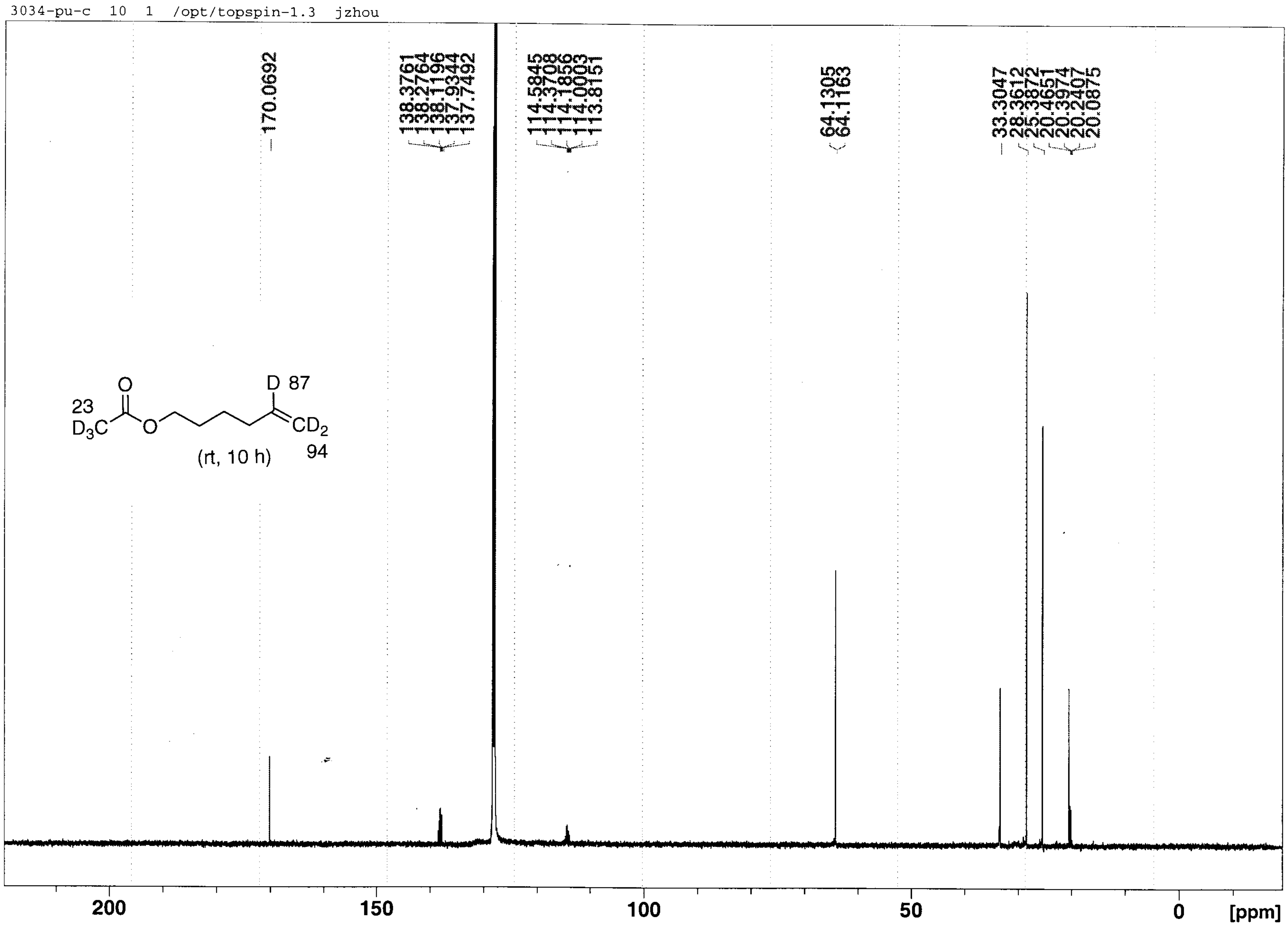
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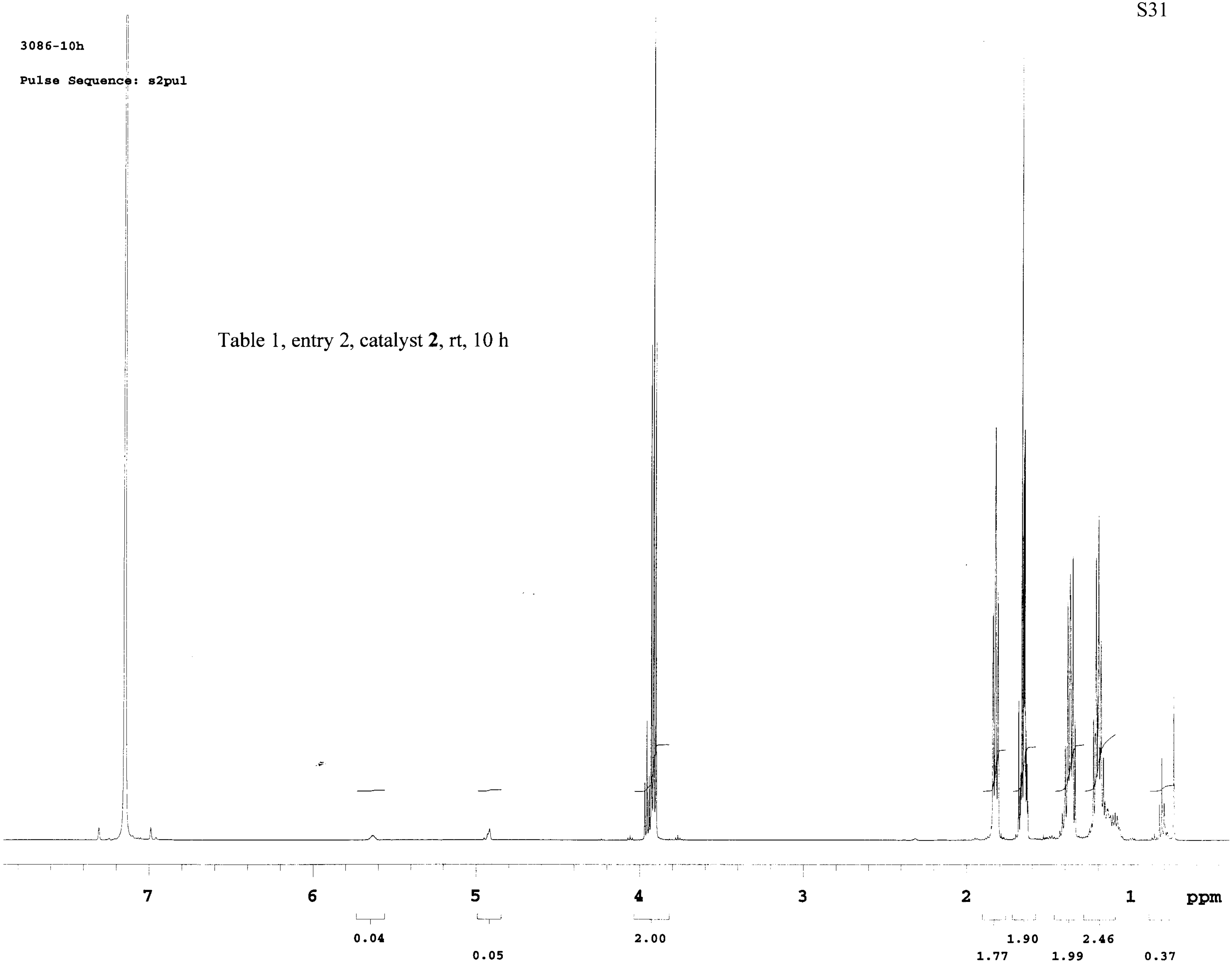

3095-3h-h

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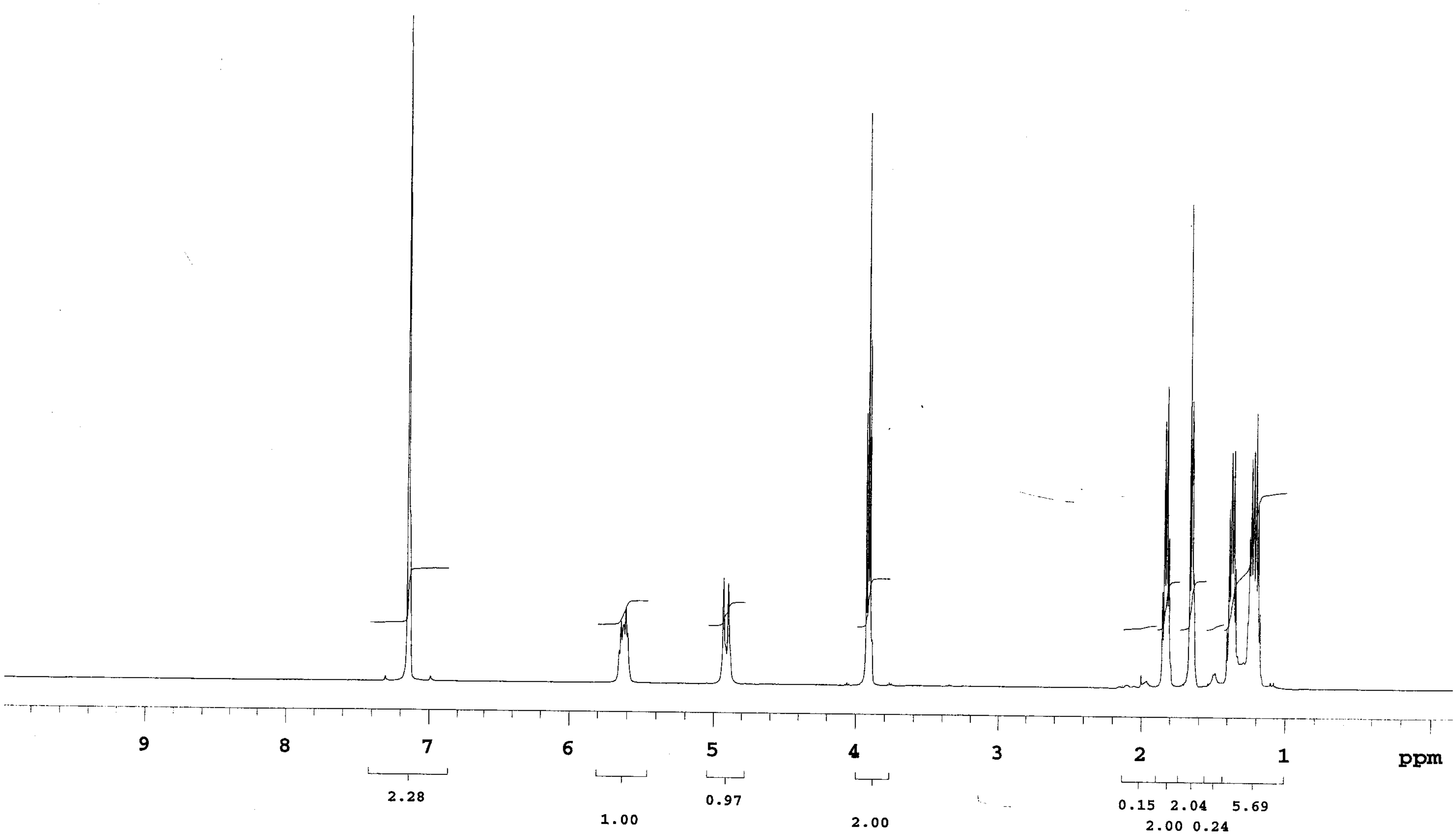

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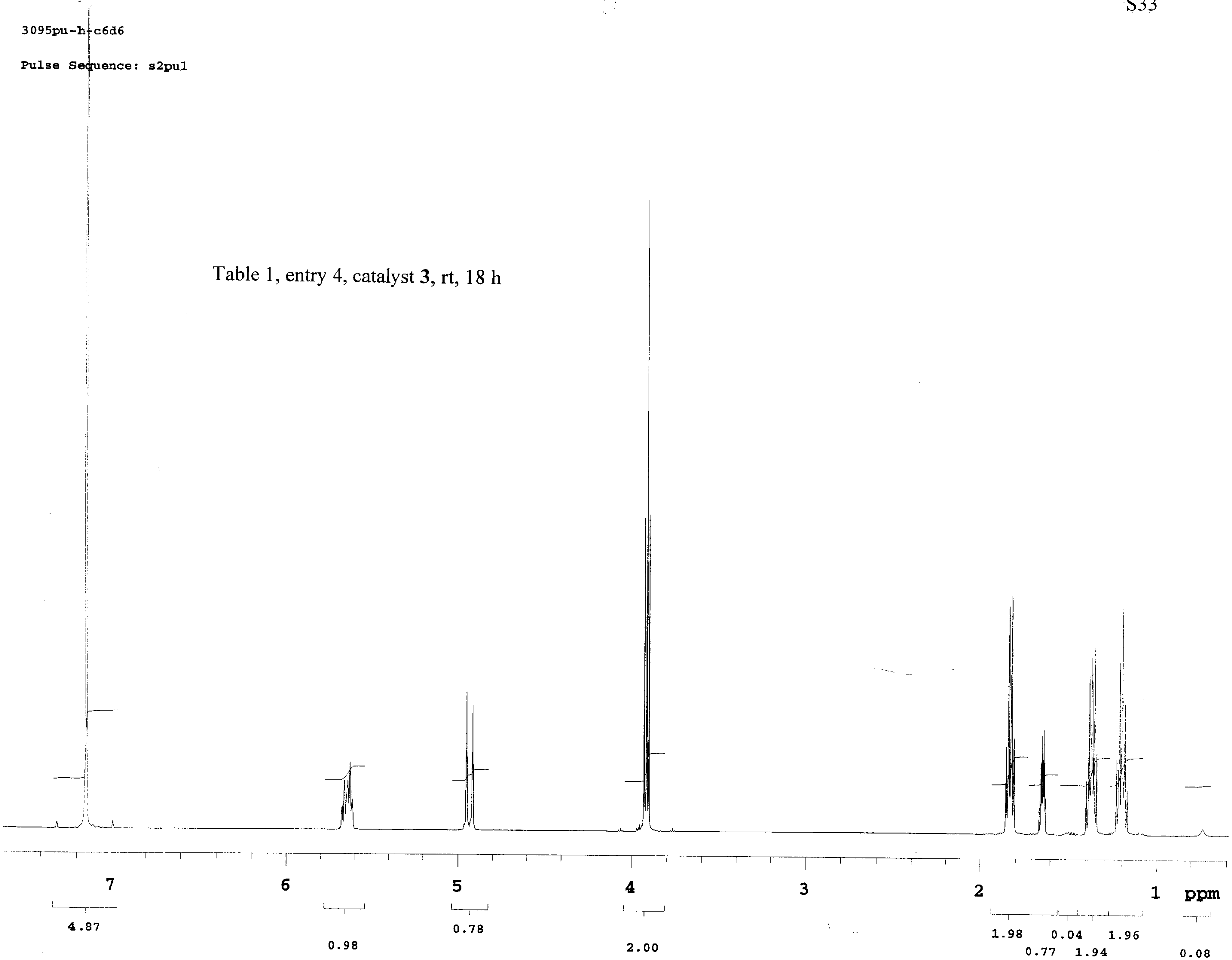
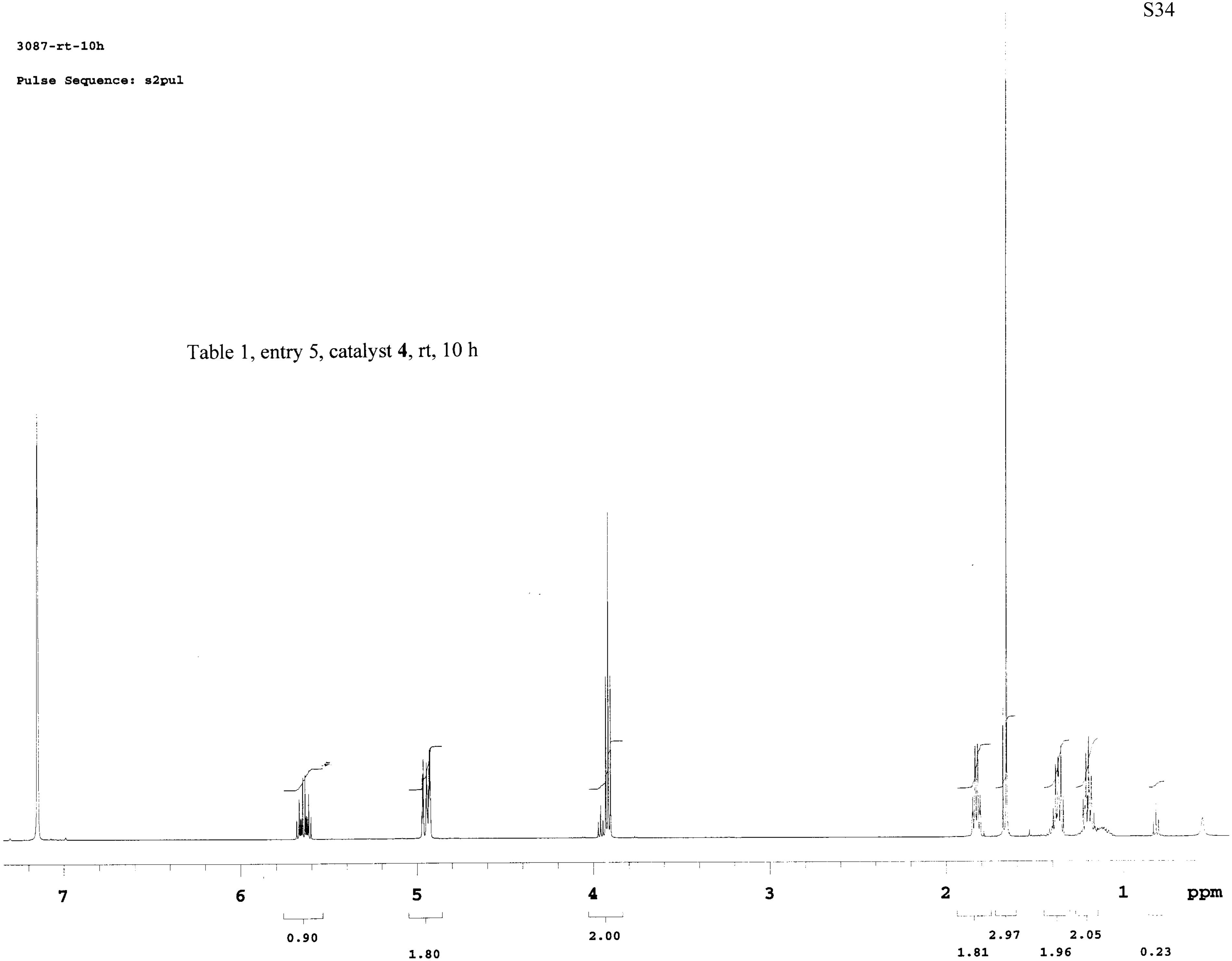
Table 1, entry 4, catalyst **3**, rt, 18 h

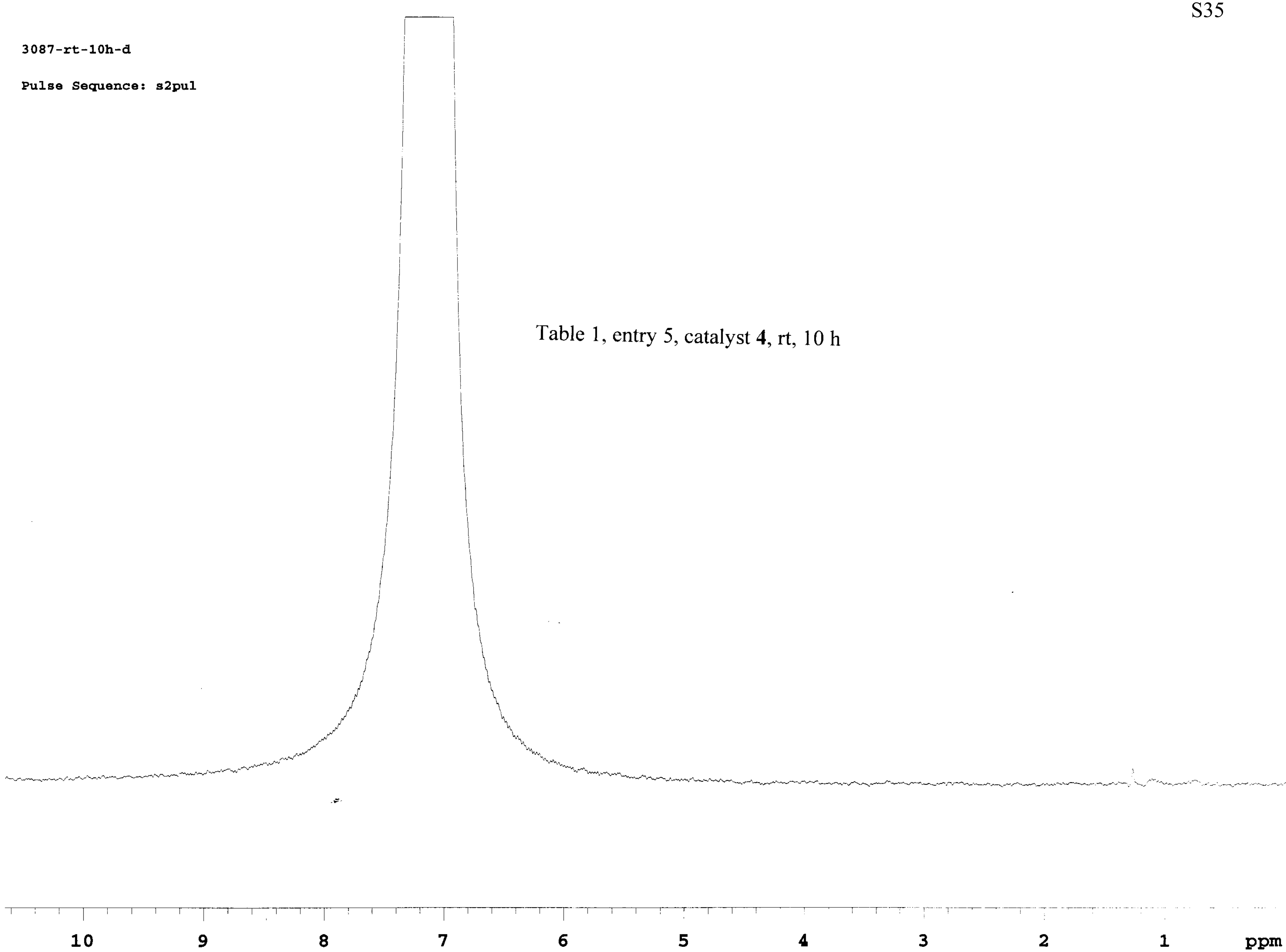


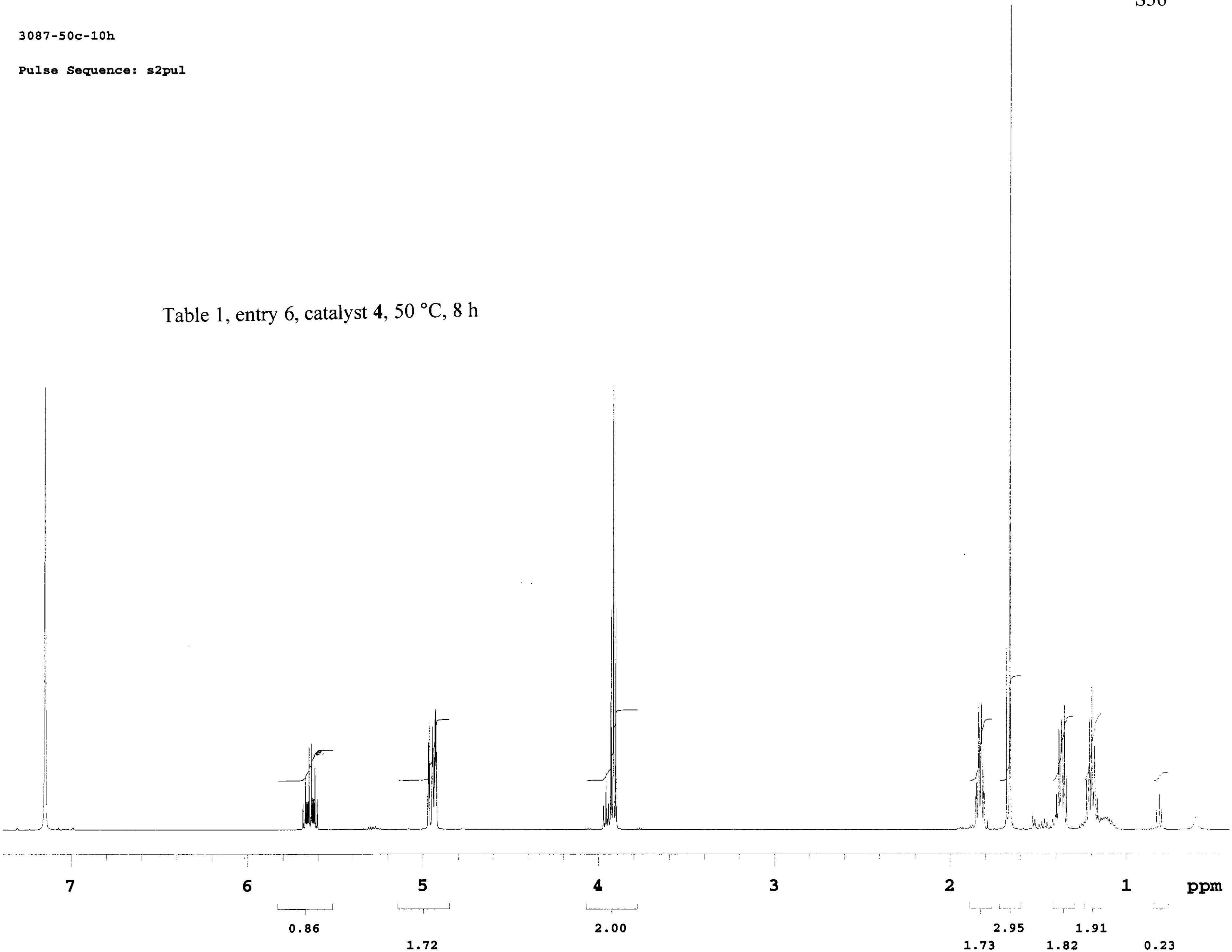
3087-rt-10h

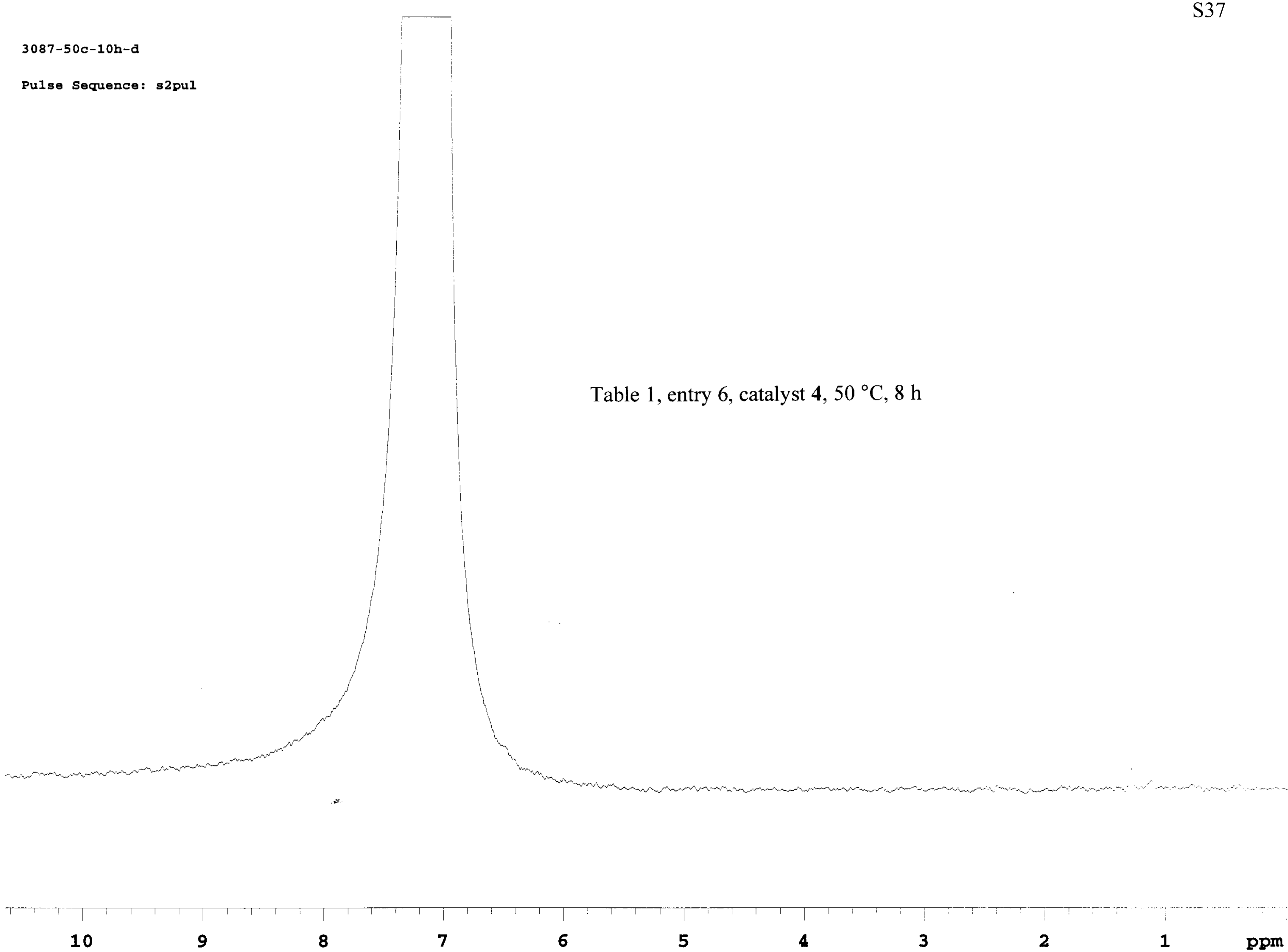
Pulse Sequence: s2pul

Table 1, entry 5, catalyst **4**, rt, 10 h




3087-rt-10h-d
Pulse Sequence: s2pul
Table 1, entry 5, catalyst 4, rt, 10 h
10
9
8
7
6
5
4
3
2
1
ppm


3087-50c-10h
Pulse Sequence: s2pul
Table 1, entry 6, catalyst **4**, 50 °C, 8 h
7
6
5
4
3
2
1
ppm
0.86
1.72
2.00
2.95
1.91
1.73
1.82
0.23


3087-50c-10h-d
Pulse Sequence: s2pul
Table 1, entry 6, catalyst **4**, 50 °C, 8 h
10
9
8
7
6
5
4
3
2
1
ppm

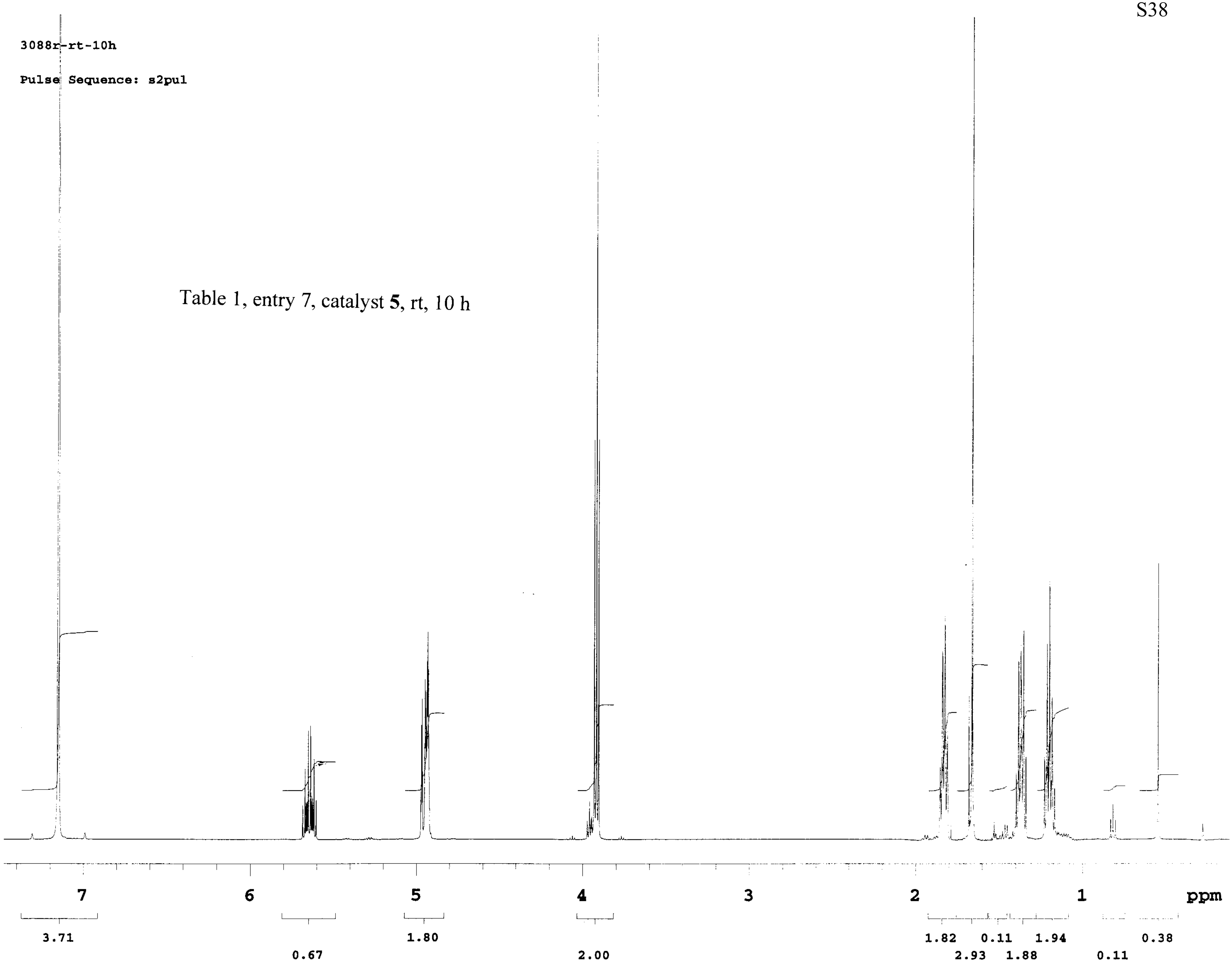


Table 1, entry 7, catalyst **5**, rt, 10 h

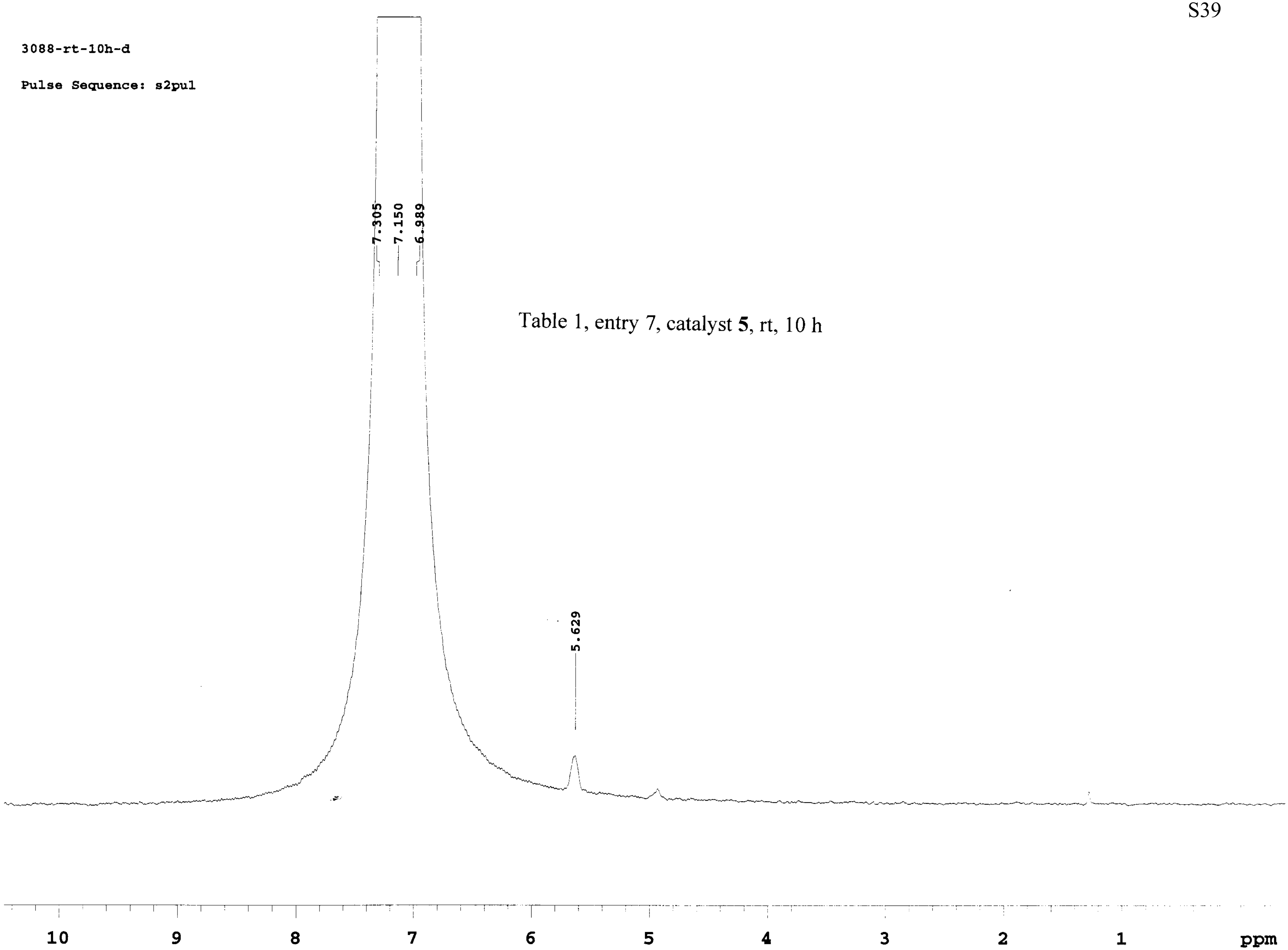


Table 1, entry 7, catalyst **5**, rt, 10 h

3088-50c-10h

Pulse Sequence: s2pul

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

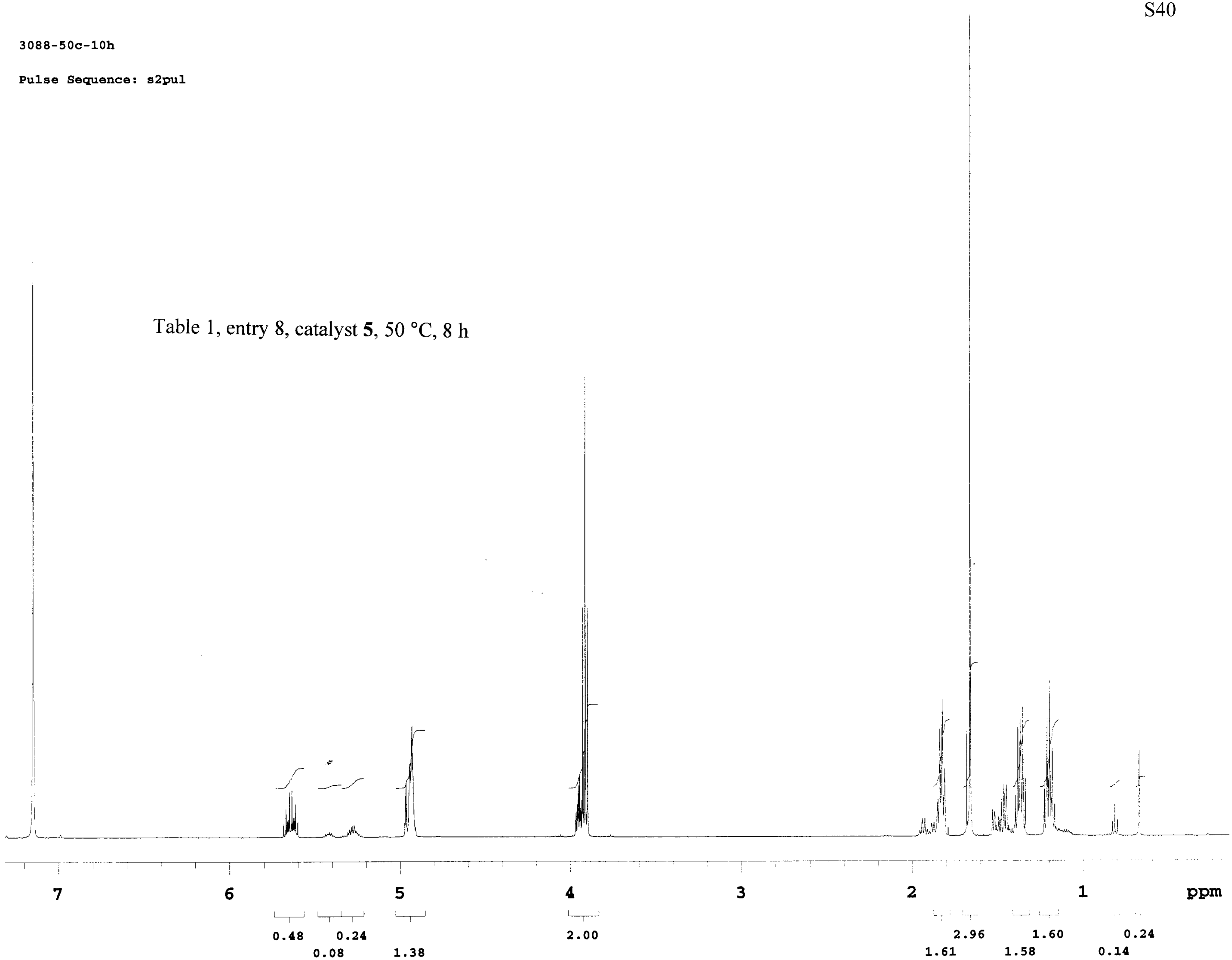
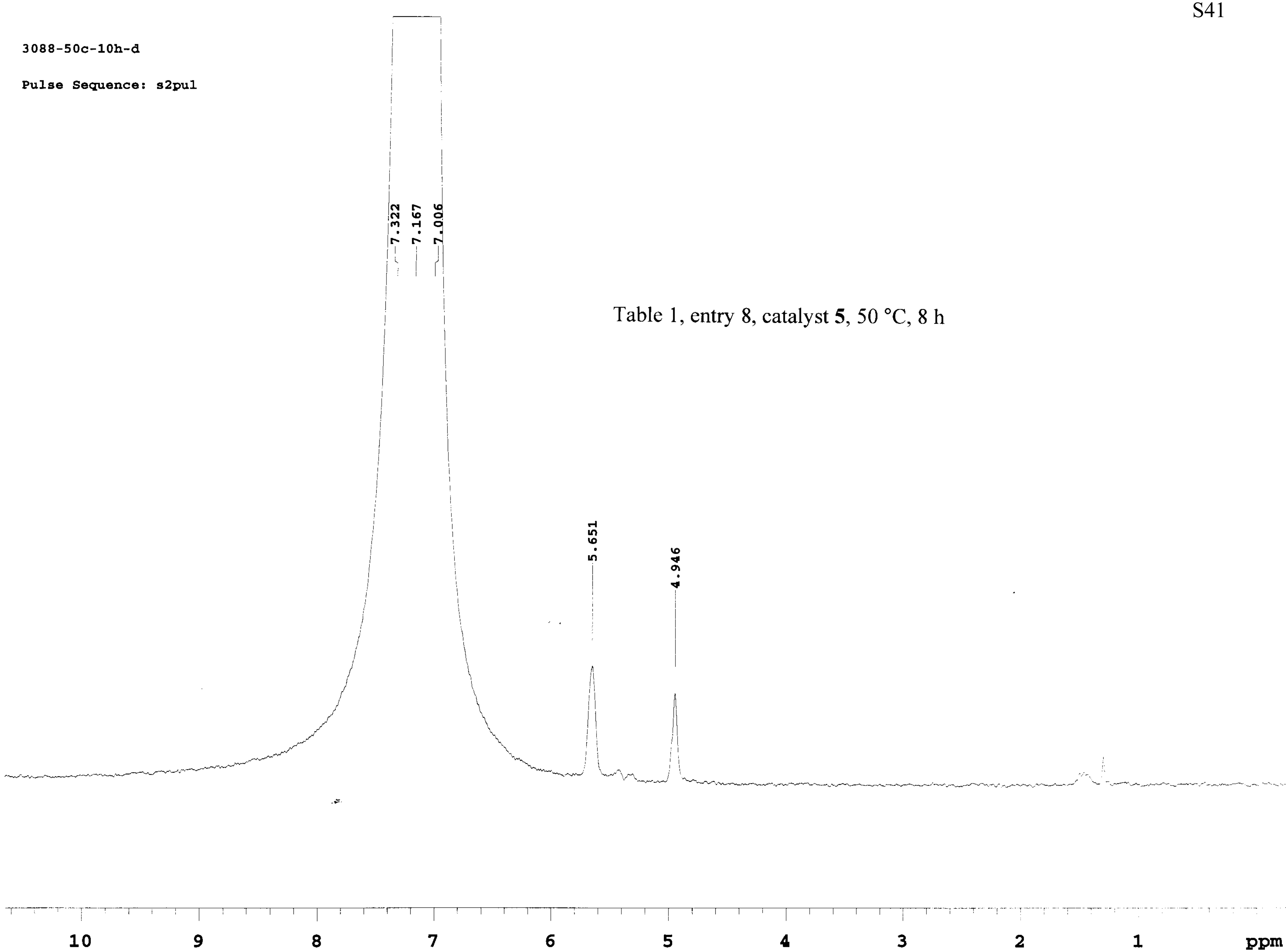
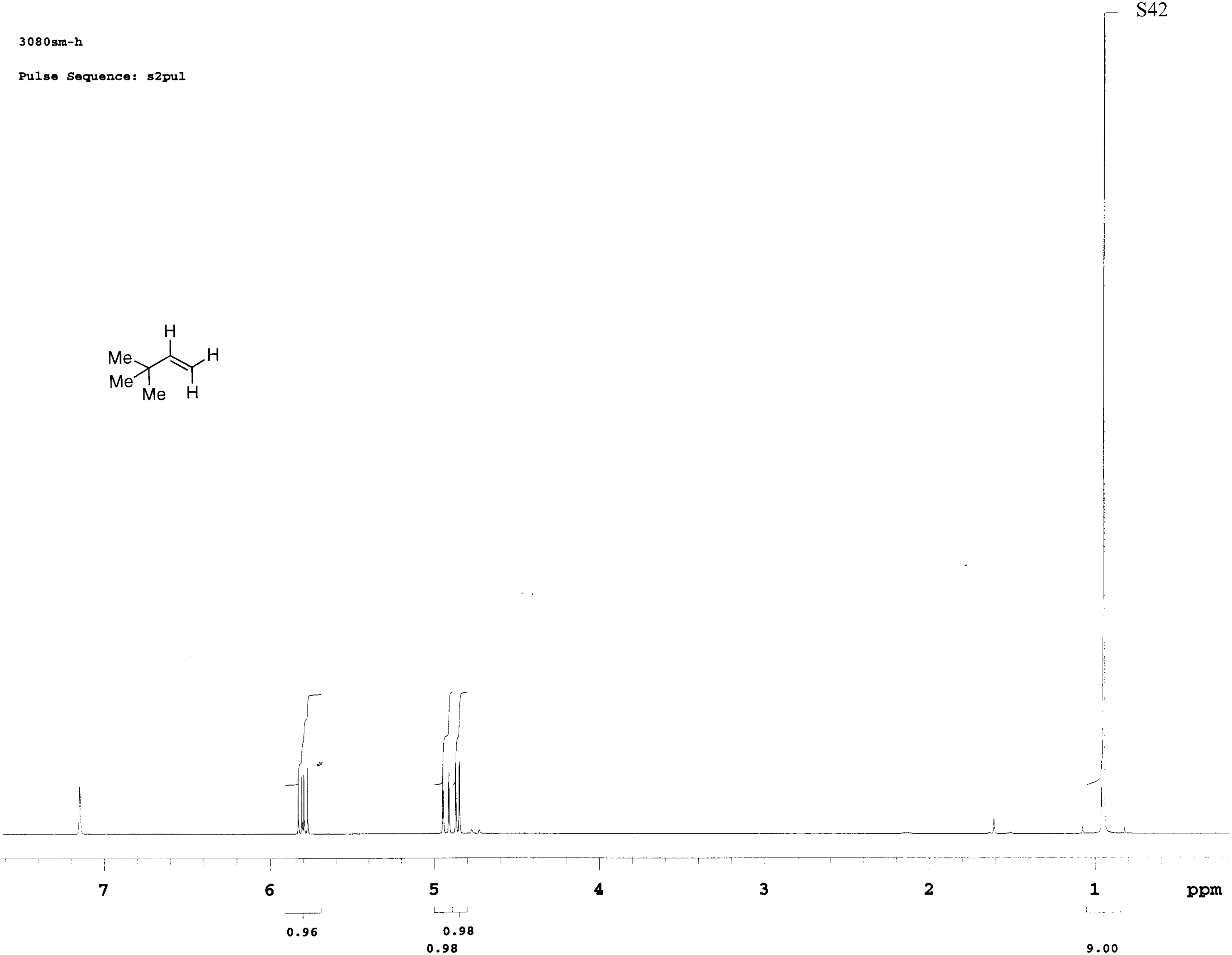


Table 1, entry 8, catalyst **5**, 50 °C, 8 h



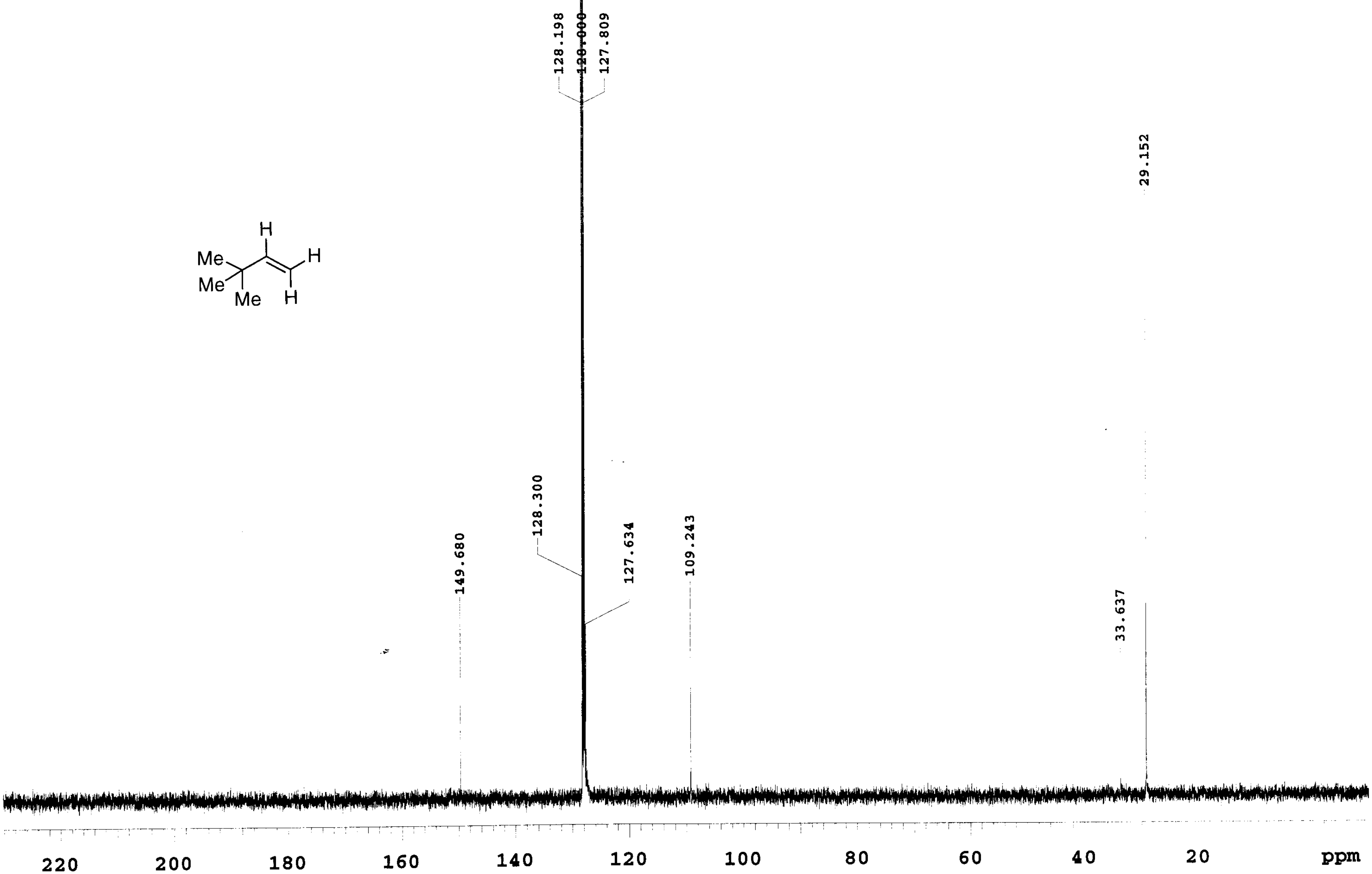
3080sm-h

Pulse Sequence: s2pul



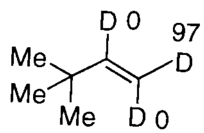
3080sm-c

Pulse Sequence: s2pul

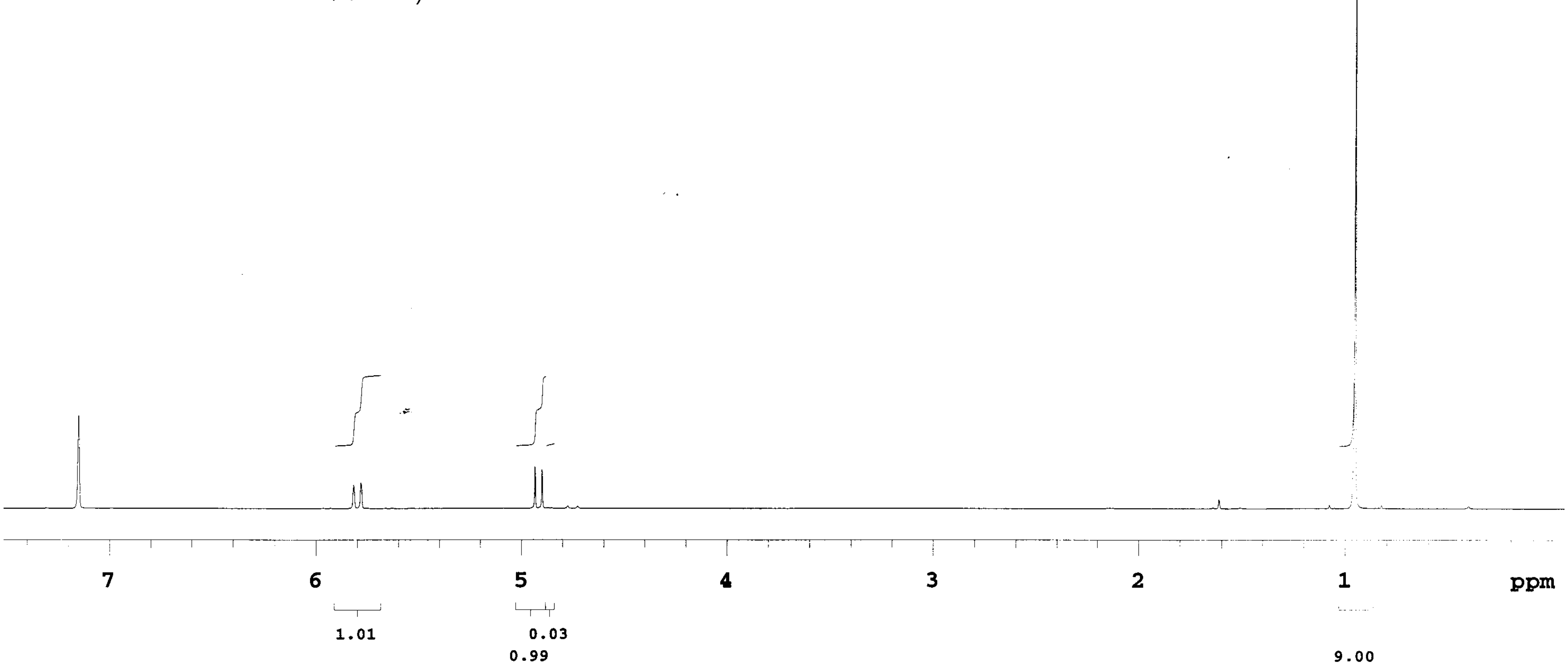


3080-1min

Pulse Sequence: s2pul

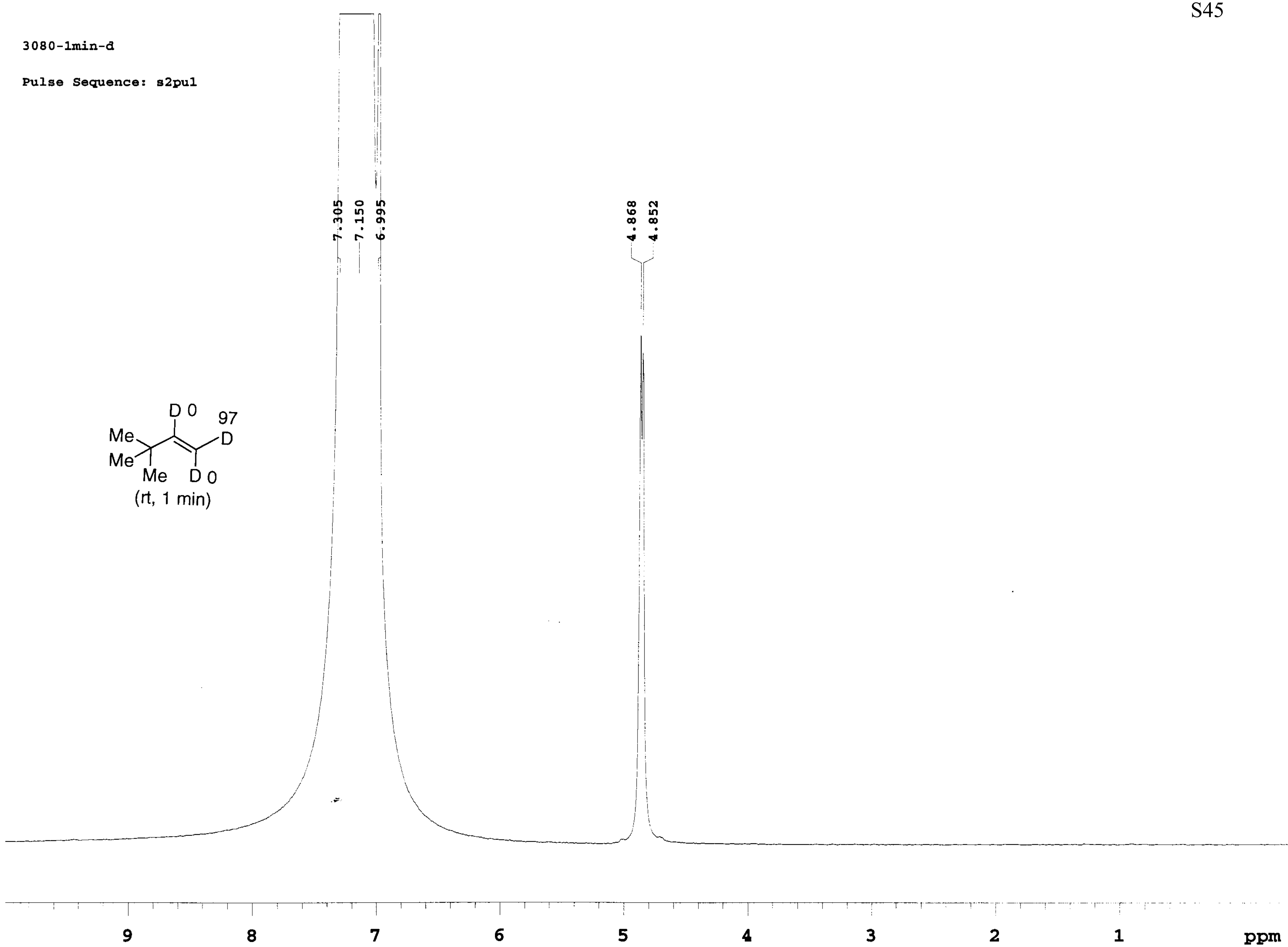


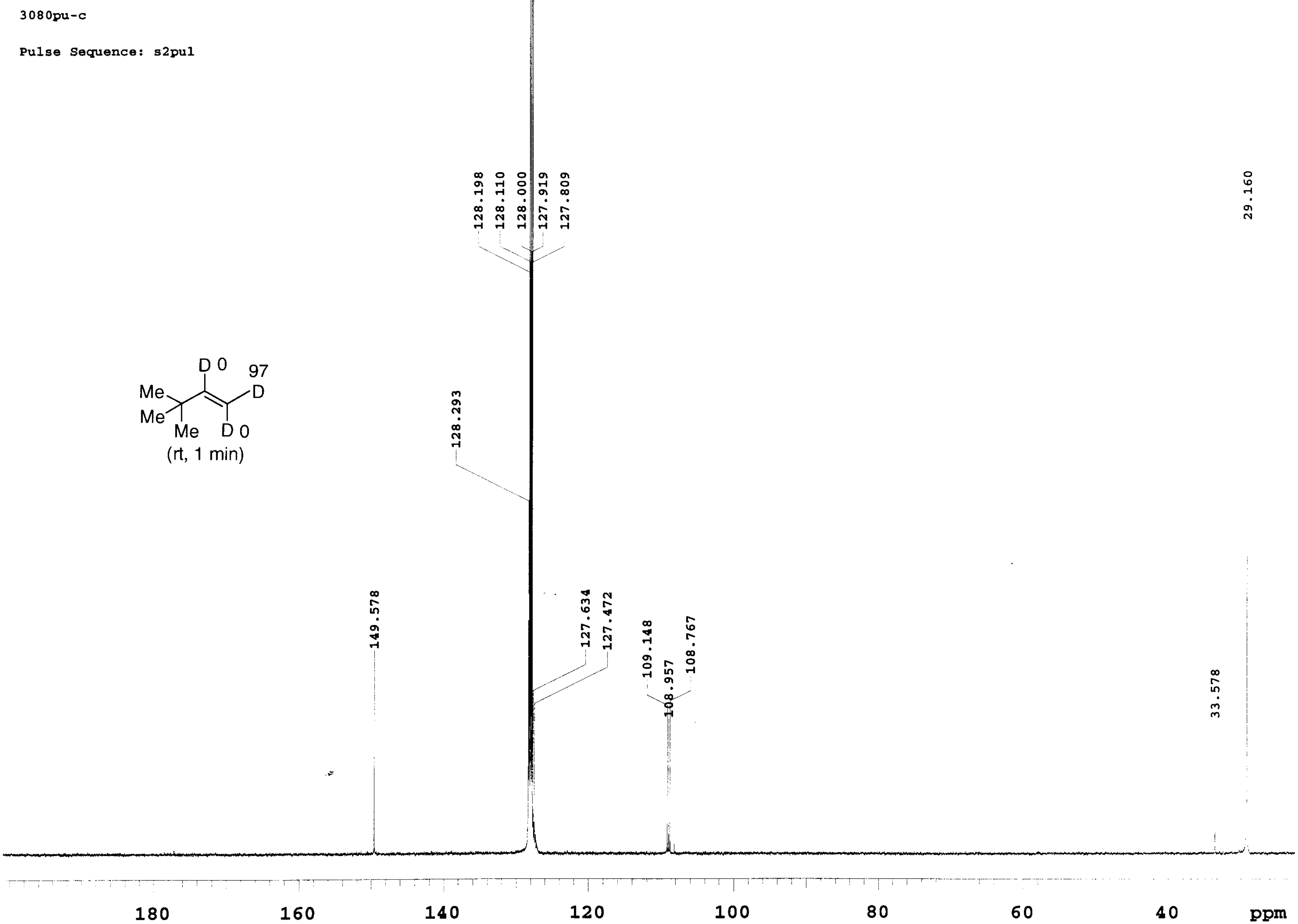
(rt, 1 min)



3080-1min-d

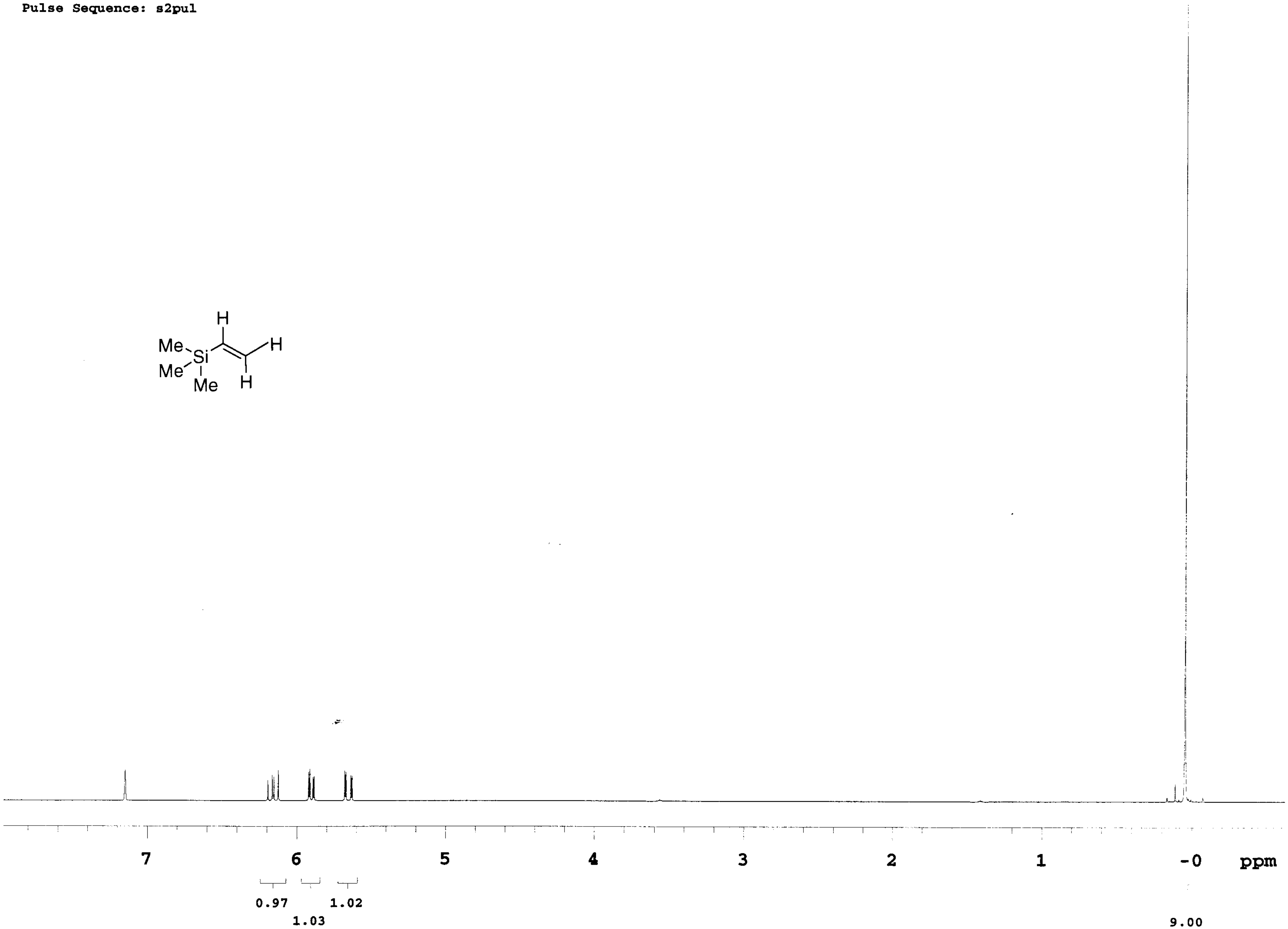
Pulse Sequence: s2pul




3080pu-c
Pulse Sequence: s2pul
D 0
97
D
Me
Me
Me
D 0
(rt, 1 min)
128.198
128.110
128.000
127.919
127.809
128.293
149.578
127.634
127.472
109.148
108.957
108.767
33.578
29.160
180
160
140
120
100
80
60
40
ppm

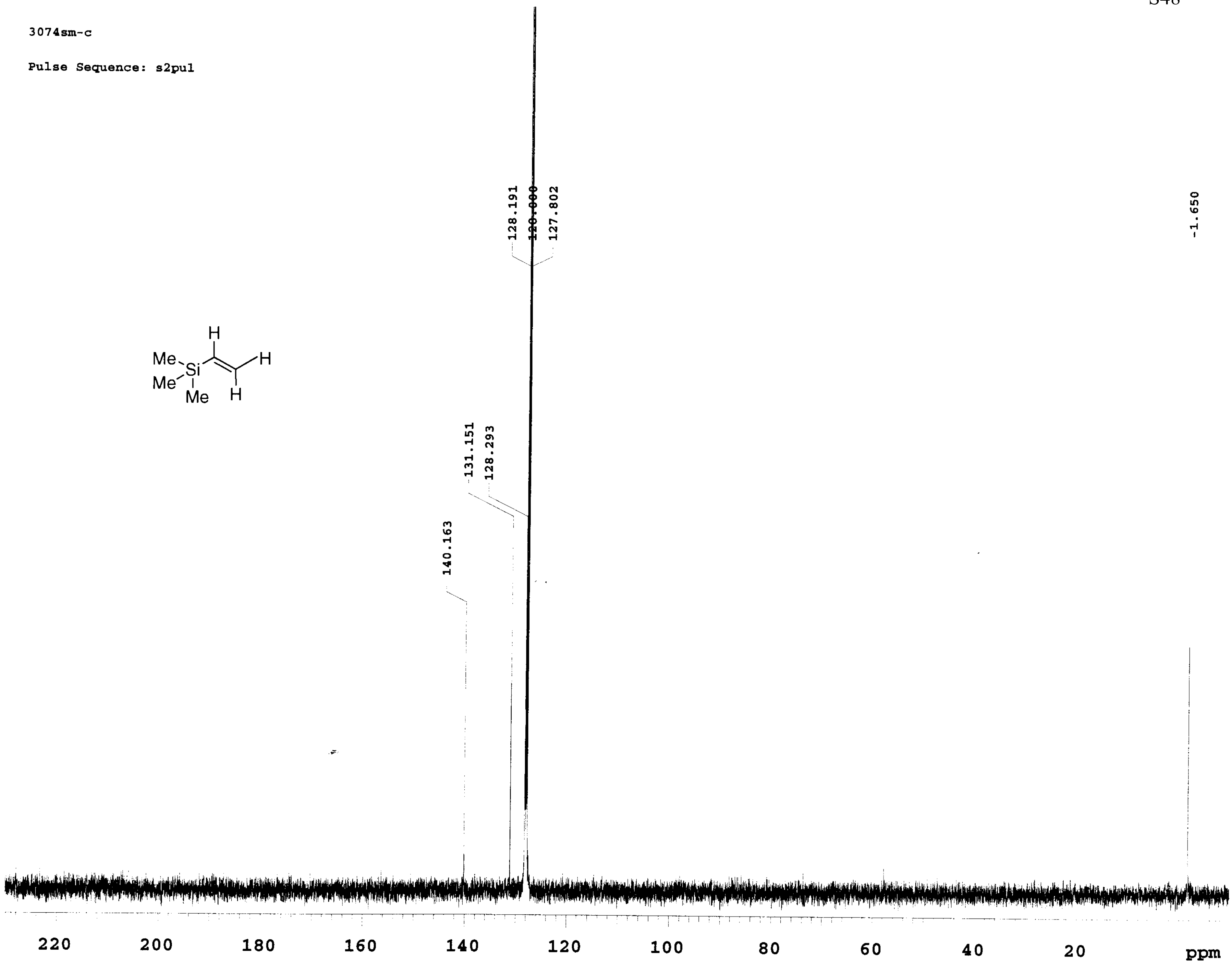
3074sm-h

Pulse Sequence: s2pul



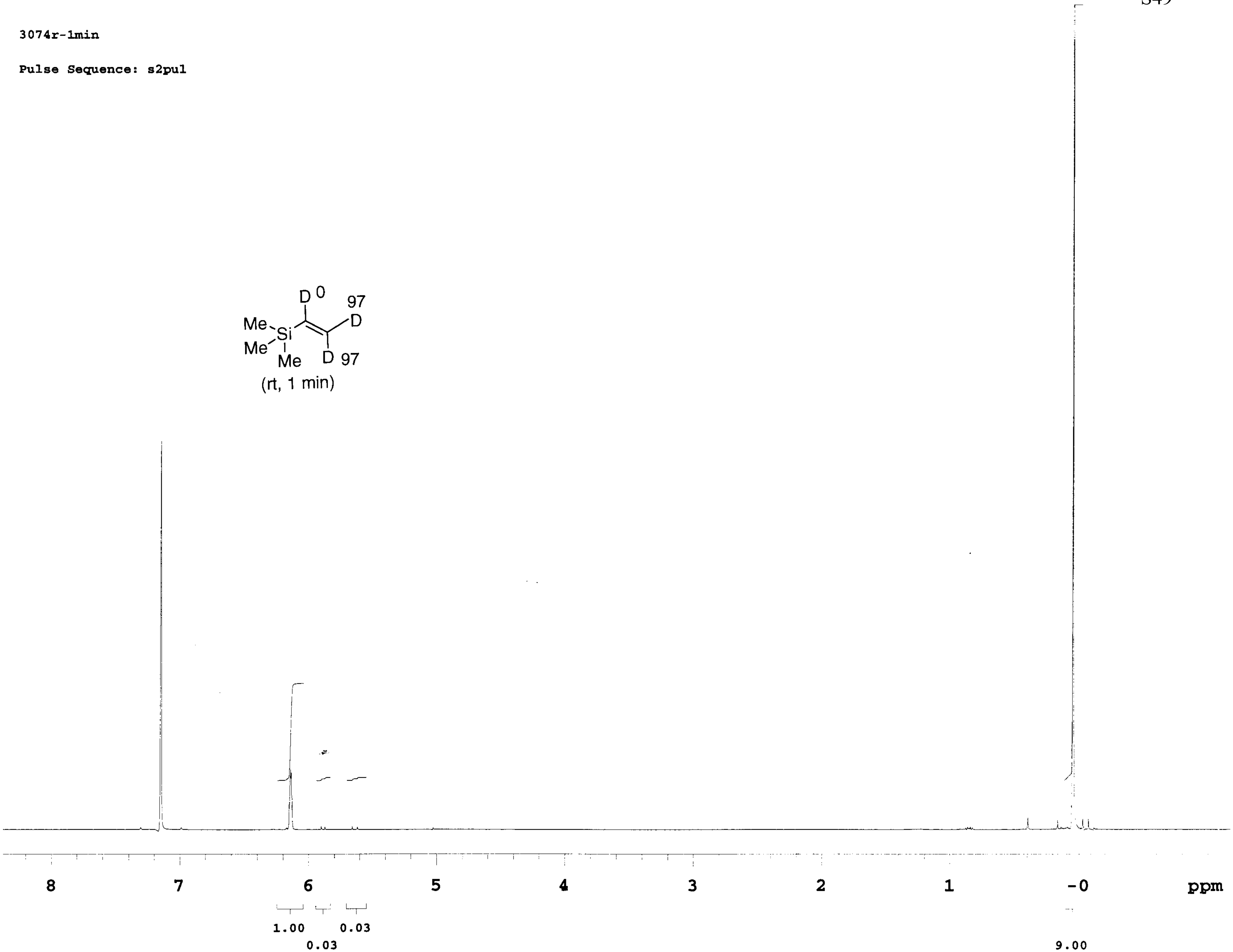
3074sm-c

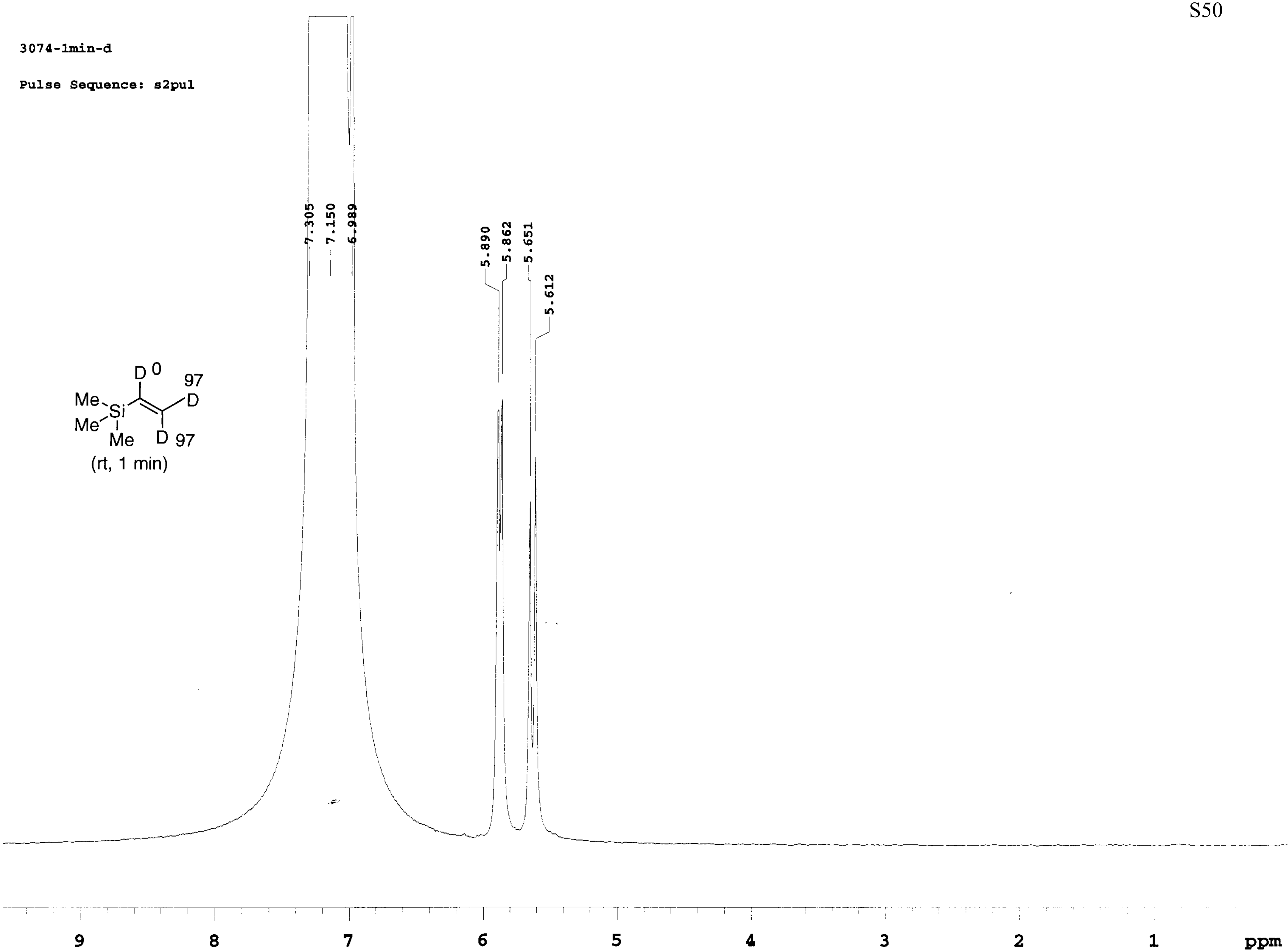
Pulse Sequence: s2pul



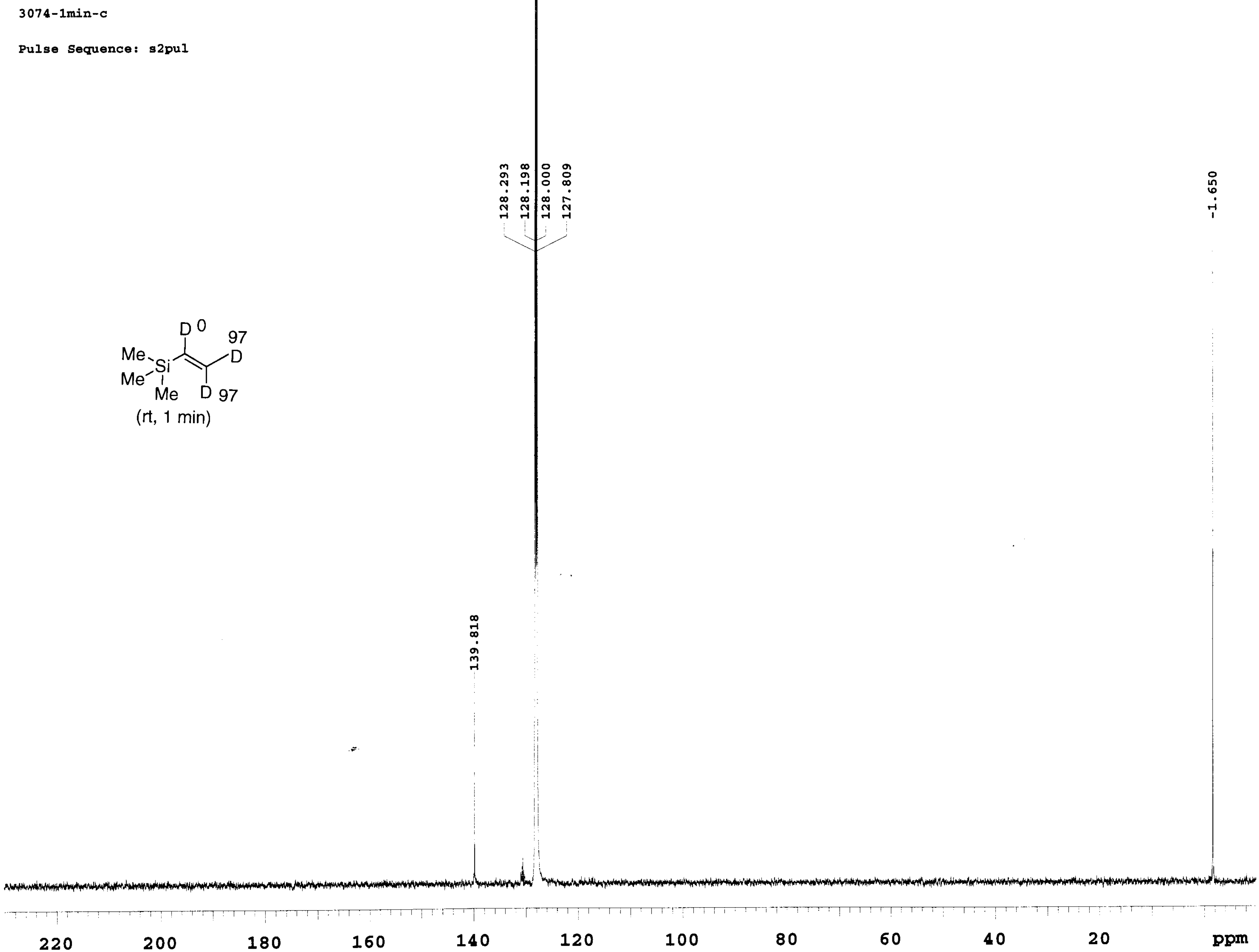
3074r-1min

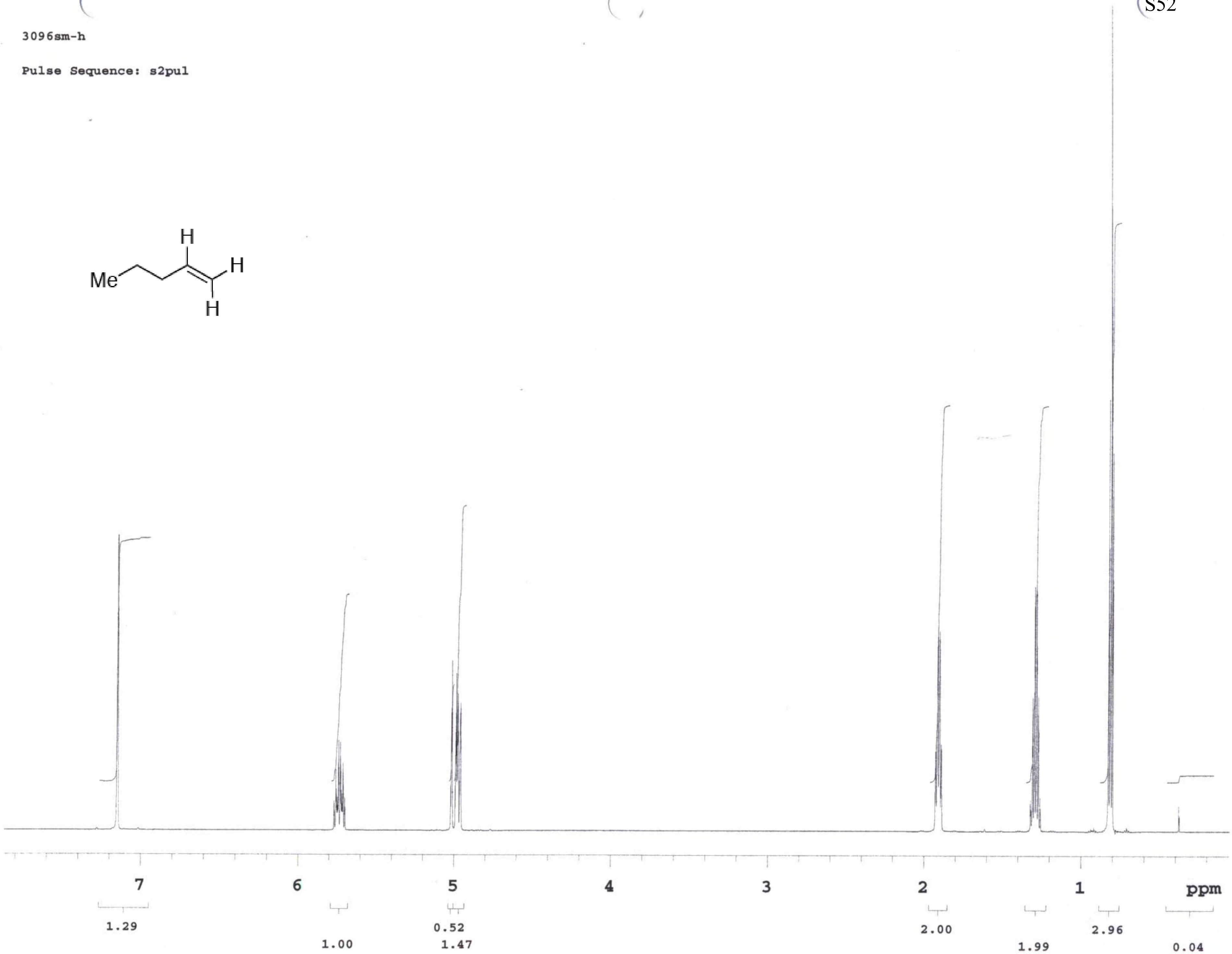
Pulse Sequence: s2pul





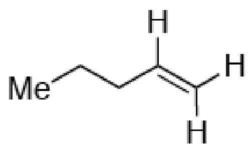
3074-1min-d
Pulse Sequence: s2pul
7.305
7.150
6.989
5.890
5.862
5.651
5.612
D 0
97
D
Me
Si
Me
Me
D 97
(rt, 1 min)
9
8
7
6
5
4
3
2
1
ppm

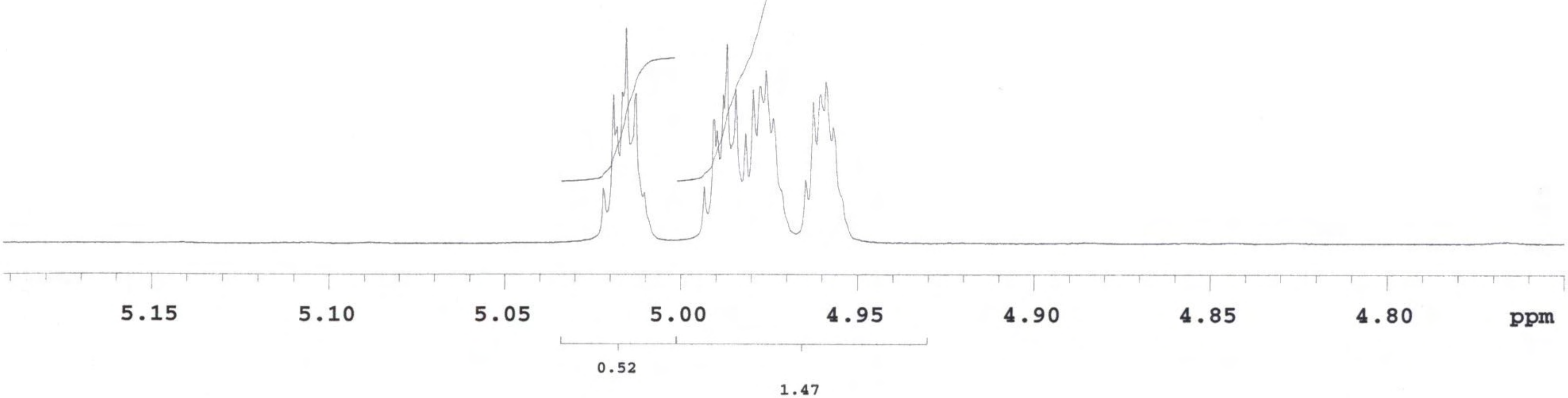

3074-1min-c
Pulse Sequence: s2pul
128.293
128.198
128.000
127.809
-1.650
139.818
D 0
97
D
Me
Si
Me
Me
D 97
(rt, 1 min)
220
200
180
160
140
120
100
80
60
40
20
ppm

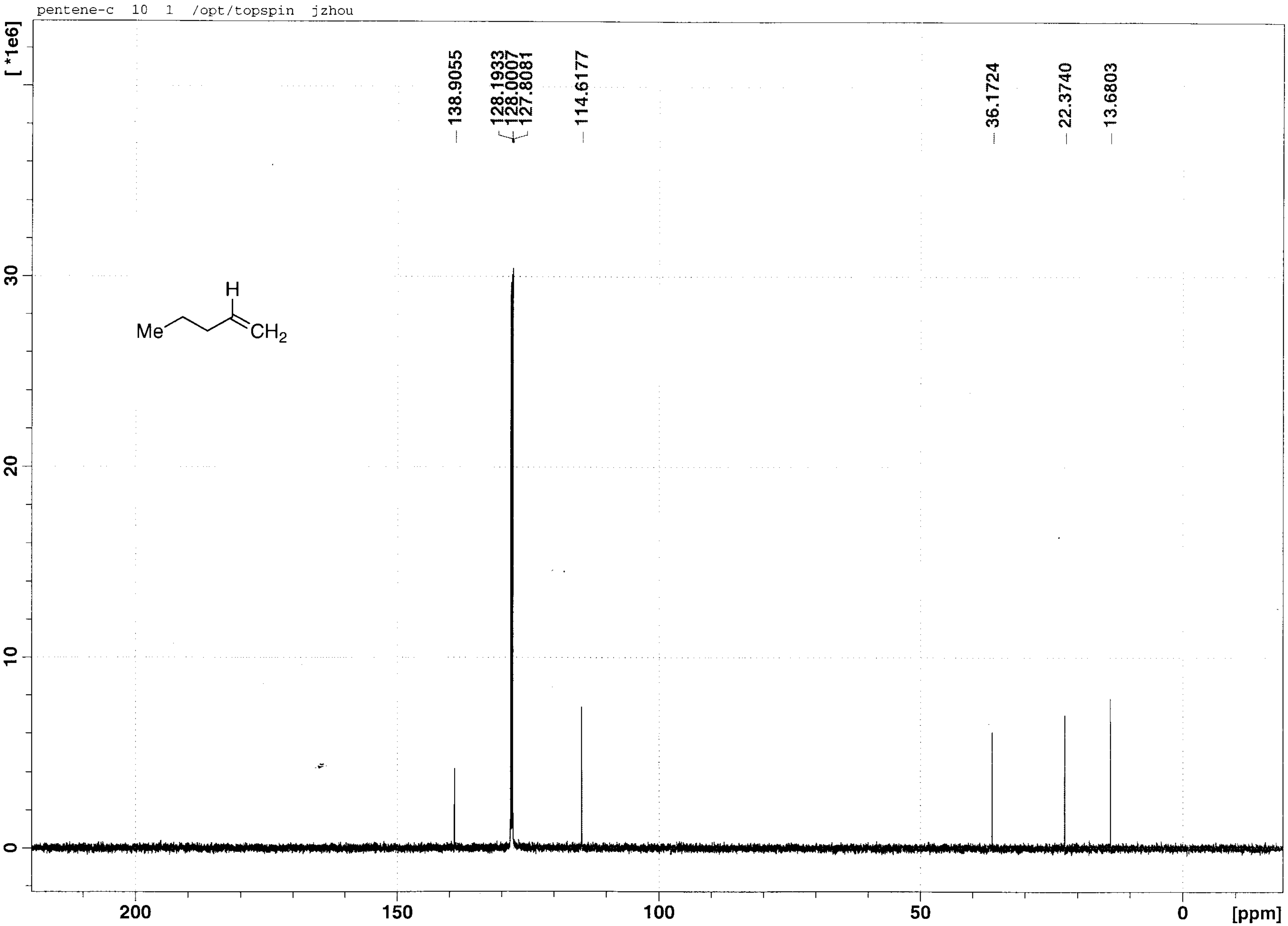

3096sm-h
Pulse Sequence: s2pul
Me
H
H
H
7
6
5
4
3
2
1
ppm
1.29
1.00
0.52
1.47
2.00
1.99
2.96
0.04

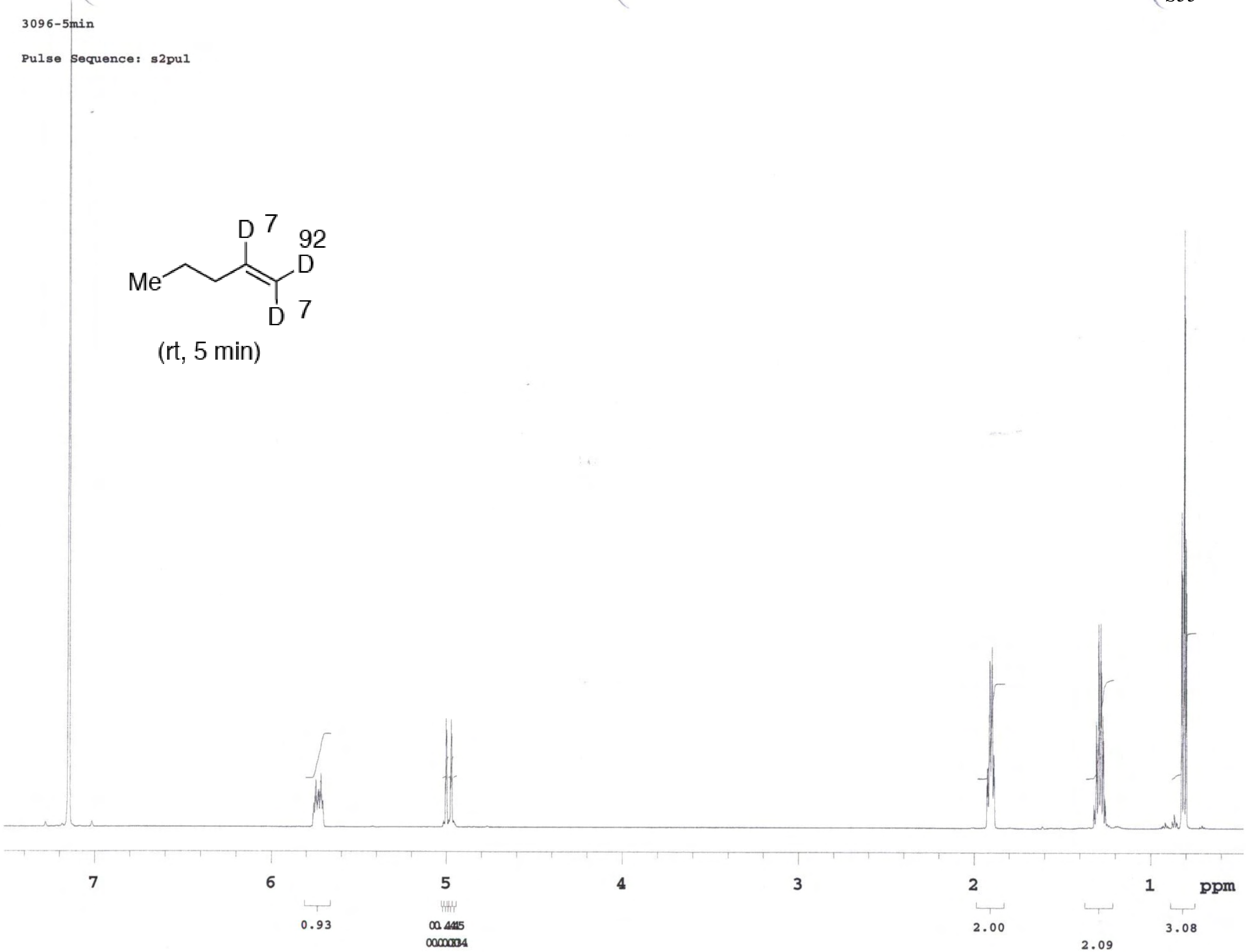
3096sm-h

Pulse Sequence: s2pul



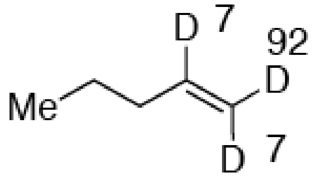



pentene-c 10 1 /opt/topspin jzhou
[*1e6]
138.9055
128.1933
128.0007
127.8081
114.6177
36.1724
22.3740
13.6803
H
Me
CH2
30
20
10
0
200
150
100
50
0
[ppm]

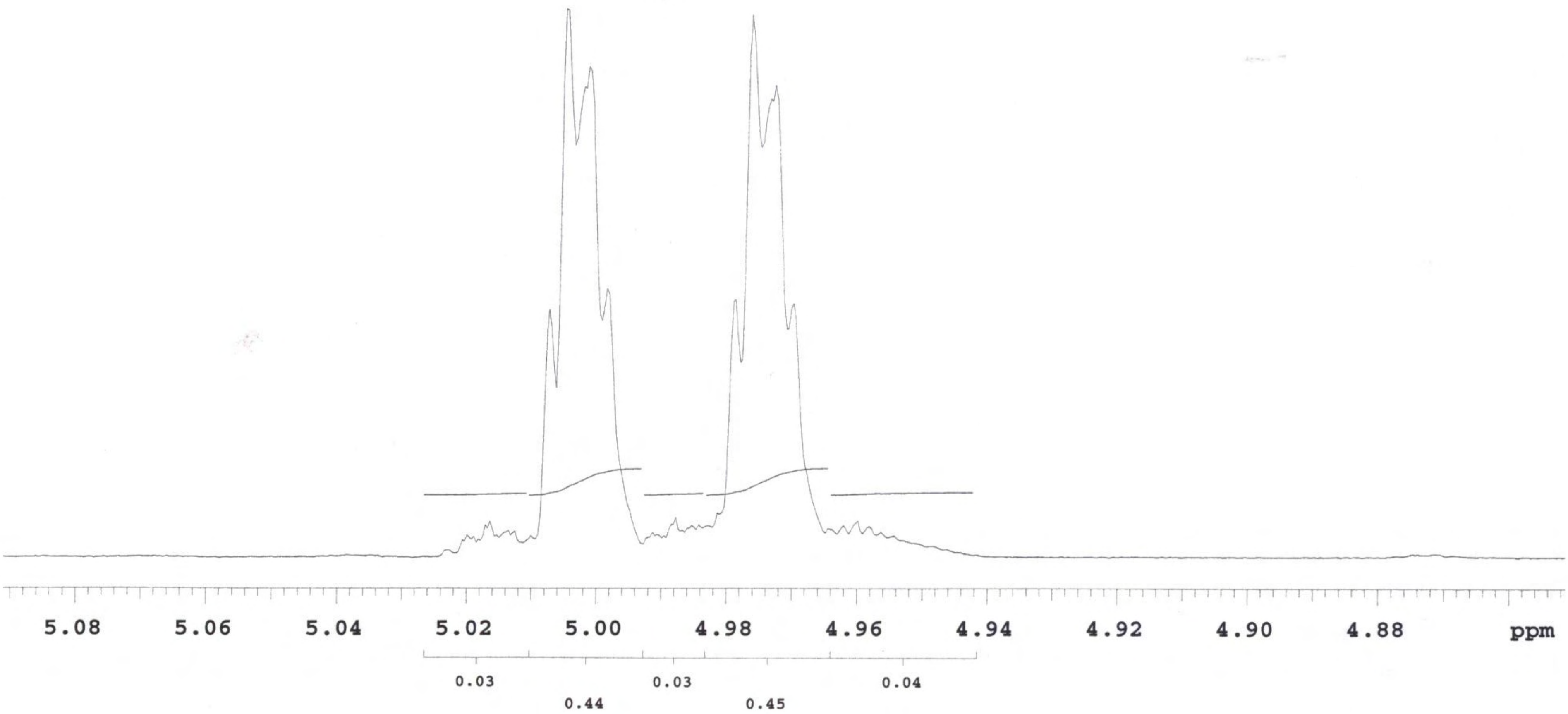

3096-5min
Pulse Sequence: s2pul
D 7
92
D
Me
D 7
(rt, 5 min)
7
6
5
4
3
2
1
ppm
0.93
2.00
2.09
3.08

3096-5min

Pulse Sequence: s2pul

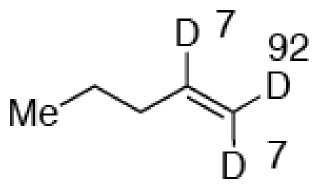


(rt, 5 min)

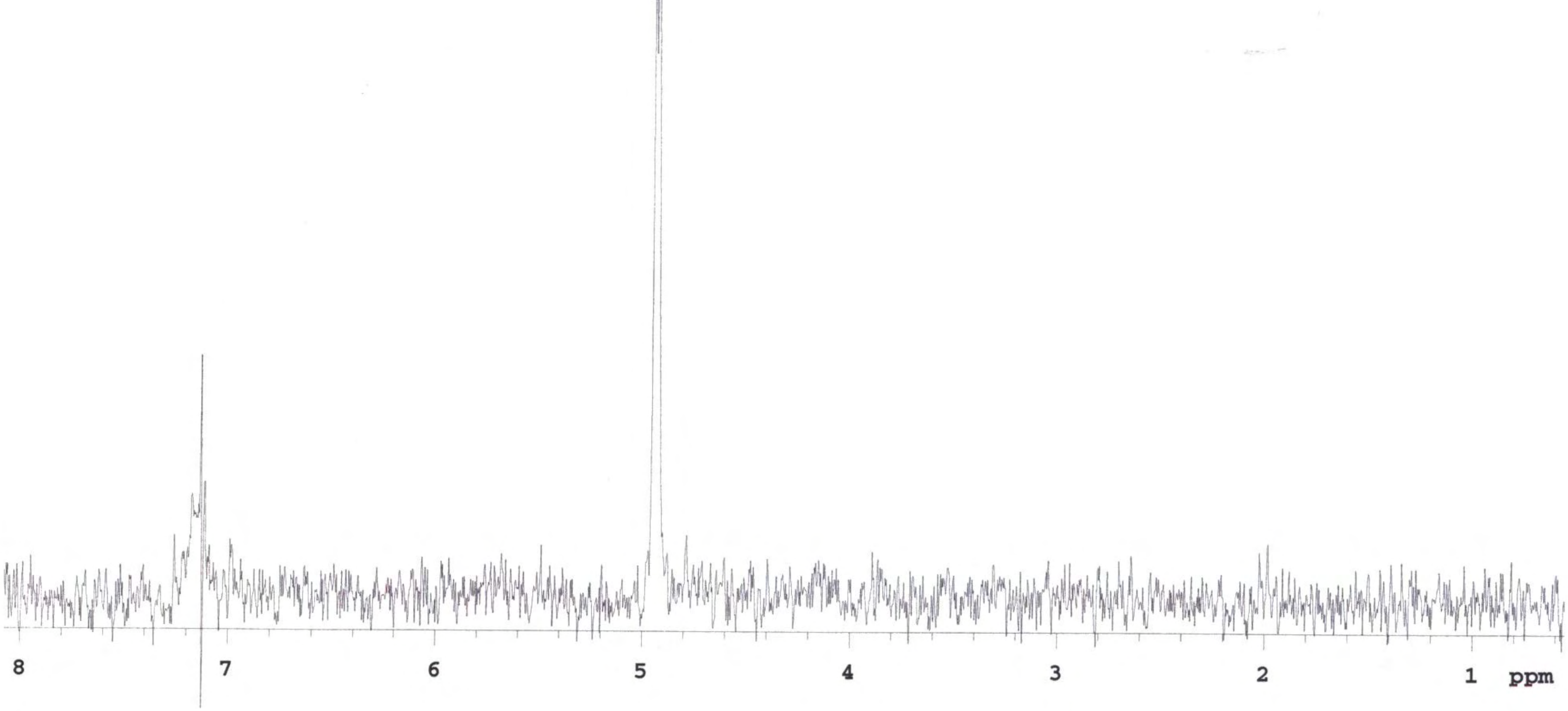


3096-5min

Pulse Sequence: presat

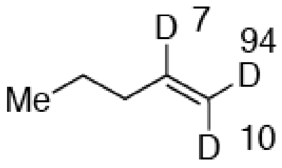


(rt, 5 min)

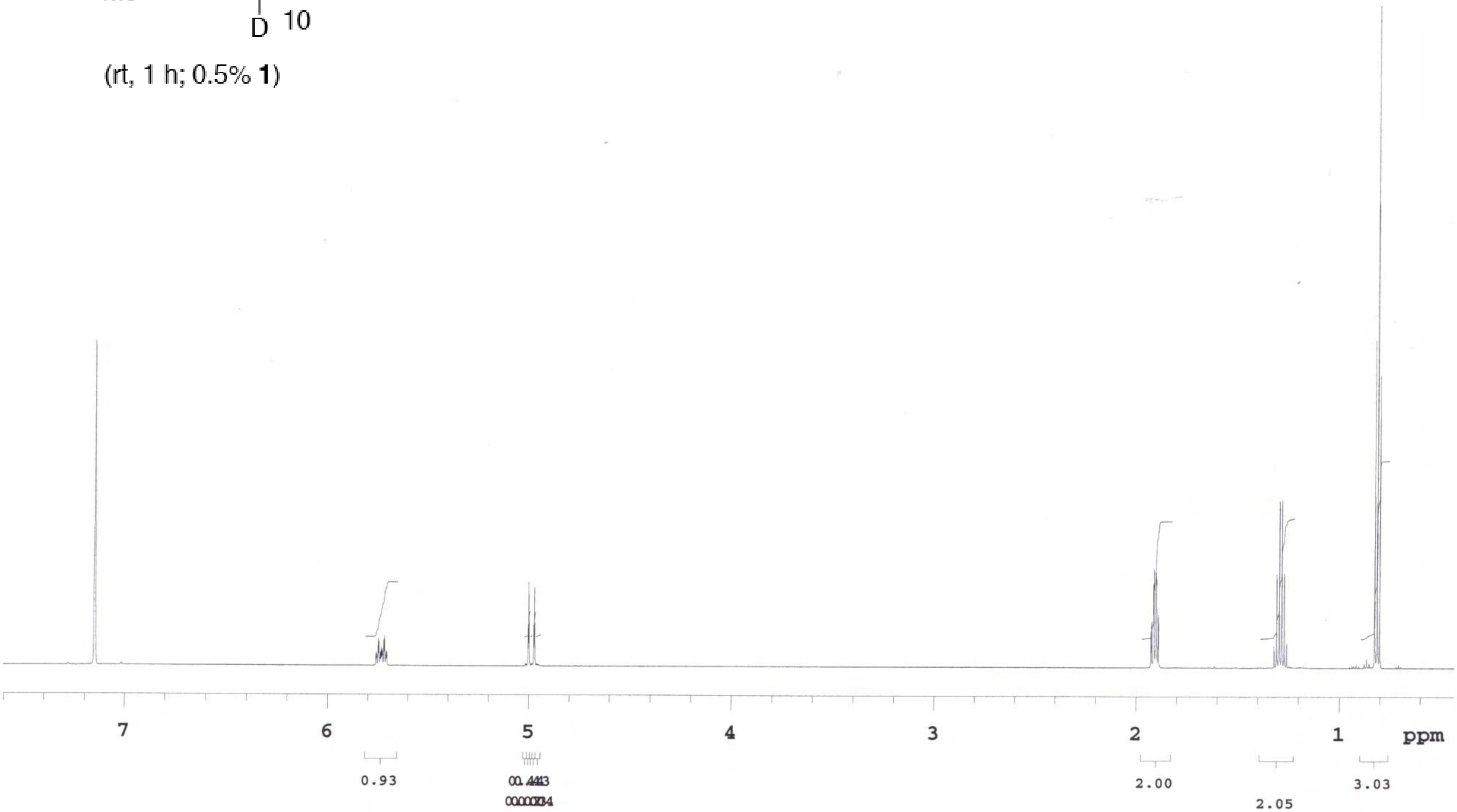


3097r-1h

Pulse Sequence: s2pul

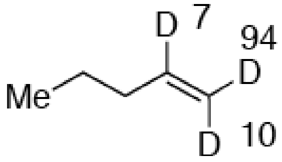


(rt, 1 h; 0.5% **1**)

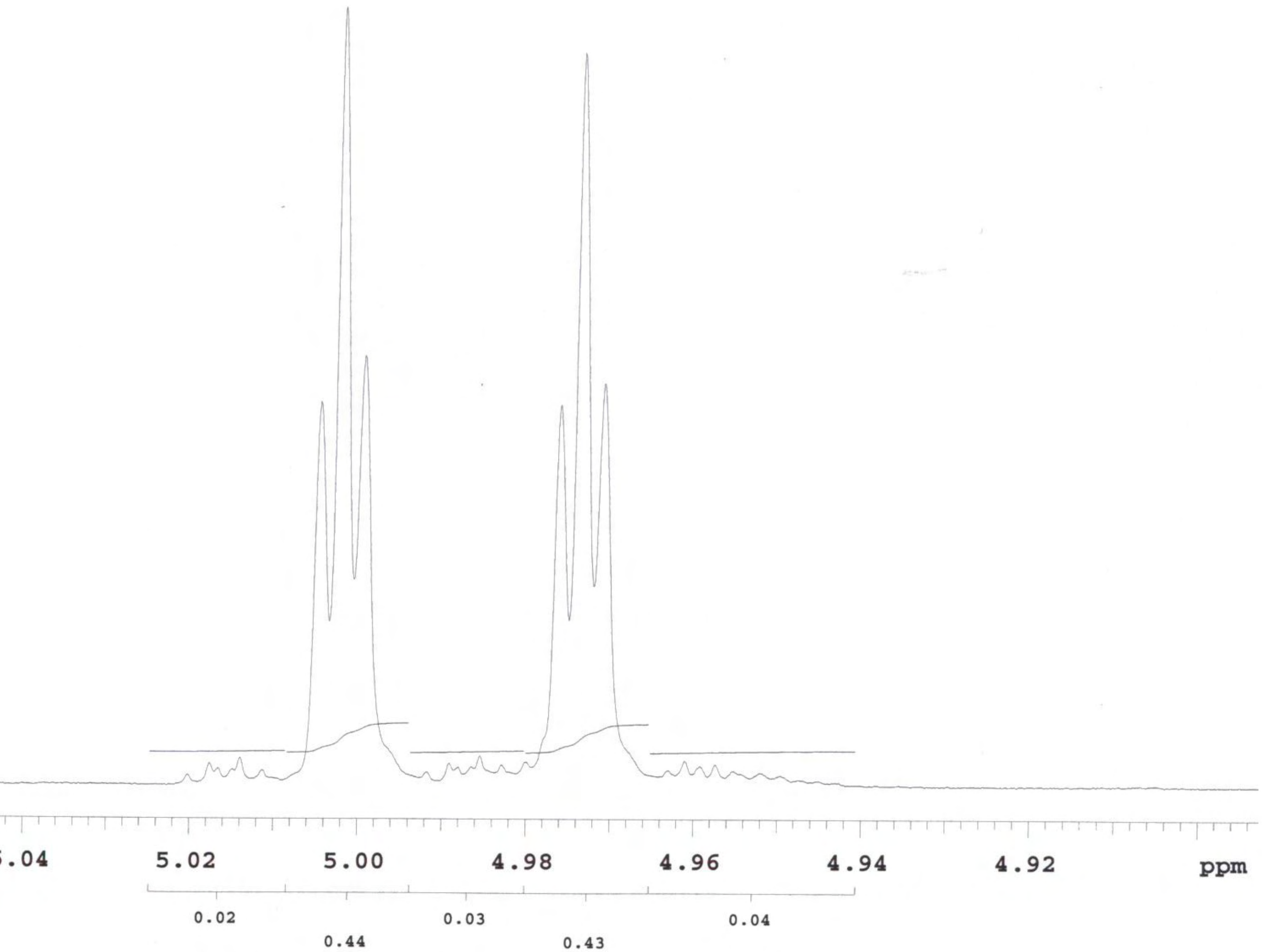


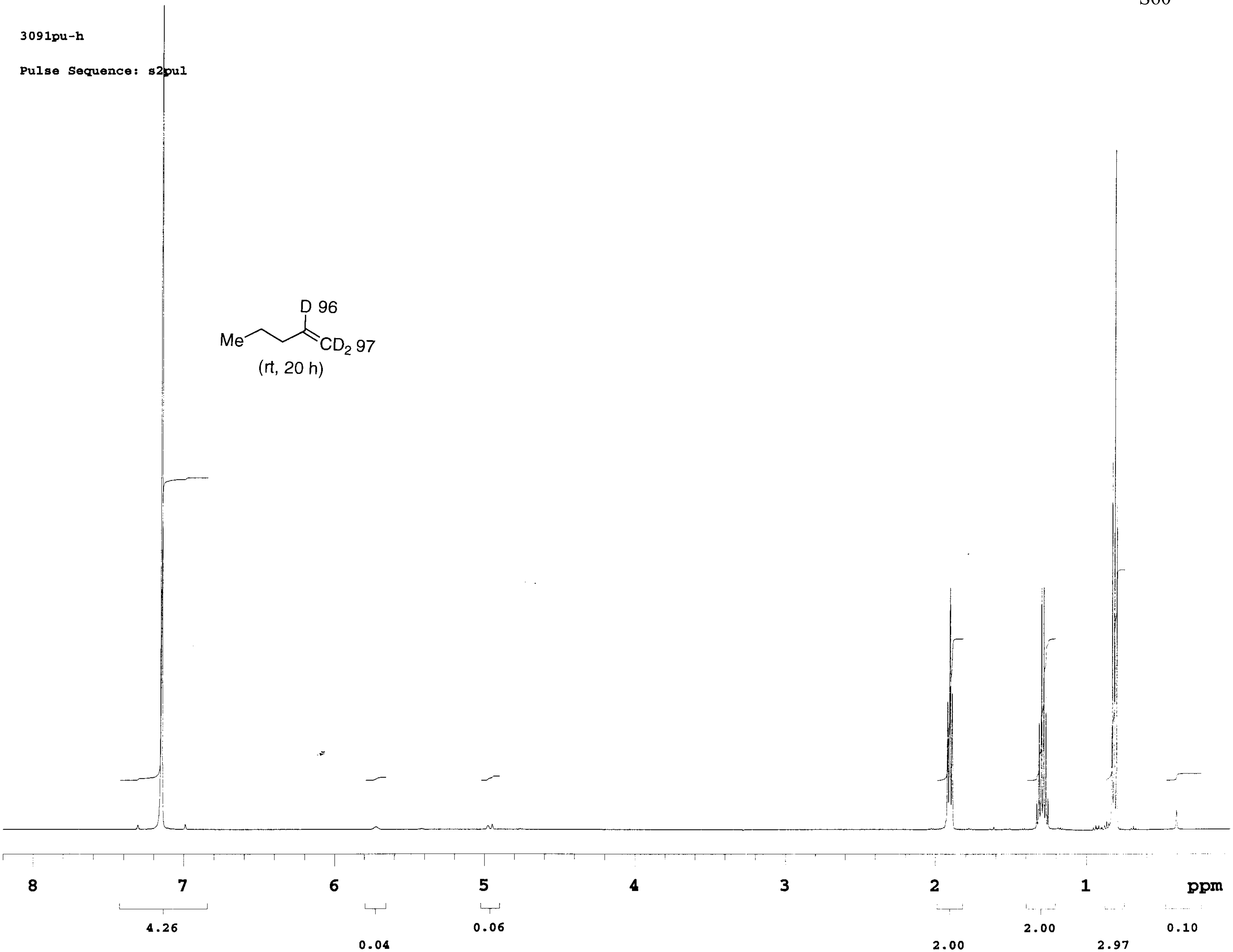
3097r-1h

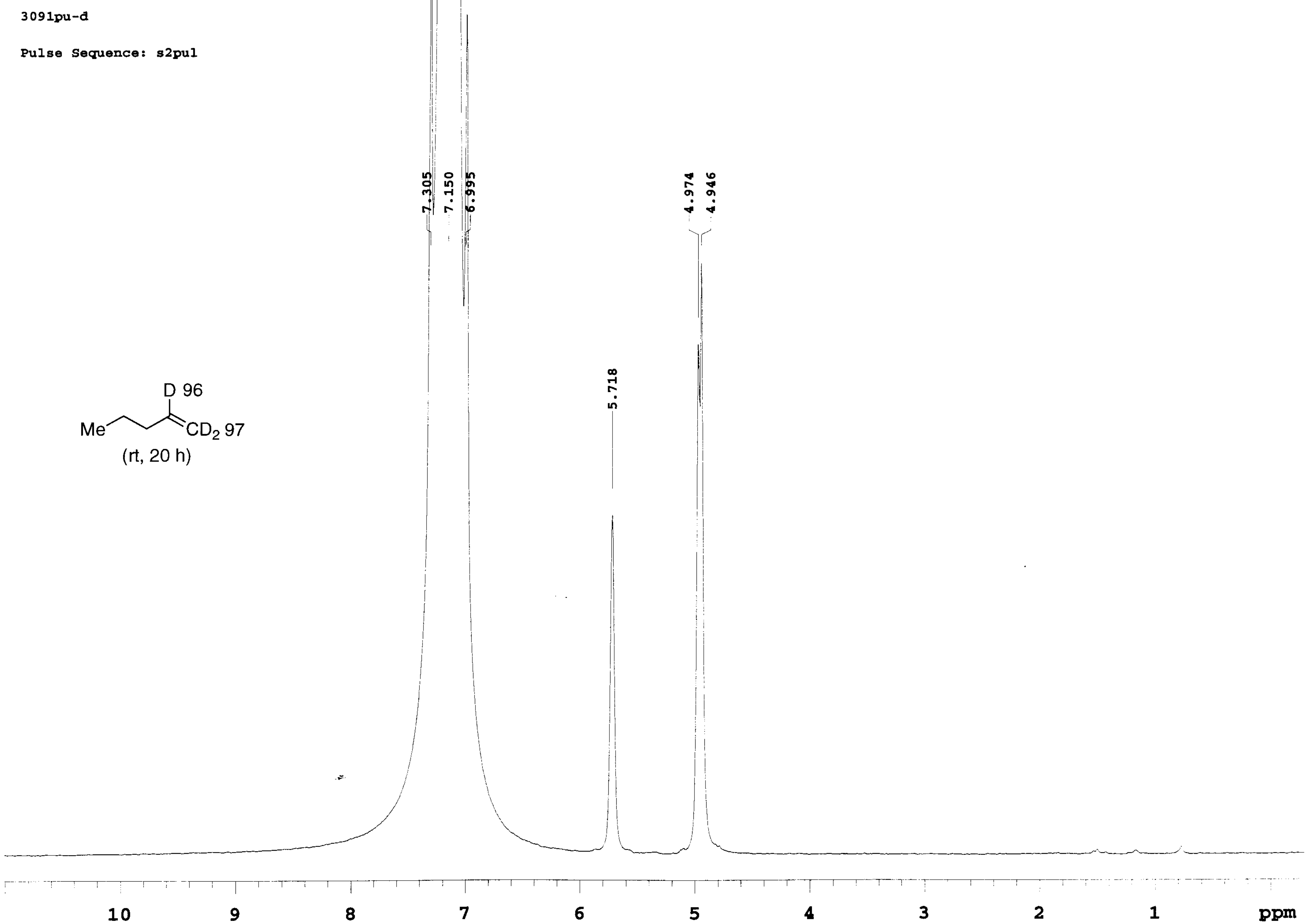
Pulse Sequence: s2pul



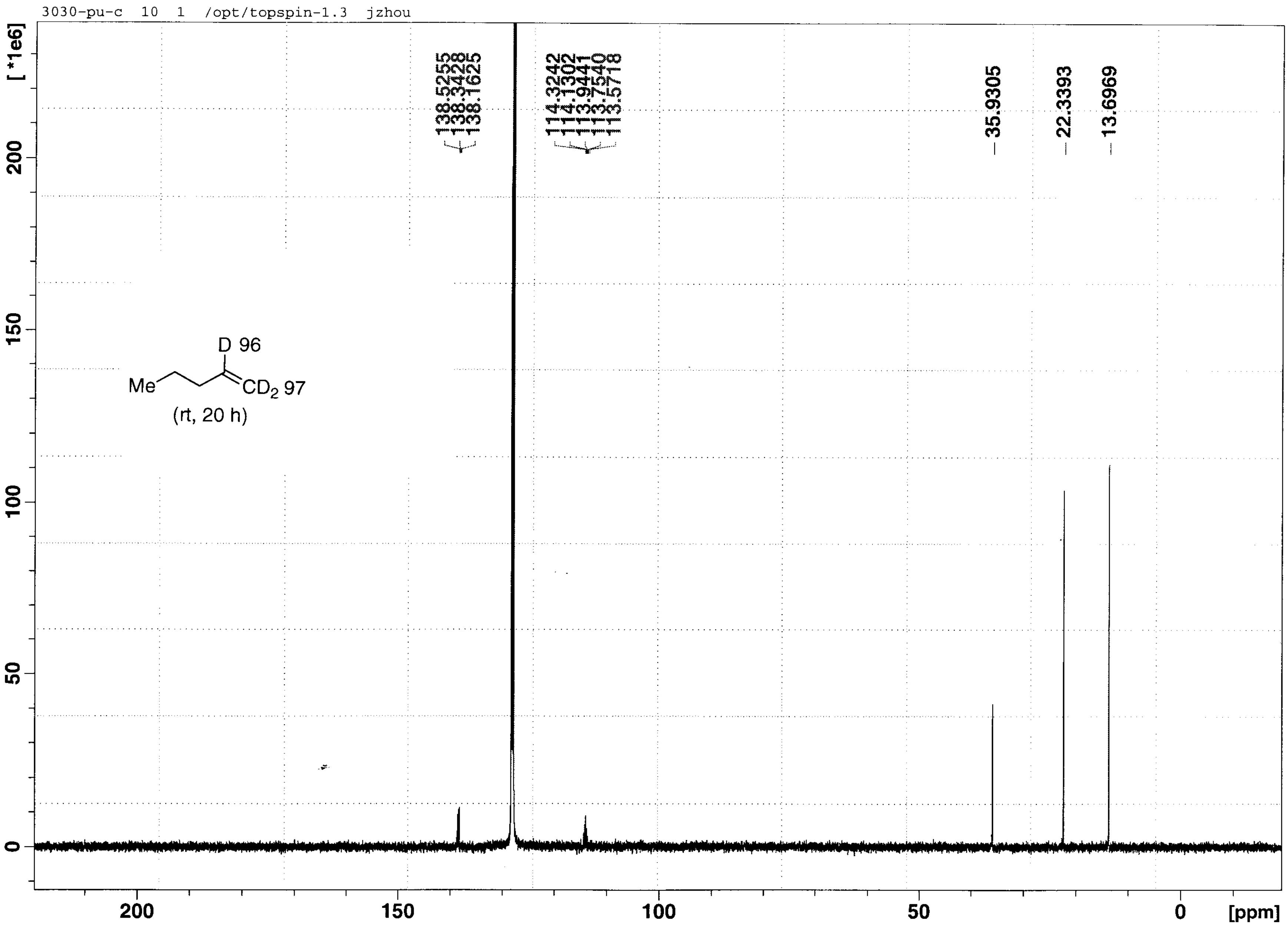
(rt, 1 h; 0.5% **1**)

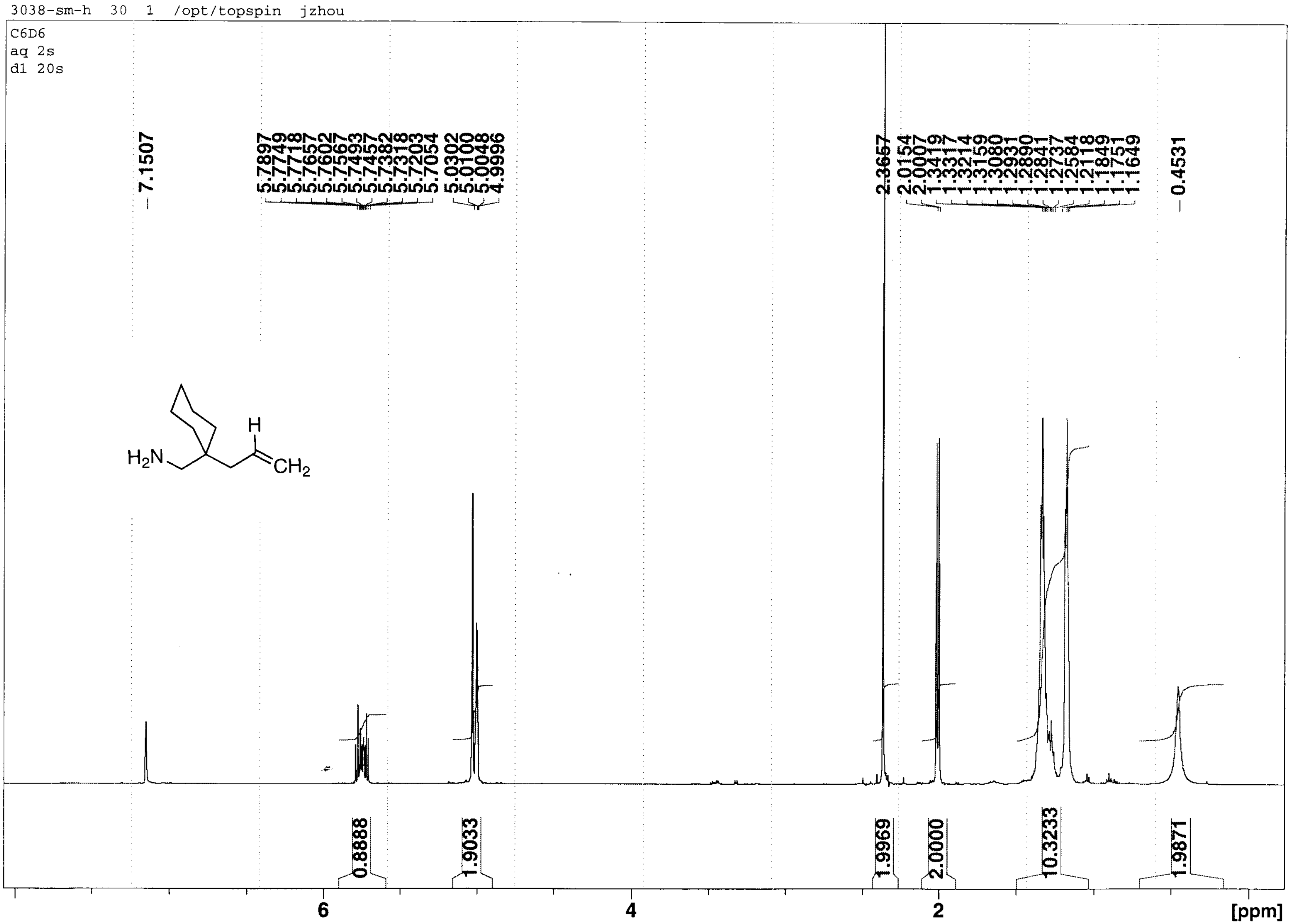


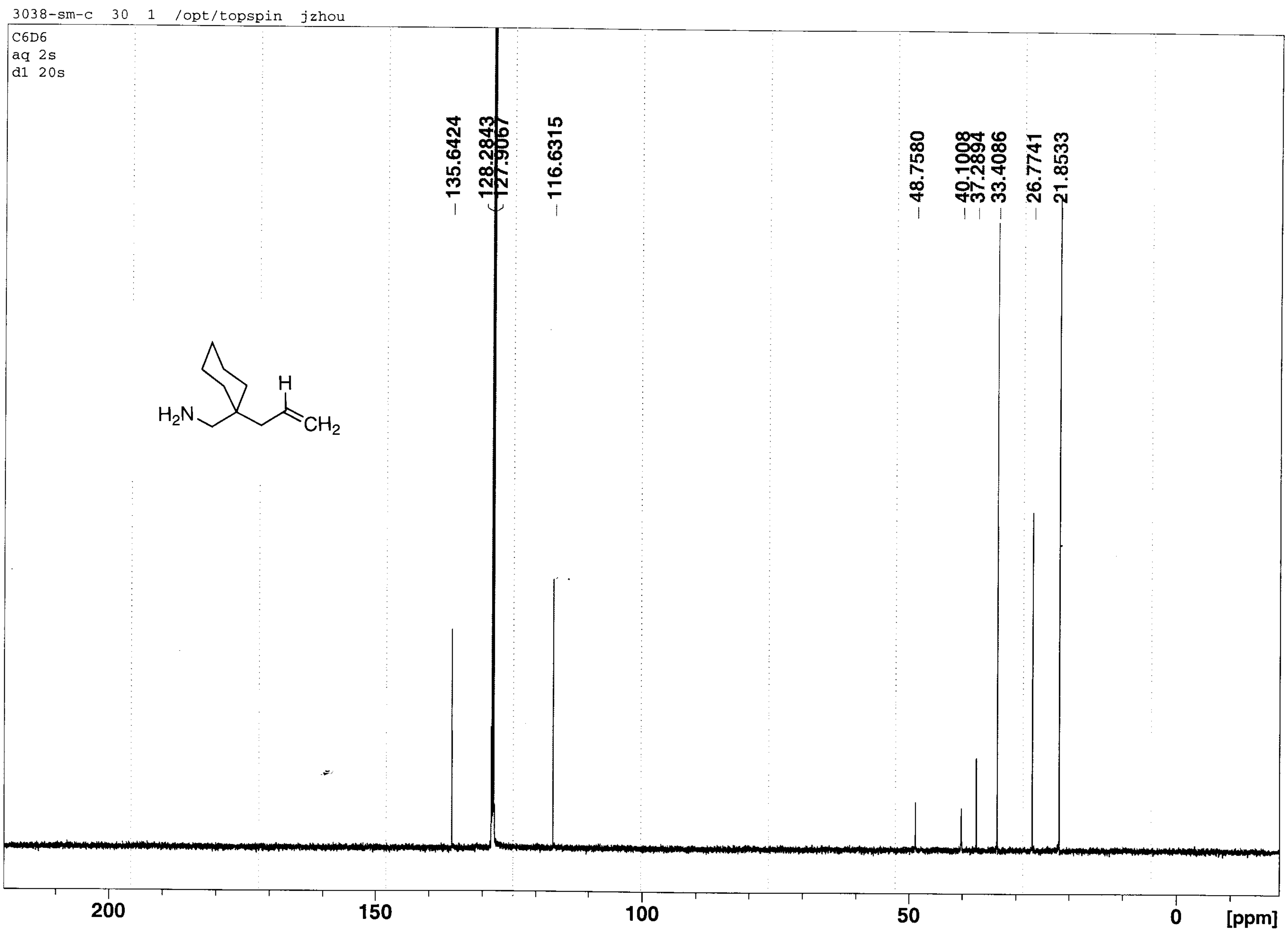

3091pu-h
Pulse Sequence: s2pul
D 96
Me
CD2 97
(rt, 20 h)
8
7
6
5
4
3
2
1
ppm
4.26
0.04
0.06
2.00
2.00
2.97
0.10


3091pu-d
Pulse Sequence: s2pul
7.305
7.150
6.995
5.718
4.974
4.946
D 96
Me
CD2 97
10
9
8
7
6
5
4
3
2
1
ppm

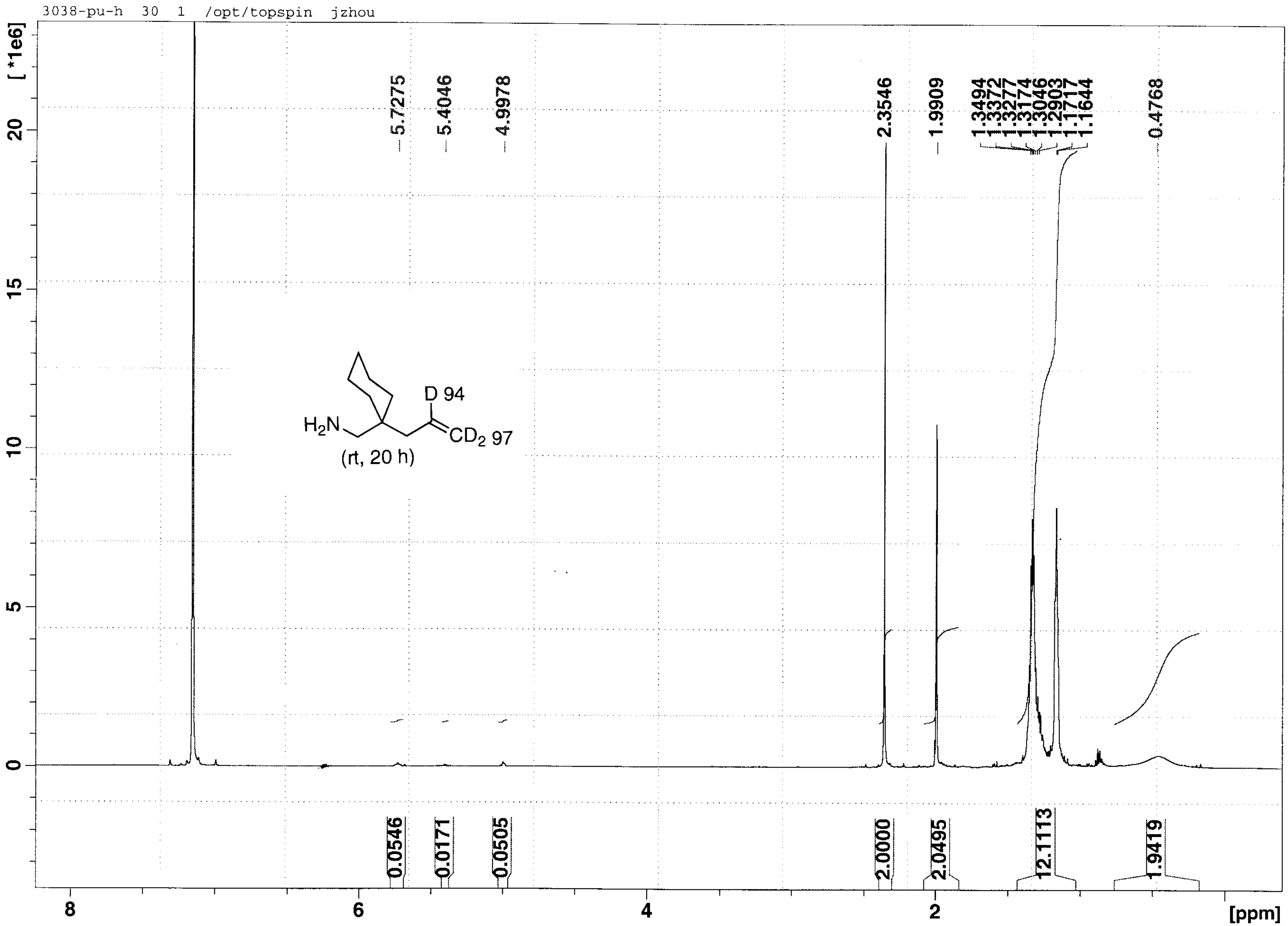
(rt, 20 h)

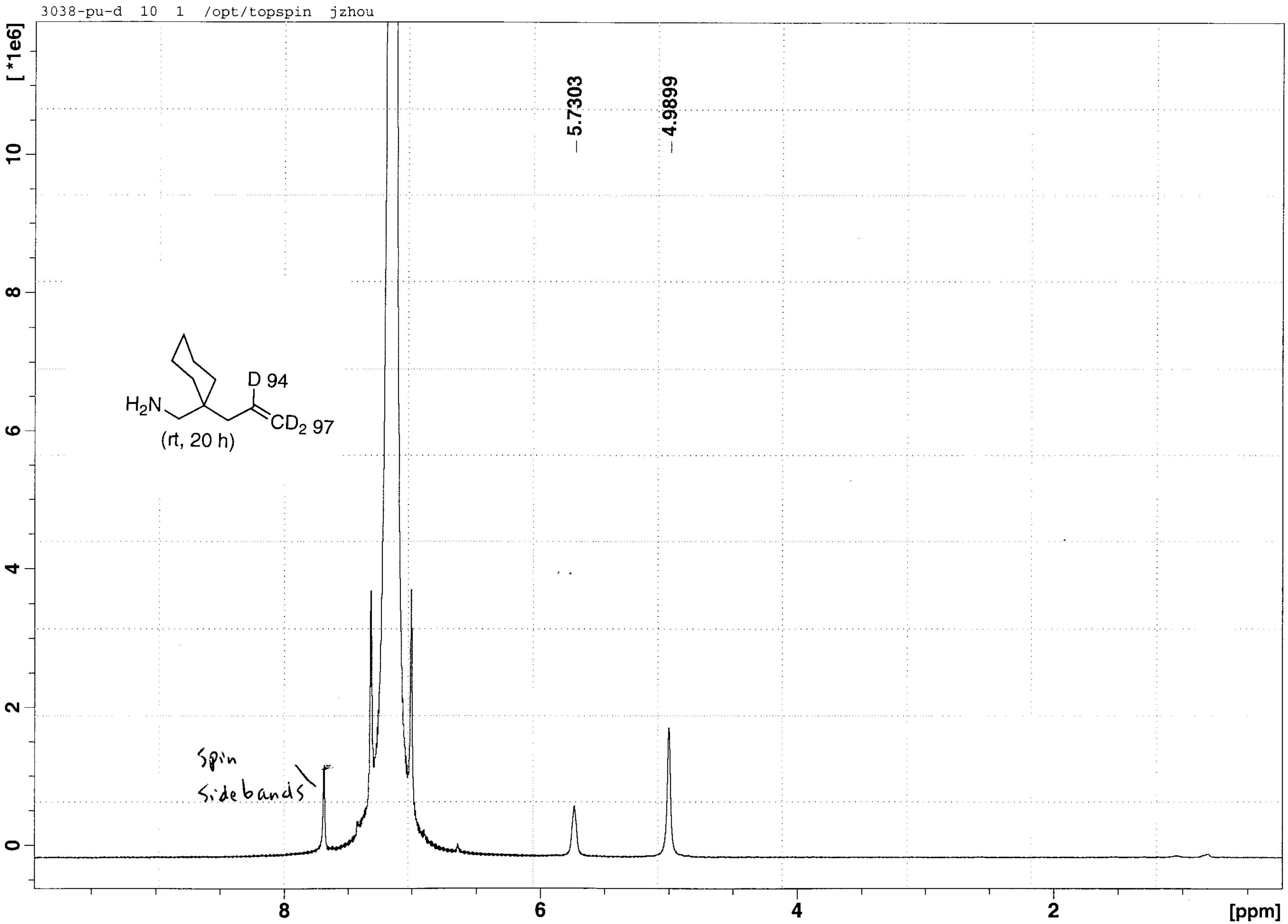

3030-pu-c 10 1 /opt/topspin-1.3 jzhou
[*1e6]
138.5255
138.3428
138.1625
114.3242
114.1302
113.9441
113.7540
113.5718
35.9305
22.3393
13.6969
D 96
Me
CD2 97
(rt, 20 h)
200
150
100
50
0
[ppm]

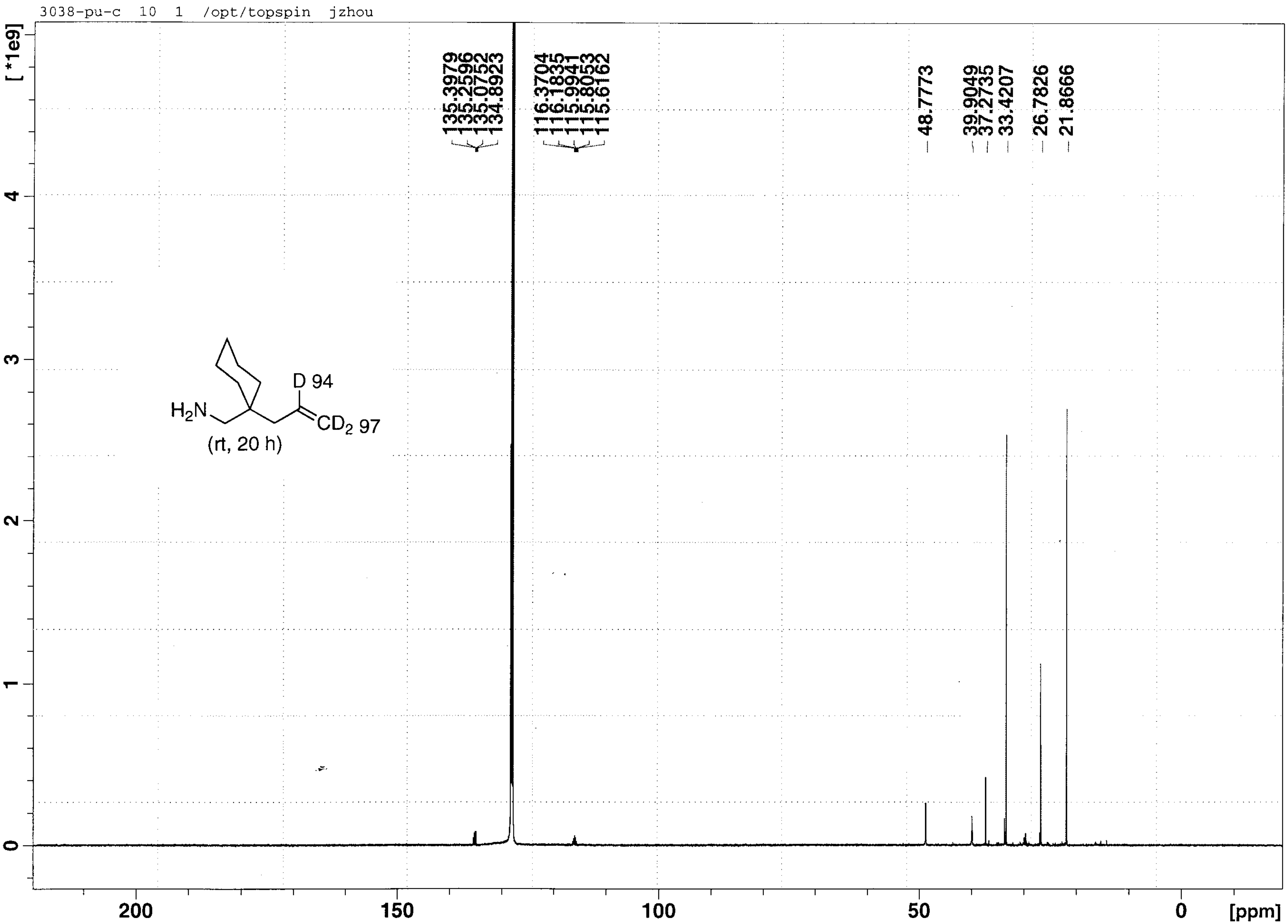

3038-sm-h 30 1 /opt/topspin jzhou
C6D6
aq 2s
d1 20s
7.1507
5.7897
5.7749
5.7718
5.7657
5.7602
5.7563
5.7493
5.7457
5.7382
5.7318
5.7203
5.7054
5.0302
5.0100
5.0048
4.9996
2.3657
2.0154
2.0007
1.3419
1.3317
1.3214
1.3159
1.3080
1.2931
1.2890
1.2841
1.2737
1.2584
1.2118
1.1849
1.1751
1.1649
0.4531
H
H2N
CH2
0.8888
1.9033
1.9969
2.0000
10.3233
1.9871
6
4
2
[ppm]

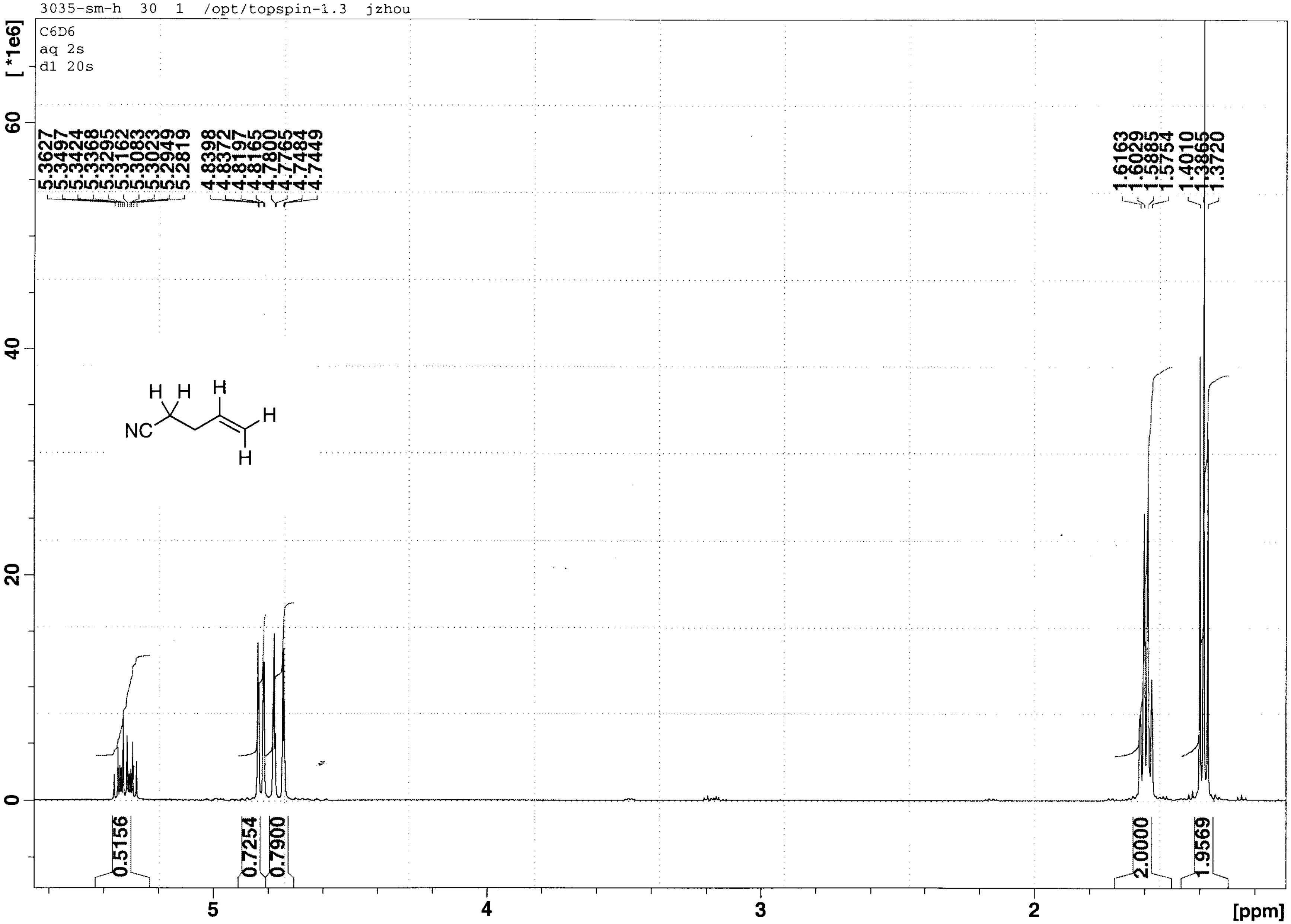


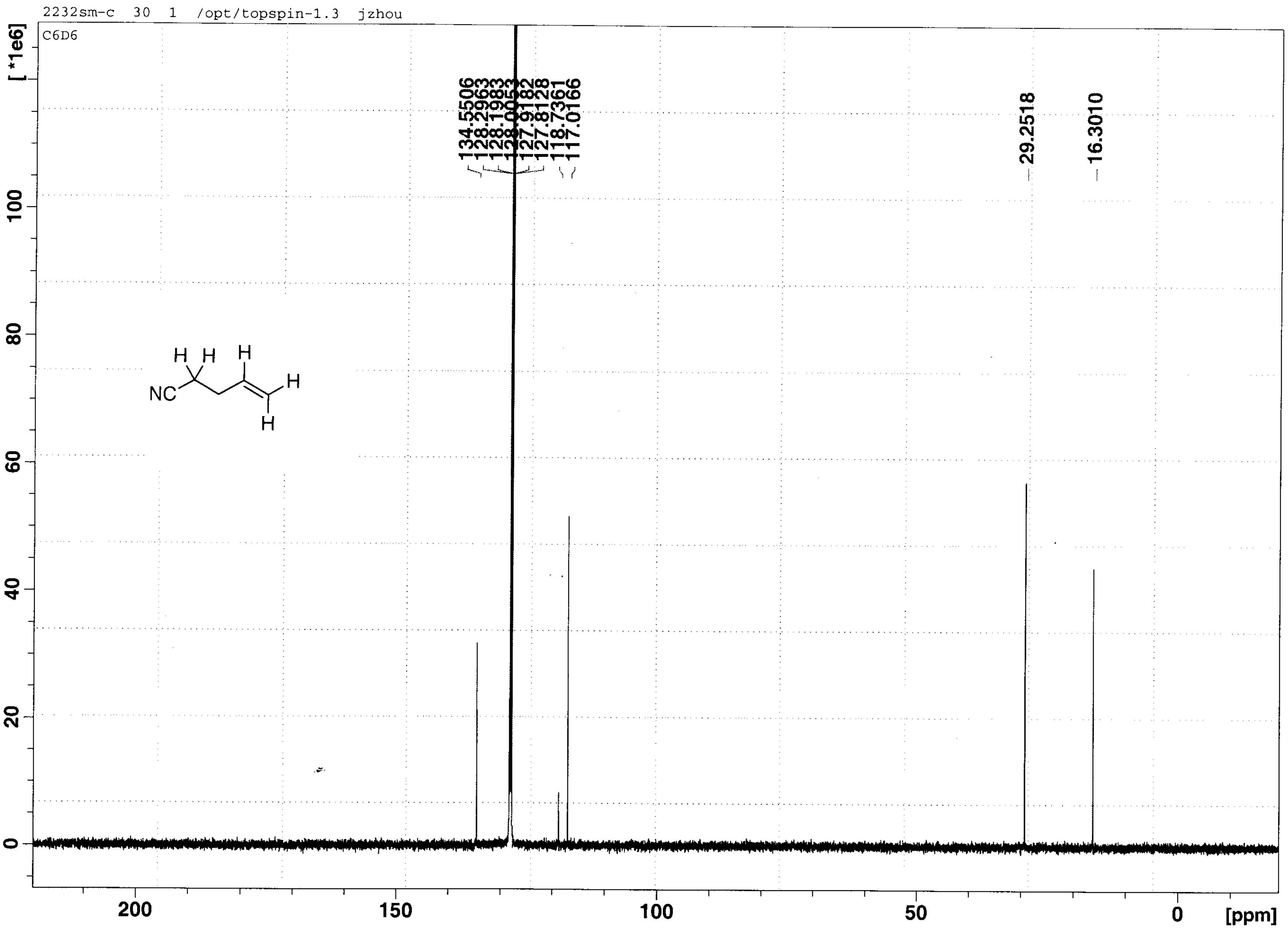
3038-sm-c 30 1 /opt/topspin jzhou
C6D6
aq 2s
d1 20s
135.6424
128.2843
127.9067
116.6315
48.7580
40.1008
37.2894
33.4086
26.7741
21.8533
H
H_2N
CH_2
200
150
100
50
0
[ppm]

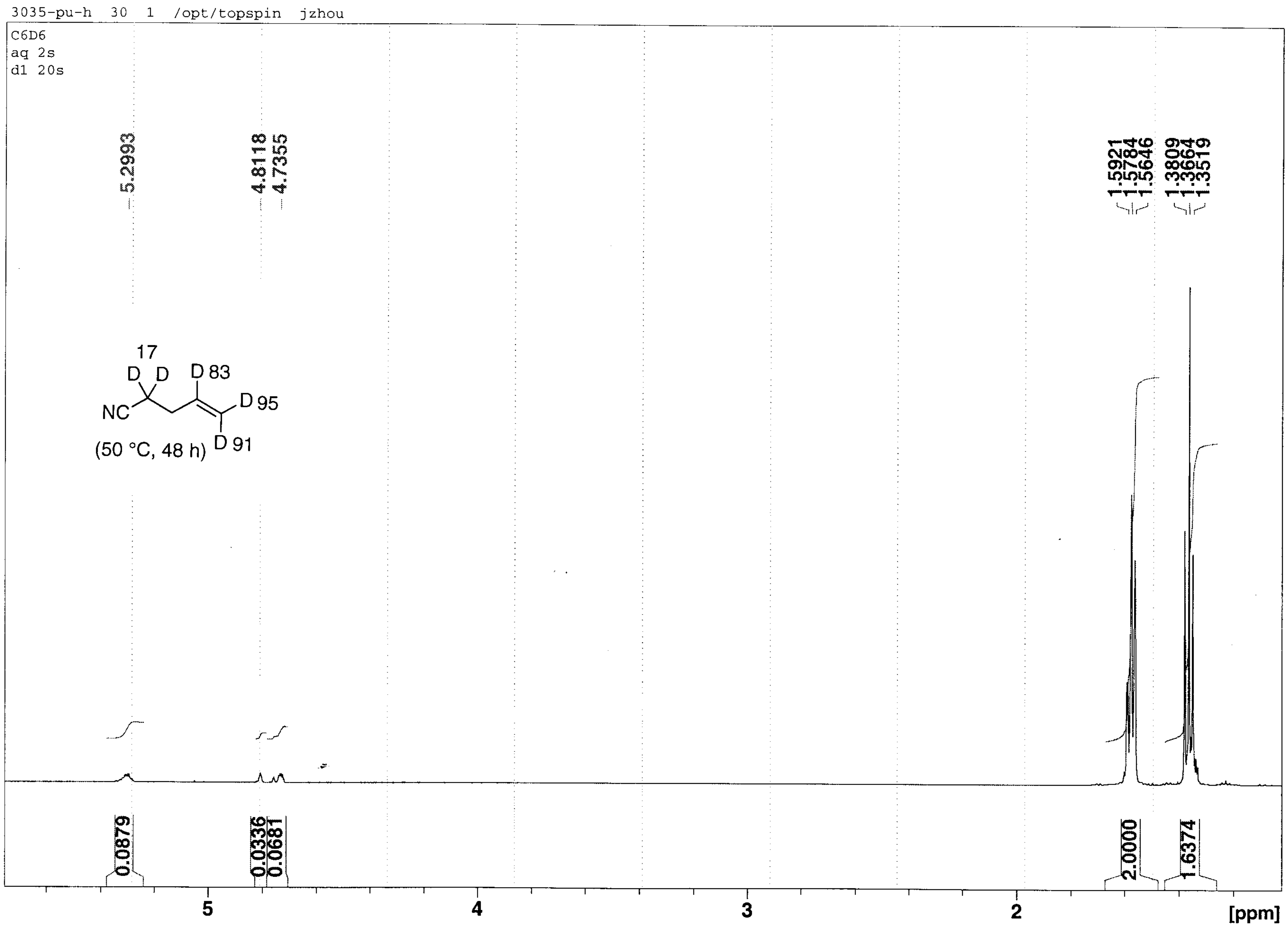

3038-pu-h 30 1 /opt/topspin jzhou
[*1e6]
5.7275
5.4046
4.9978
2.3546
1.9909
1.3494
1.3372
1.3277
1.3174
1.3046
1.2903
1.1717
1.1644
0.4768
D 94
H_2N
CD_2 97
(rt, 20 h)
0.0546
0.0171
0.0505
2.0000
2.0495
12.1113
1.9419
[ppm]

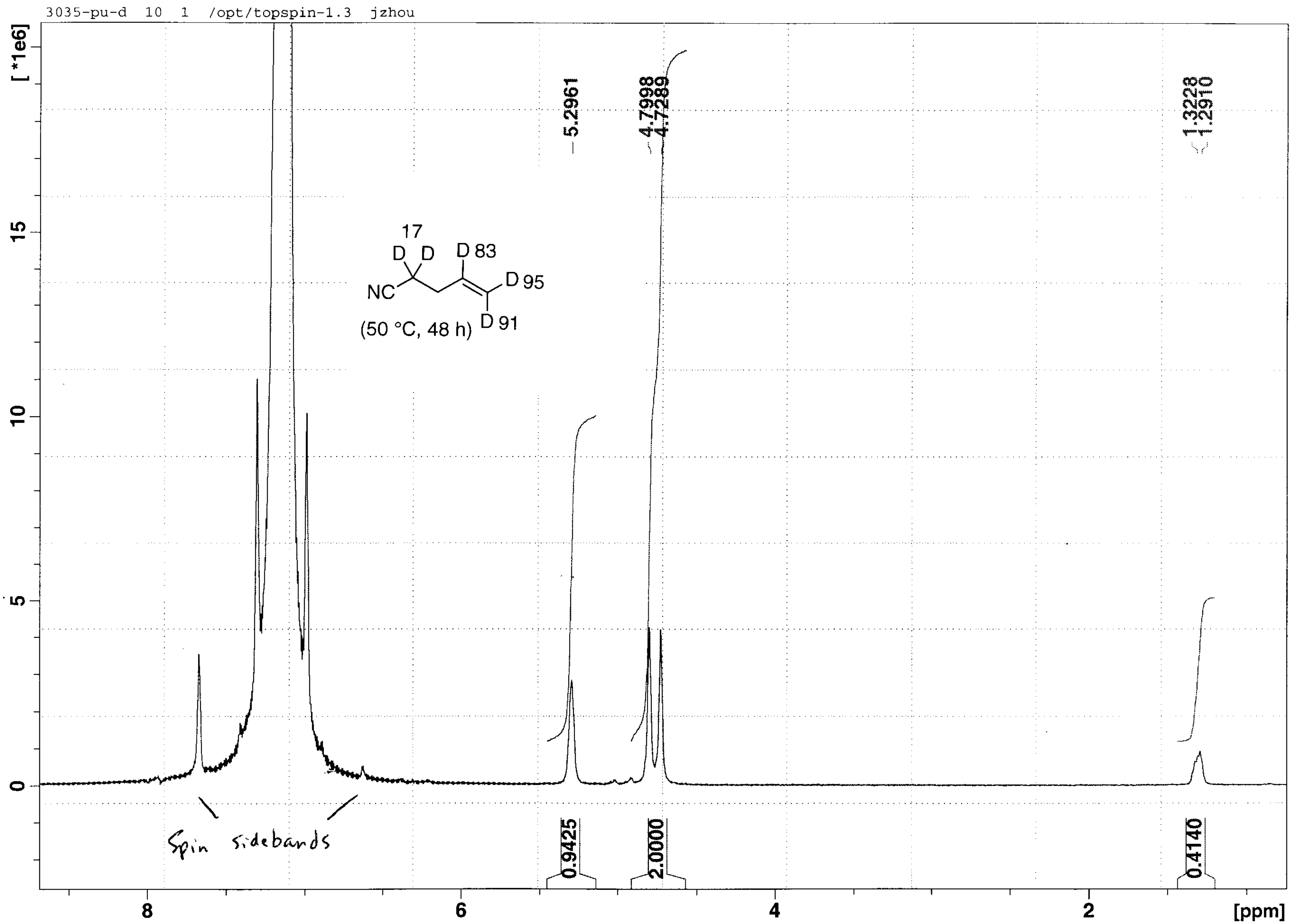

3038-pu-d 10 1 /opt/topspin jzhou
[*1e6]
5.7303
4.9899
D 94
H_2N
CD_2 97
(rt, 20 h)
Spin Sidebands
[ppm]

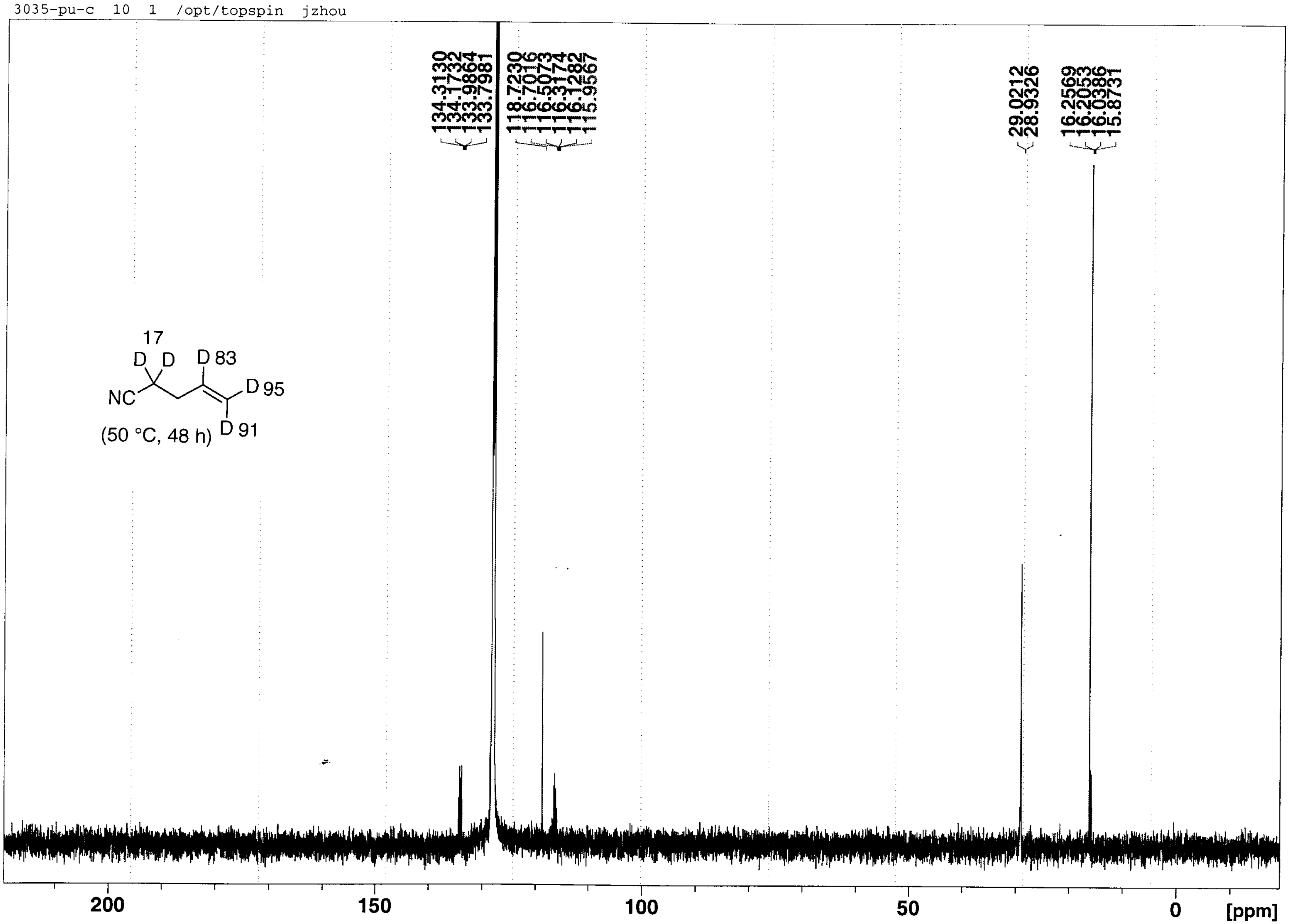

3038-pu-c 10 1 /opt/topspin jzhou
135.3979
135.2596
135.0752
134.8923
116.3704
116.1835
115.9941
115.8053
115.6162
48.7773
39.9049
37.2735
33.4207
26.7826
21.8666
[*1e9]
H2N
D 94
CD2 97
(rt, 20 h)
200
150
100
50
0
[ppm]


3035-sm-h 30 1 /opt/topspin-1.3 jzhou
C6D6
aq 2s
d1 20s
[*1e6]
5.3627
5.3497
5.3424
5.3368
5.3295
5.3162
5.3083
5.3023
5.2949
5.2819
4.8398
4.8372
4.8197
4.8165
4.7800
4.7765
4.7484
4.7449
1.6163
1.6029
1.5885
1.5754
1.4010
1.3865
1.3720
H H H
H
NC
H
0.5156
0.7254
0.7900
2.0000
1.9569
[ppm]


2232sm-c 30 1 /opt/topspin-1.3 jzhou
C6D6
[*1e6]
134.5506
128.2963
128.1983
128.0053
127.9182
127.8128
118.7361
117.0166
29.2518
16.3010
NC
H
[ppm]
200
150
100
50
0
20
40
60
80
100

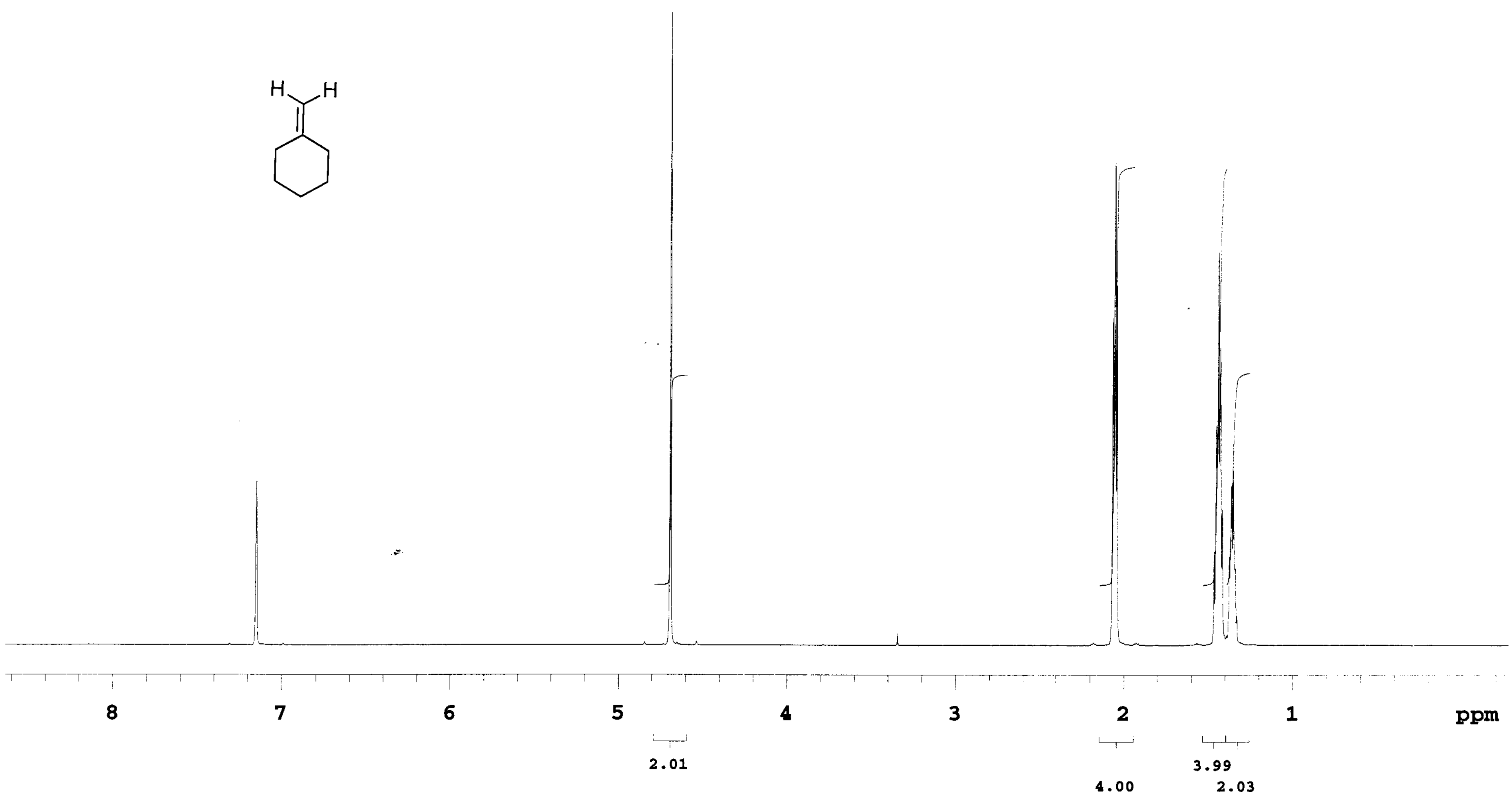

3035-pu-h 30 1 /opt/topspin jzhou
C6D6
aq 2s
d1 20s
5.2993
4.8118
4.7355
1.5921
1.5784
1.5646
1.3809
1.3664
1.3519
17
D D
D 83
D 95
NC
D 91
(50 °C, 48 h)
0.0879
0.0336
0.0681
2.0000
1.6374
5
4
3
2
[ppm]

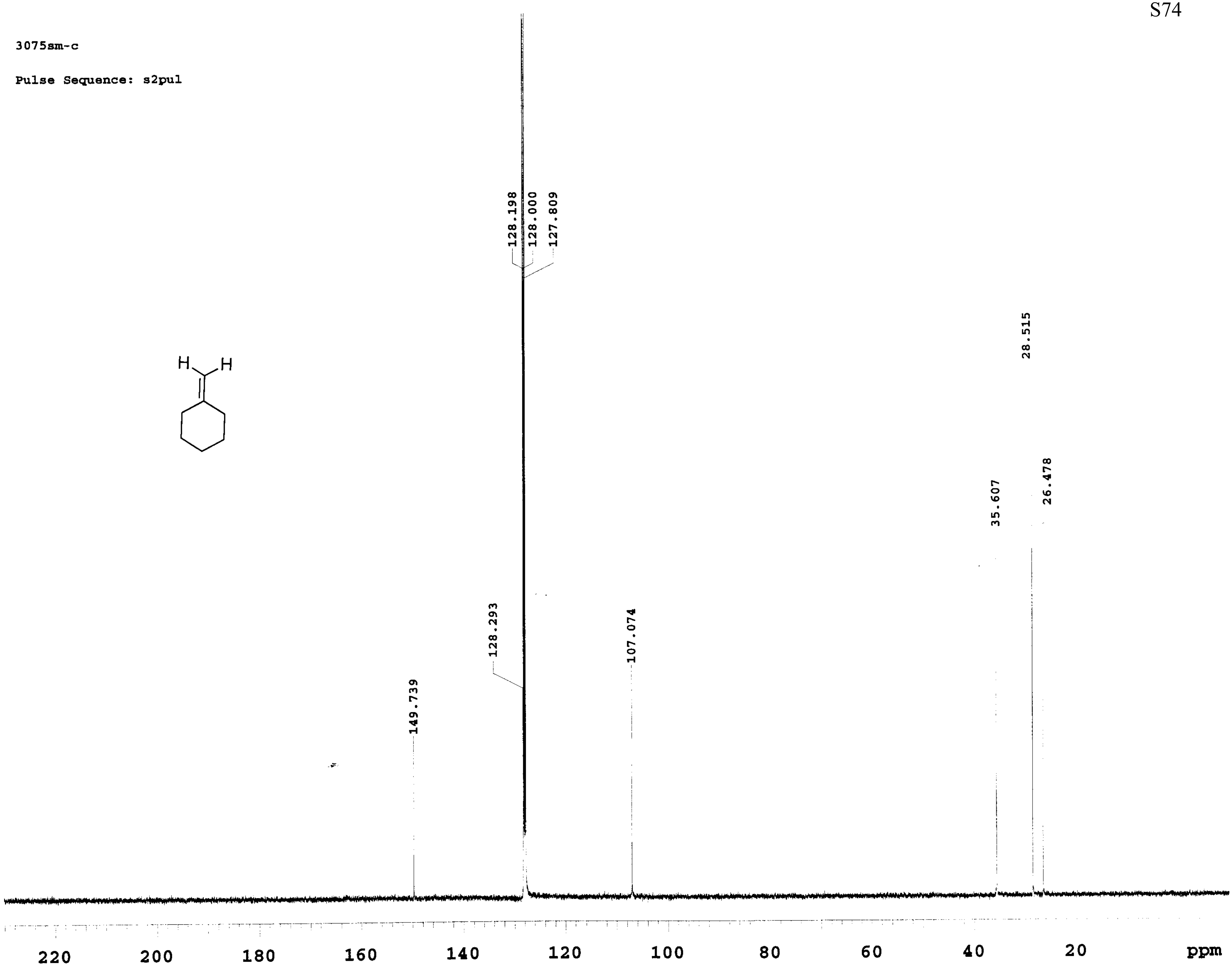

3035-pu-d 10 1 /opt/topspin-1.3 jzhou
[*1e6]
15
10
5
0
5.2961
4.7998
4.7289
1.3228
1.2910
17
D D
D 83
D 95
NC
D 91
(50 °C, 48 h)
Spin sidebands
0.9425
2.0000
0.4140
8
6
4
2
[ppm]


3035-pu-c 10 1 /opt/topspin jzhou
134.3130
134.1732
133.9864
133.7981
118.7230
116.7016
116.5073
116.3174
116.1282
115.9567
29.0212
28.9326
16.2569
16.2053
16.0386
15.8731
17
D D
D 83
D 95
NC
D 91
(50 °C, 48 h)
200
150
100
50
0
[ppm]

3075sm-h

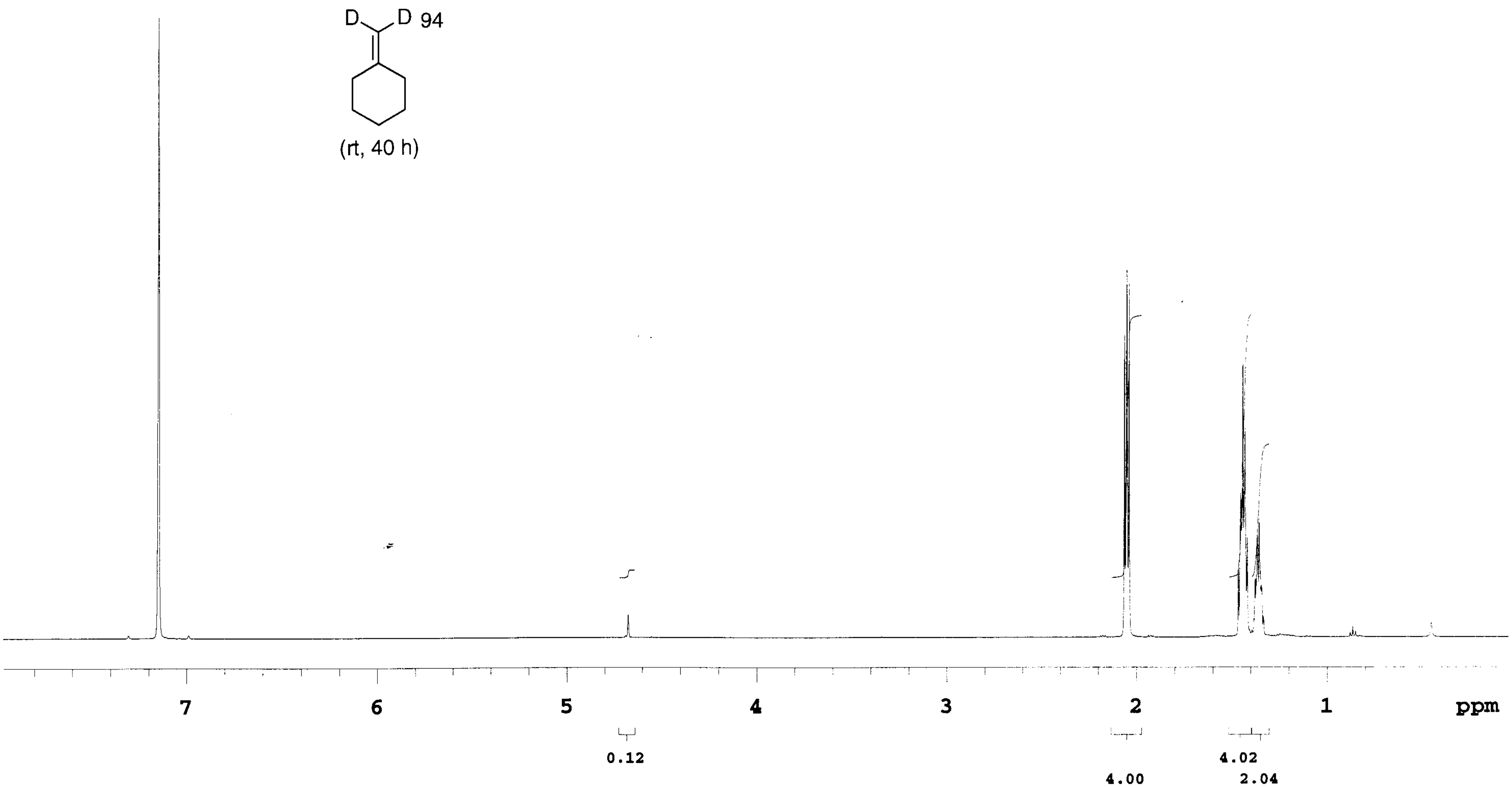
Pulse Sequence: s2pul

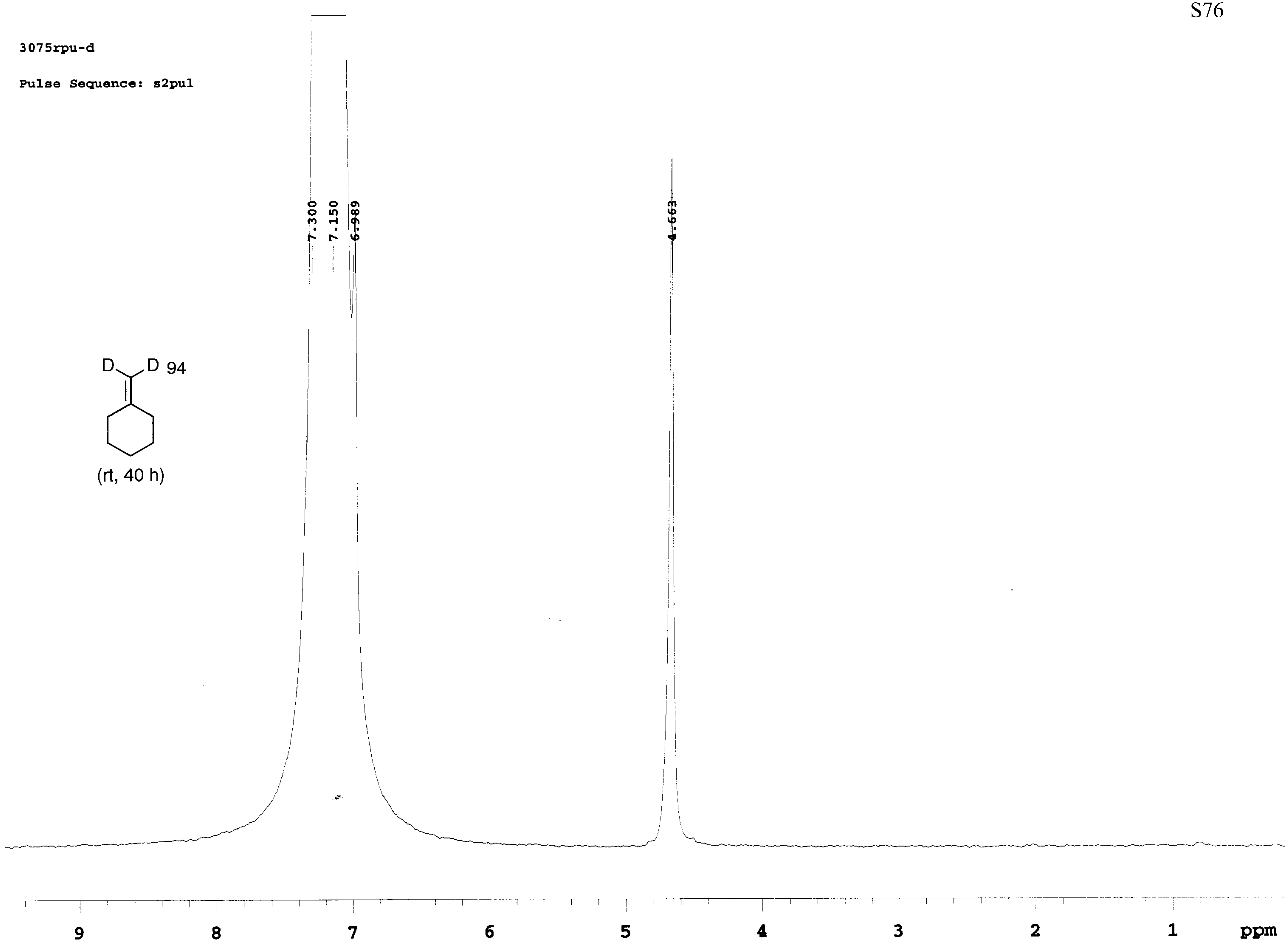


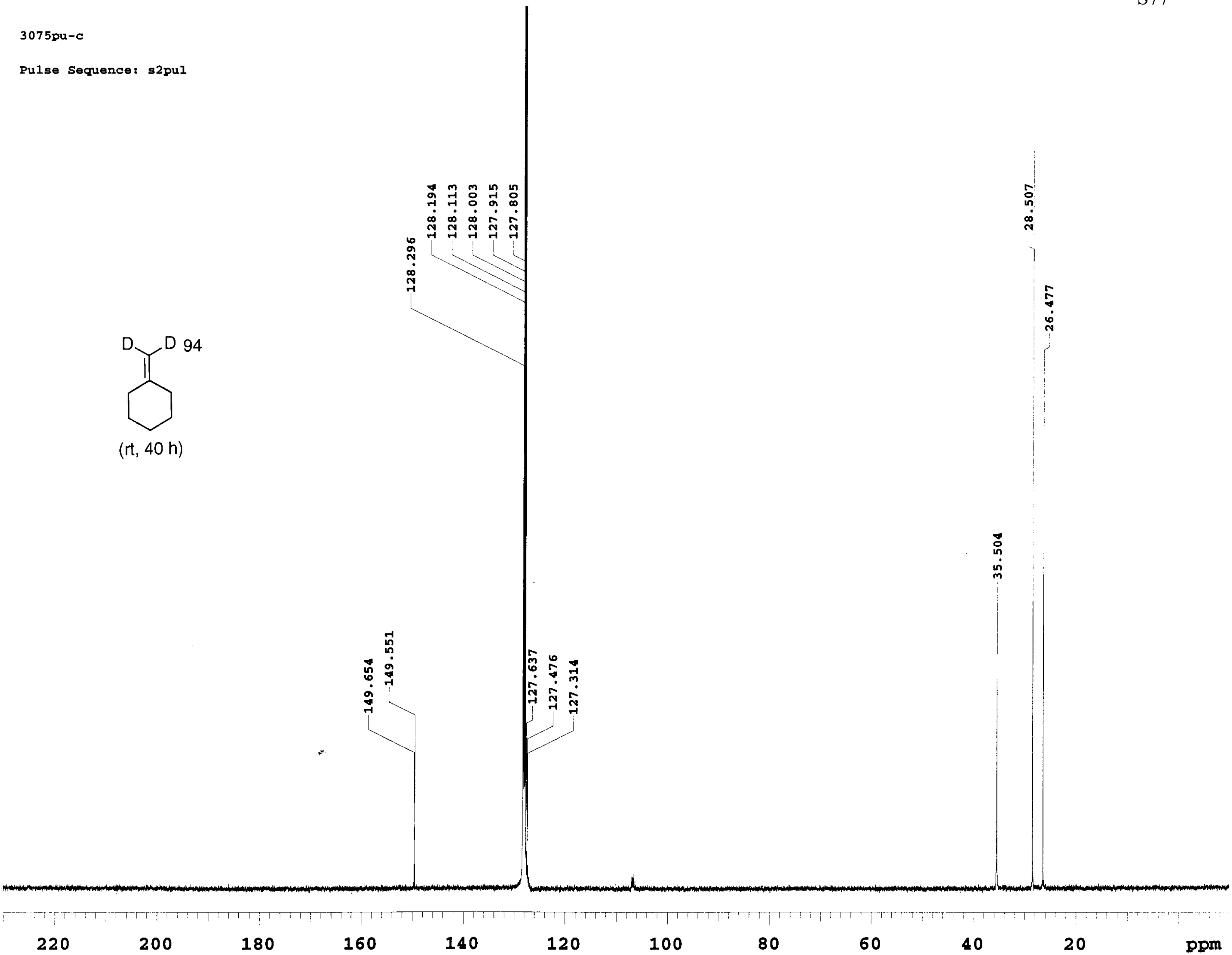

3075sm-c
Pulse Sequence: s2pul
H
H
128.198
128.000
127.809
28.515
35.607
26.478
128.293
107.074
149.739
220
200
180
160
140
120
100
80
60
40
20
ppm

3075rpu-h

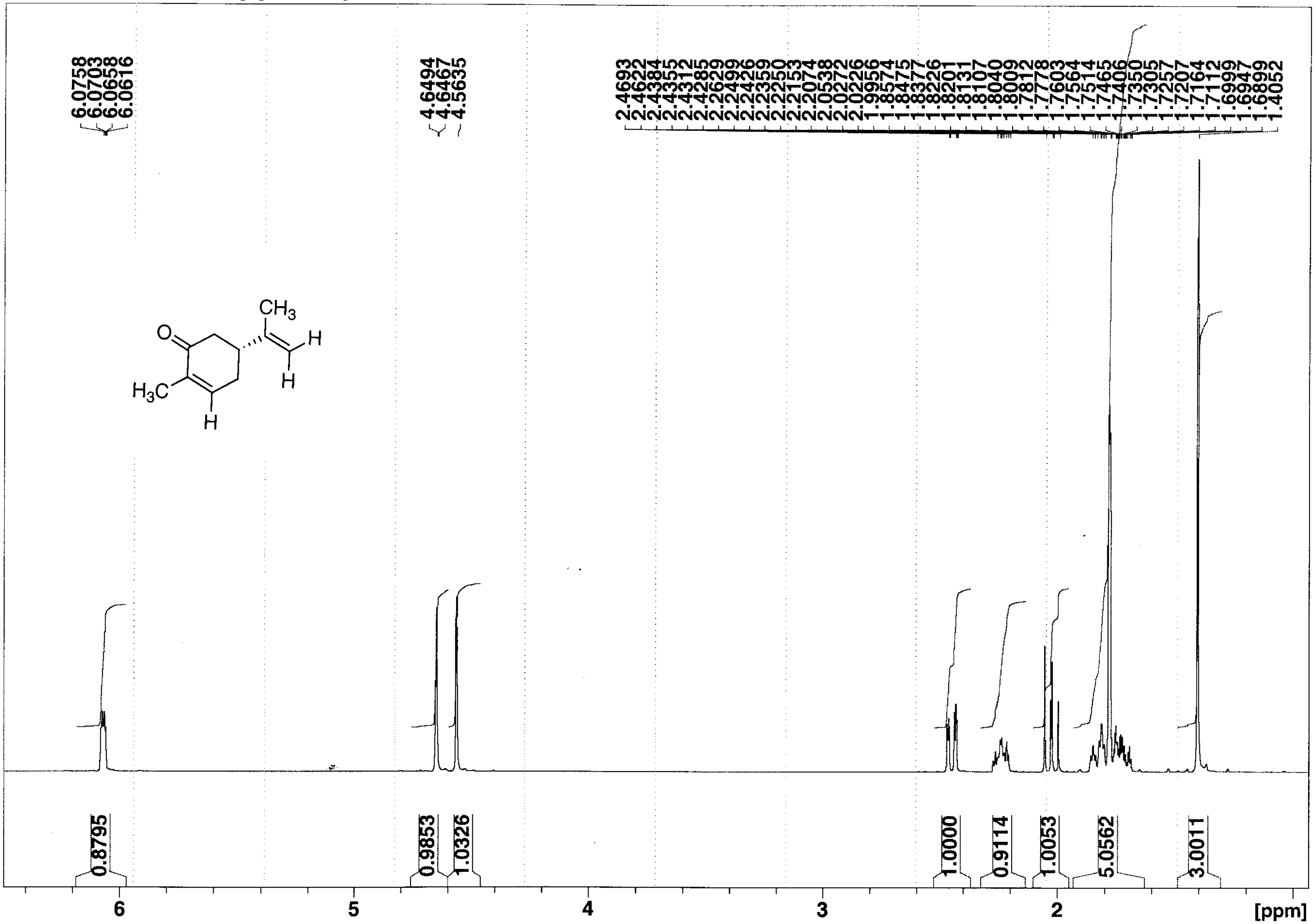
Pulse Sequence: s2pul

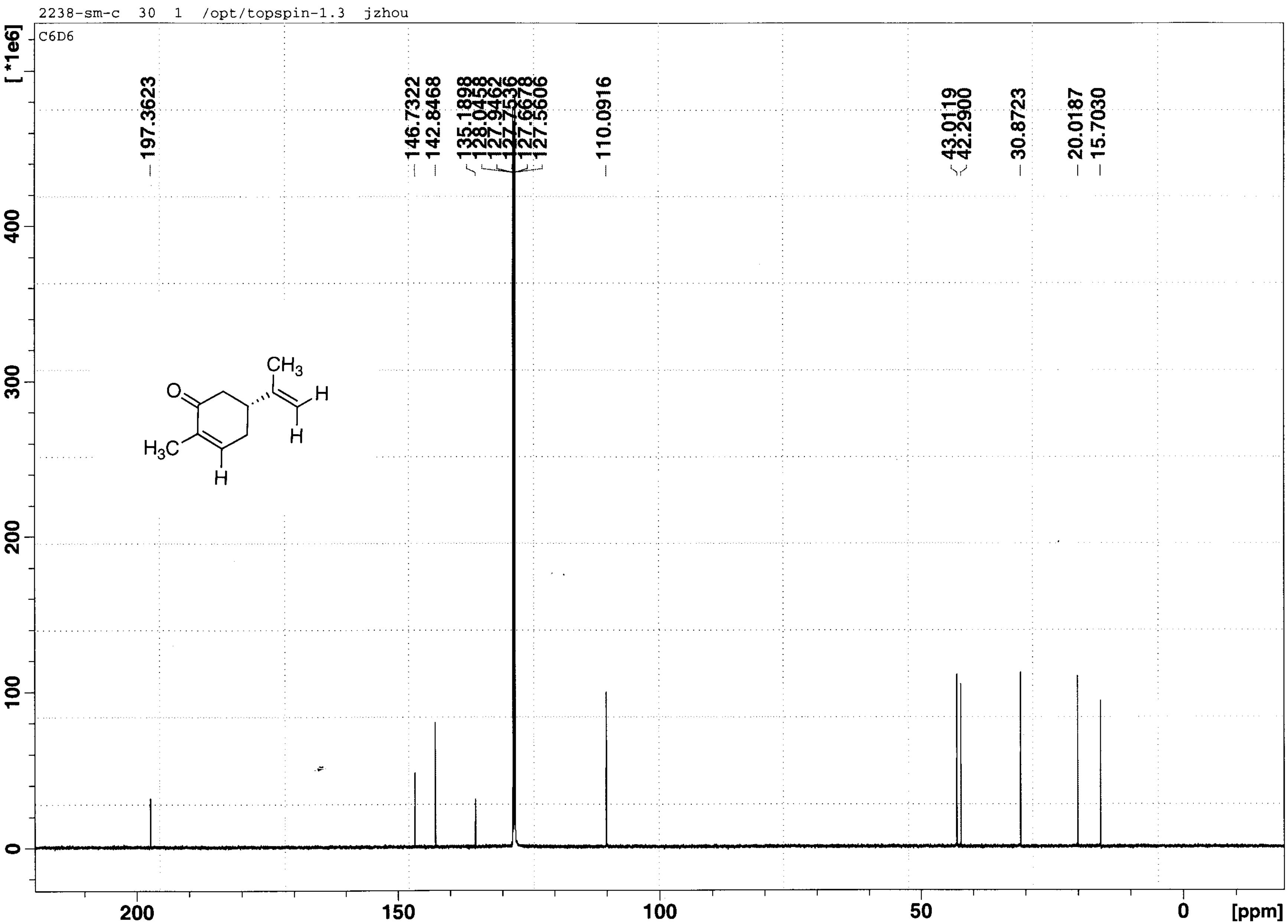


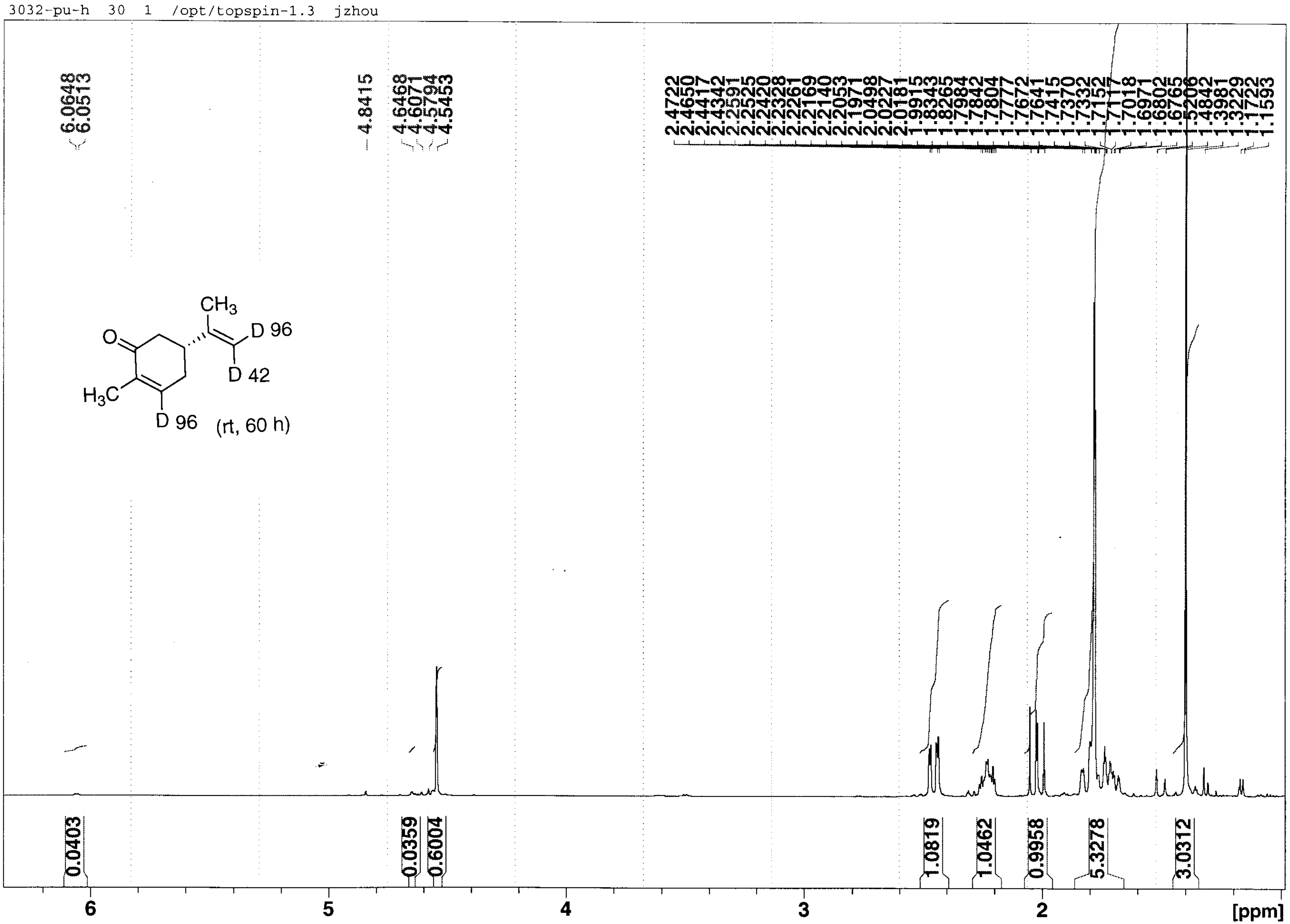

3075rpu-d
Pulse Sequence: s2pul
7.300
7.150
6.989
4.663
D
D
94
(rt, 40 h)
9
8
7
6
5
4
3
2
1
ppm

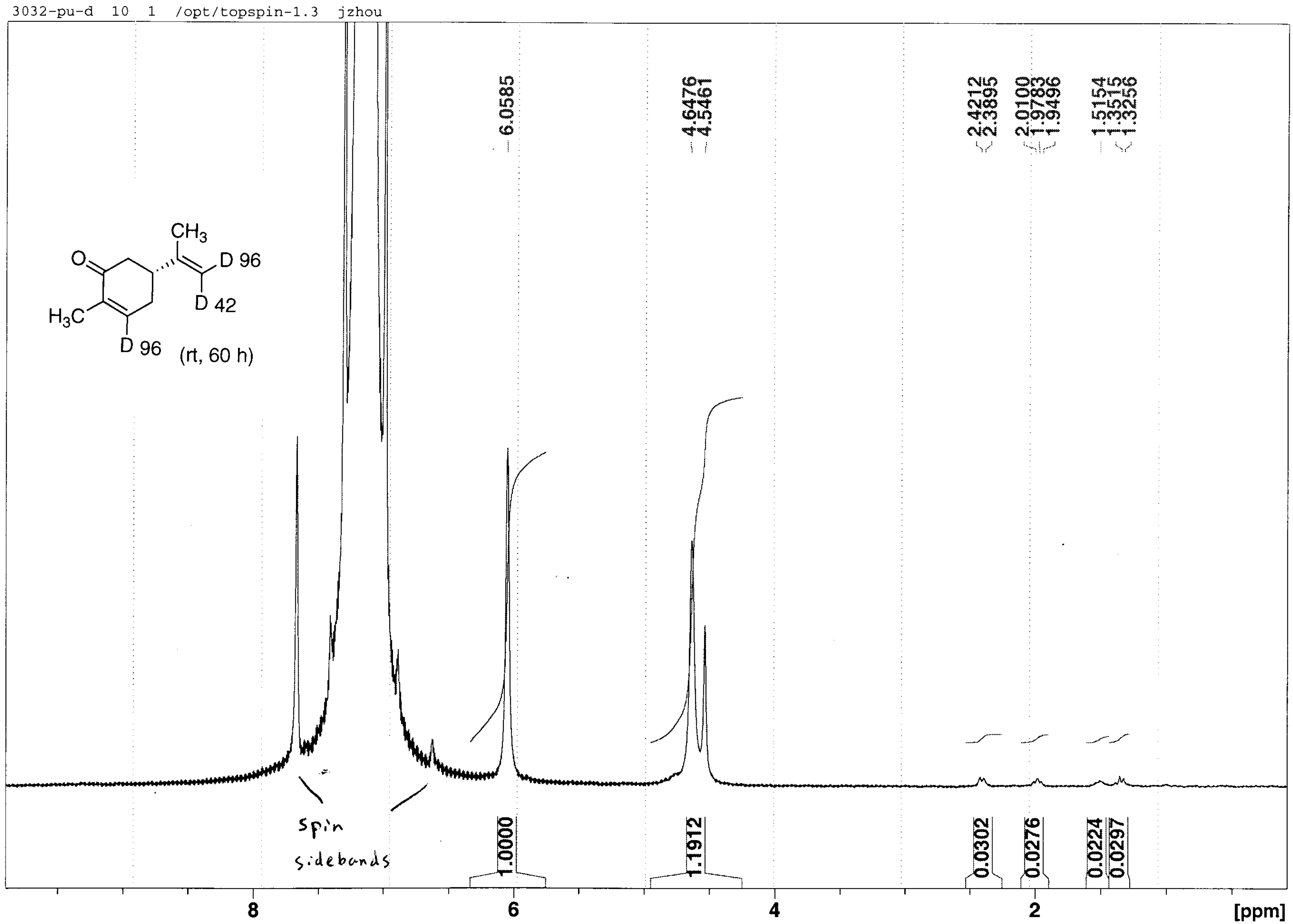

3075pu-c
Pulse Sequence: s2pul
D
D
94
(rt, 40 h)
149.654
149.551
128.296
128.194
128.113
128.003
127.915
127.805
127.637
127.476
127.314
35.504
28.507
26.477
220
200
180
160
140
120
100
80
60
40
20
ppm

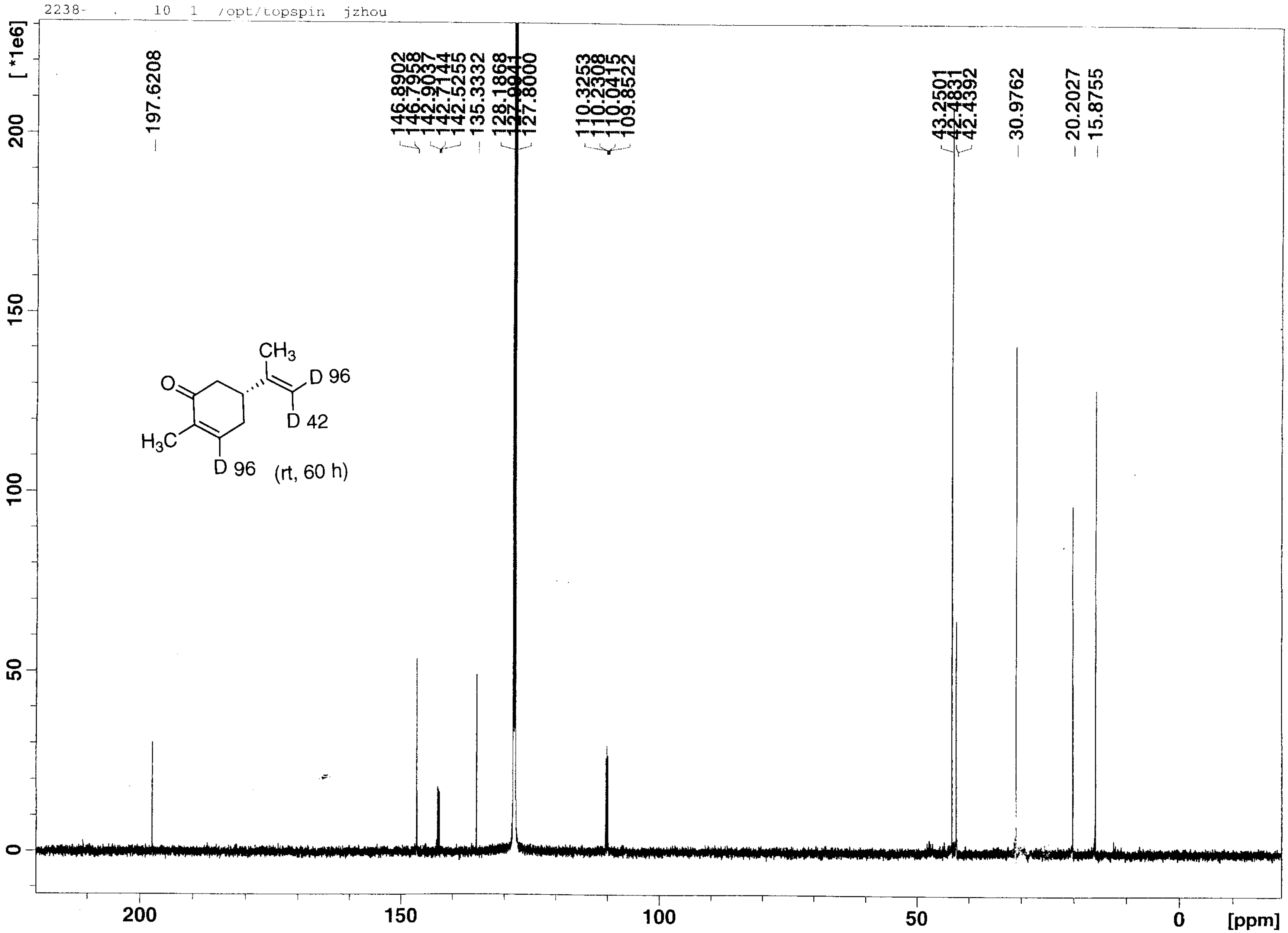
3032-sm-h 30 1 /opt/topspin-1.3 jzhou




2238-sm-c 30 1 /opt/topspin-1.3 jzhou
C6D6
[*1e6]
197.3623
146.7322
142.8468
135.1898
128.0458
127.9462
127.7536
127.6678
127.5606
110.0916
43.0119
42.2900
30.8723
20.0187
15.7030
CH3
O
H
H
H3C
H
400
300
200
100
0
200
150
100
50
0
[ppm]

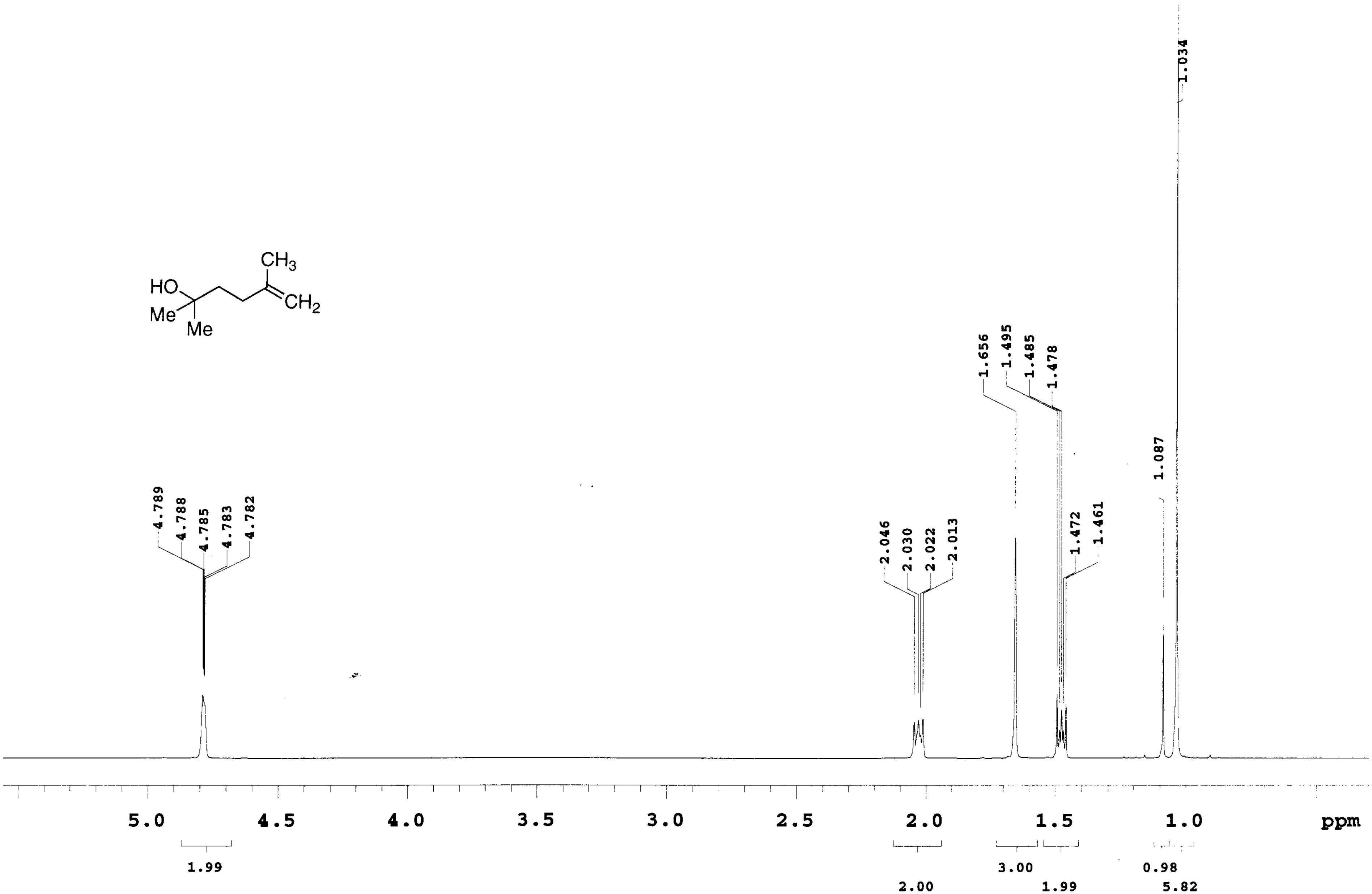

3032-pu-h 30 1 /opt/topspin-1.3 jzhou
6.0648
6.0513
4.8415
4.6468
4.6071
4.5794
4.5453
2.4722
2.4650
2.4417
2.4342
2.2591
2.2525
2.2420
2.2328
2.2261
2.2169
2.2140
2.2053
2.1971
2.0498
2.0227
2.0181
1.9915
1.8343
1.8265
1.7984
1.7842
1.7804
1.7777
1.7672
1.7641
1.7415
1.7370
1.7332
1.7152
1.7117
1.7018
1.6971
1.6802
1.6765
1.5206
1.4842
1.3981
1.3229
1.1722
1.1593
CH3
O
D 96
D 42
H3C
D 96
(rt, 60 h)
0.0403
0.0359
0.6004
1.0819
1.0462
0.9958
5.3278
3.0312
6
5
4
3
2
[ppm]

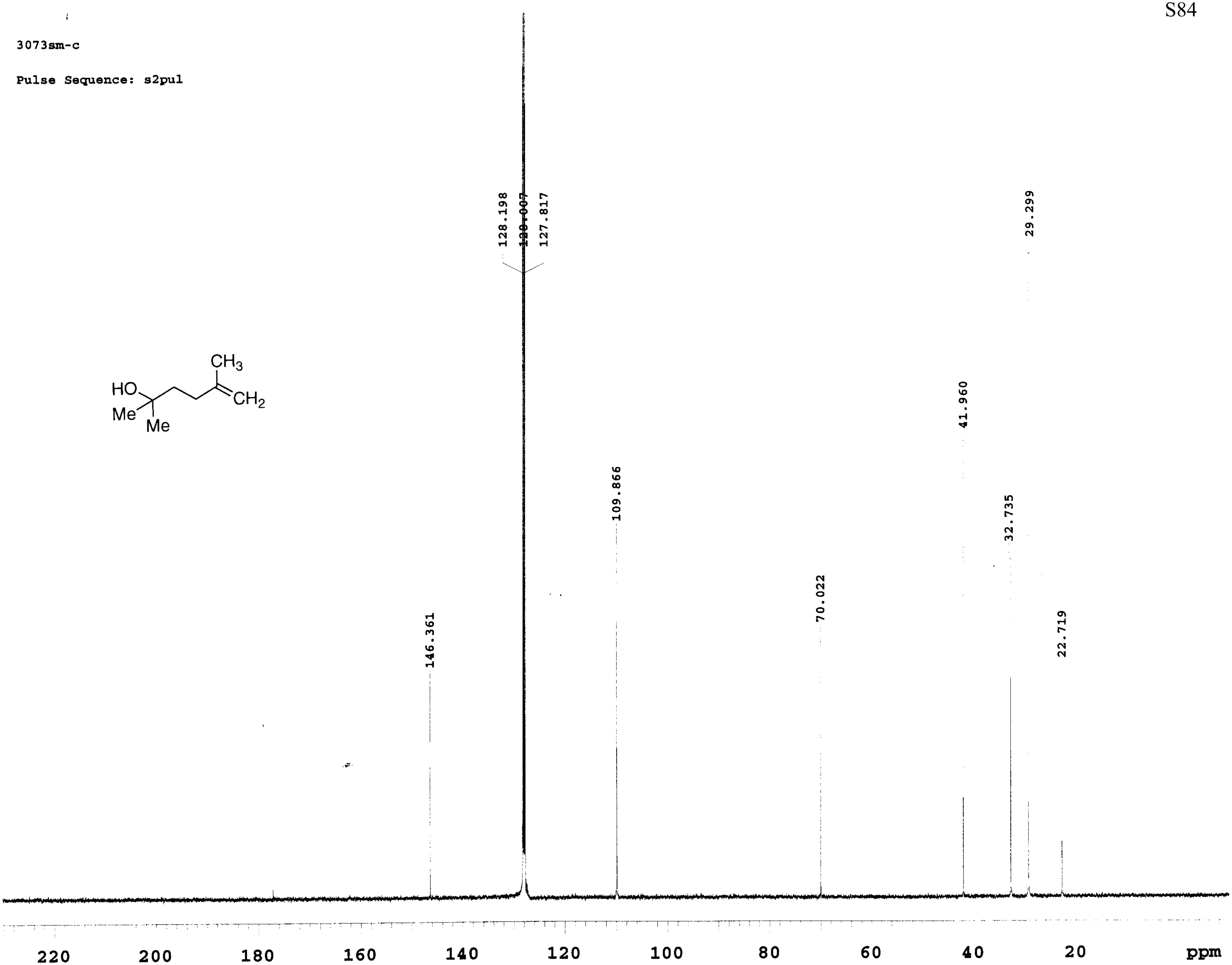

3032-pu-d 10 1 /opt/topspin-1.3 jzhou
6.0585
4.6476
4.5461
2.4212
2.3895
2.0100
1.9783
1.9496
1.5154
1.3515
1.3256
CH3
O
D 96
D 42
H3C
D 96
(rt, 60 h)
spin sidebands
1.0000
1.1912
0.0302
0.0276
0.0224
0.0297
8
6
4
2
[ppm]


2238- . 10 1 /opt/topspin jzhou
197.6208
146.8902
146.7958
142.9037
142.7144
142.5255
135.3332
128.1868
127.9941
127.8000
110.3253
110.2308
110.0415
109.8522
43.2501
42.4831
42.4392
30.9762
20.2027
15.8755
CH3
O
D 96
D 42
H3C
D 96
(rt, 60 h)
[*1e6]
[ppm]

3073sm-h

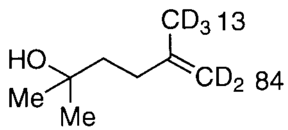
Pulse Sequence: s2pul



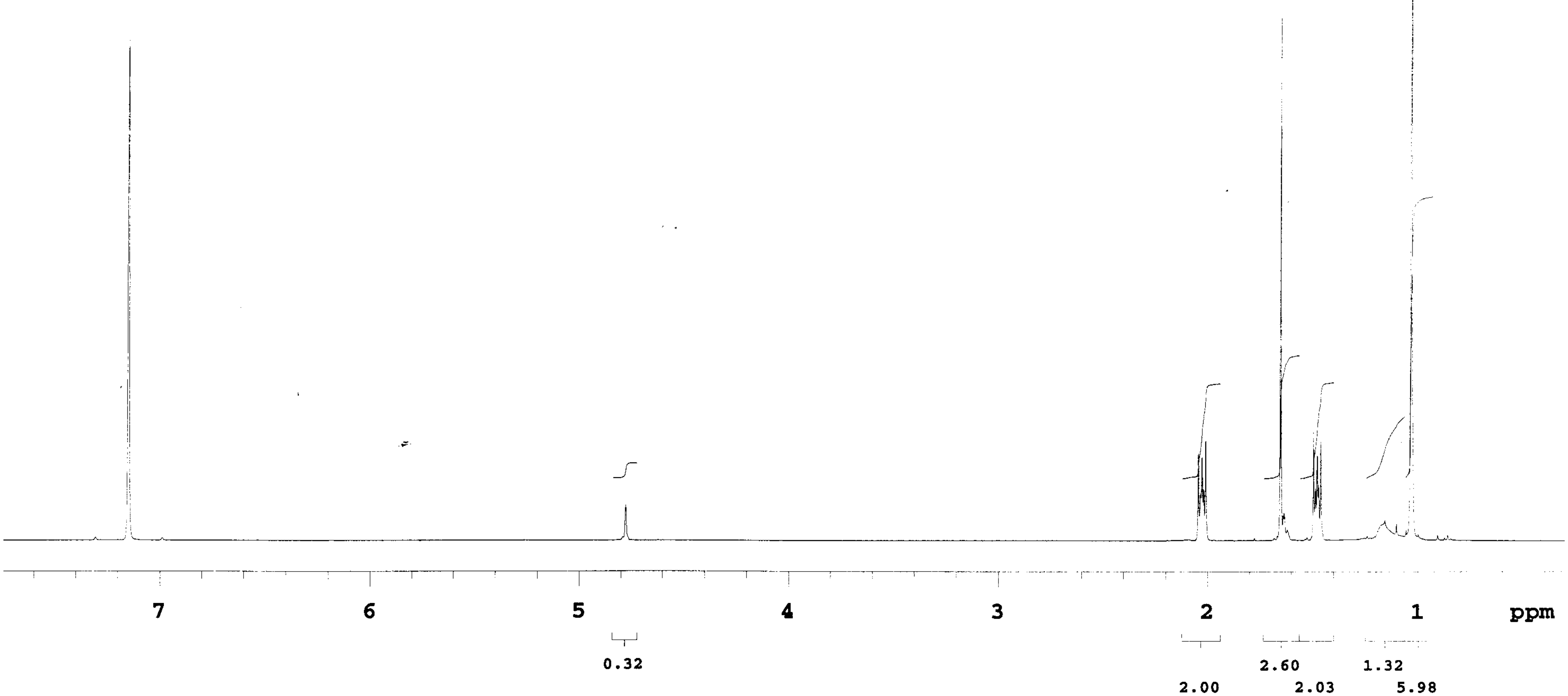

3073sm-c
Pulse Sequence: s2pul
128.198
128.007
127.817
29.299
CH_3
HO
CH_2
Me
Me
41.960
109.866
32.735
70.022
146.361
22.719
220
200
180
160
140
120
100
80
60
40
20
ppm

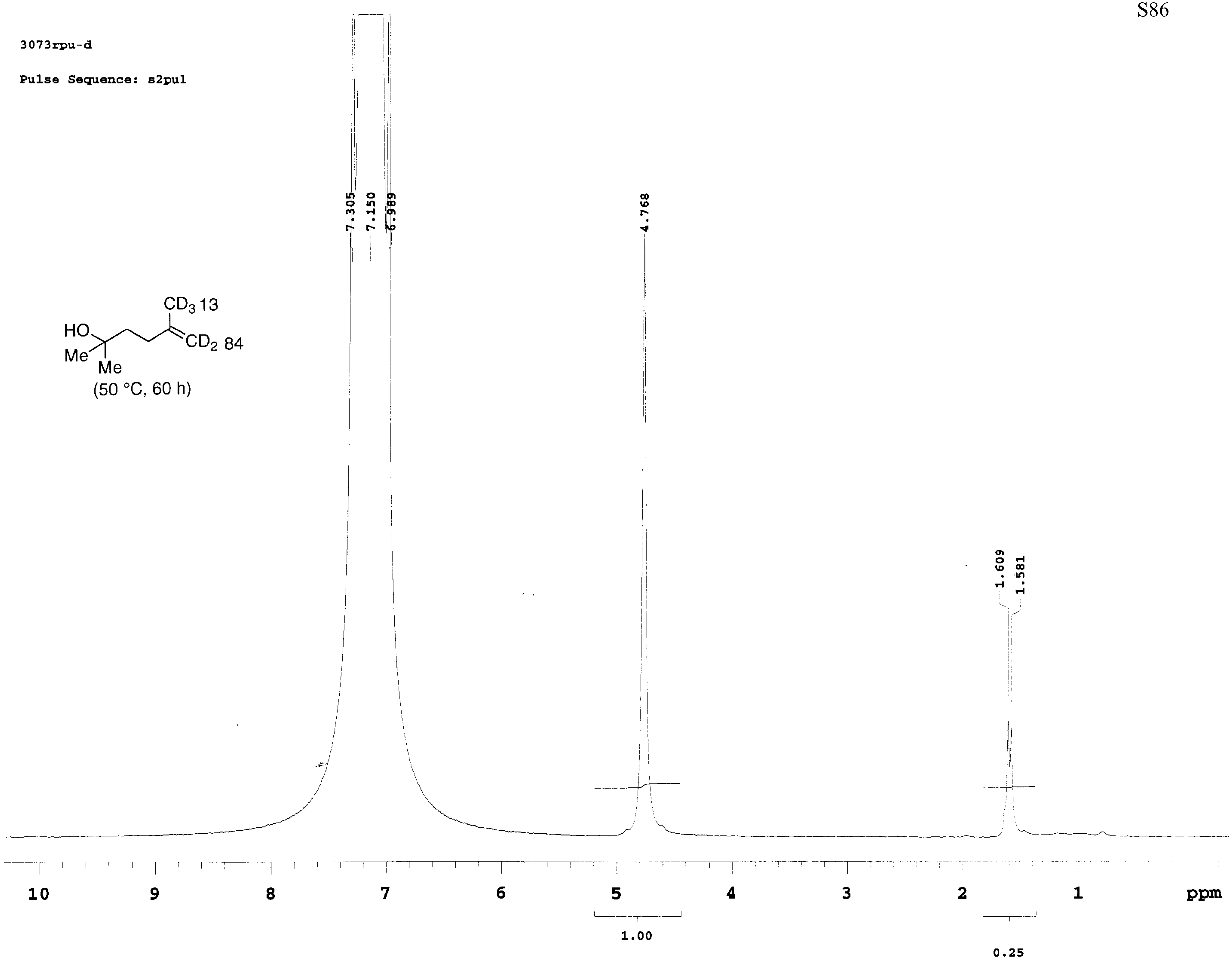
3073rpu-h

Pulse Sequence: s2pul



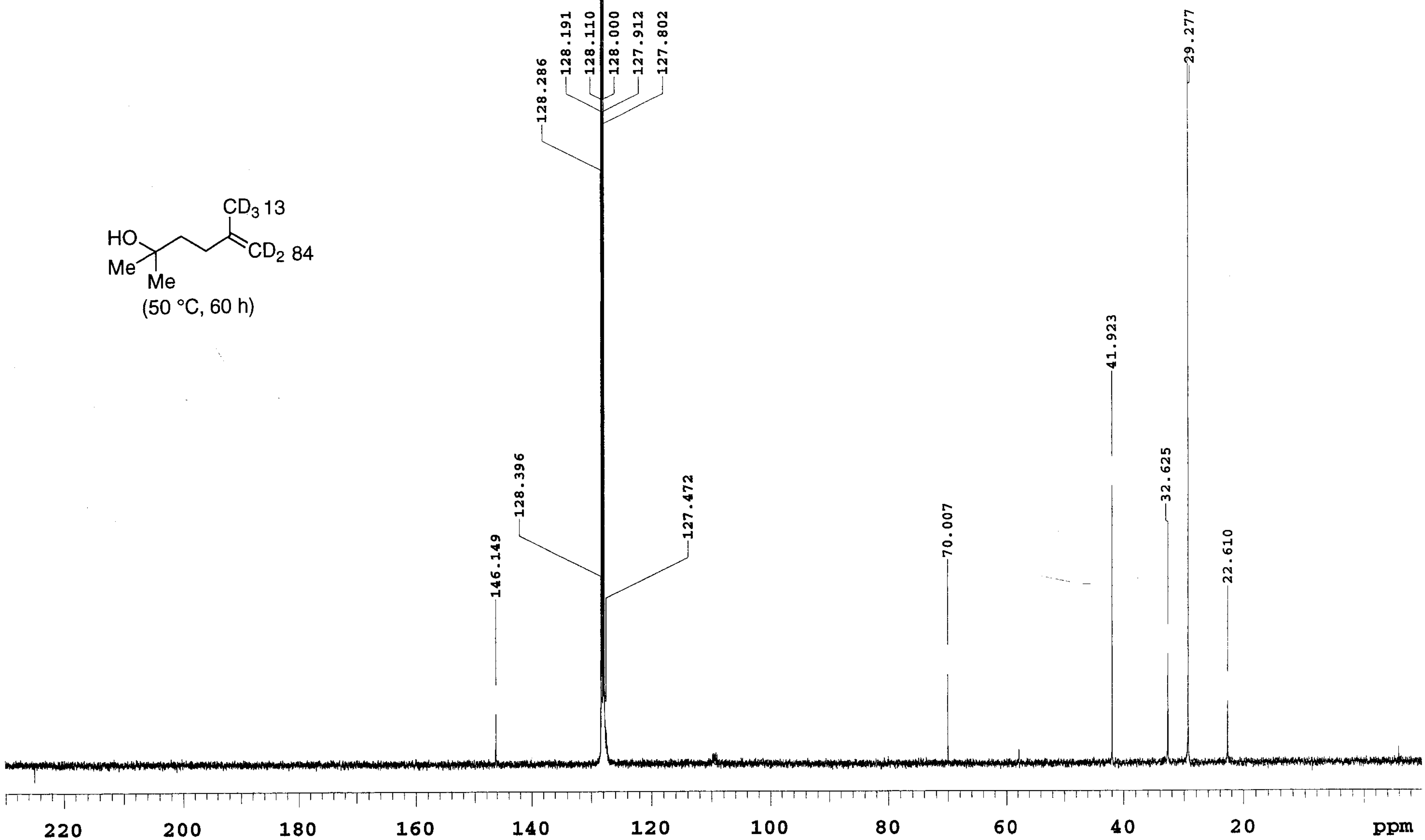
(50 °C, 60 h)




3073rpu-d
Pulse Sequence: s2pul
7.305
7.150
6.989
4.768
1.609
1.581
CD_3 13
HO
Me
Me
CD_2 84
(50 °C, 60 h)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.25

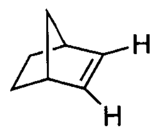
3073rpu-c

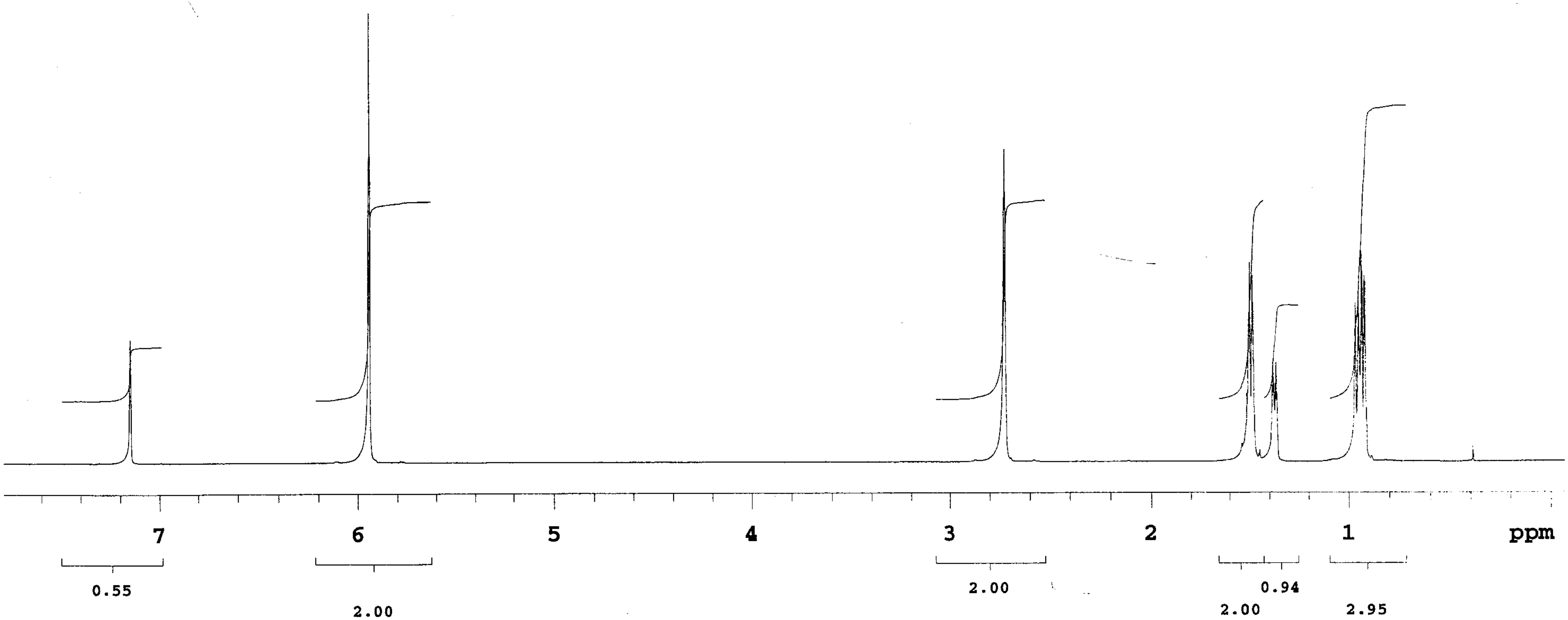
Pulse Sequence: s2pul

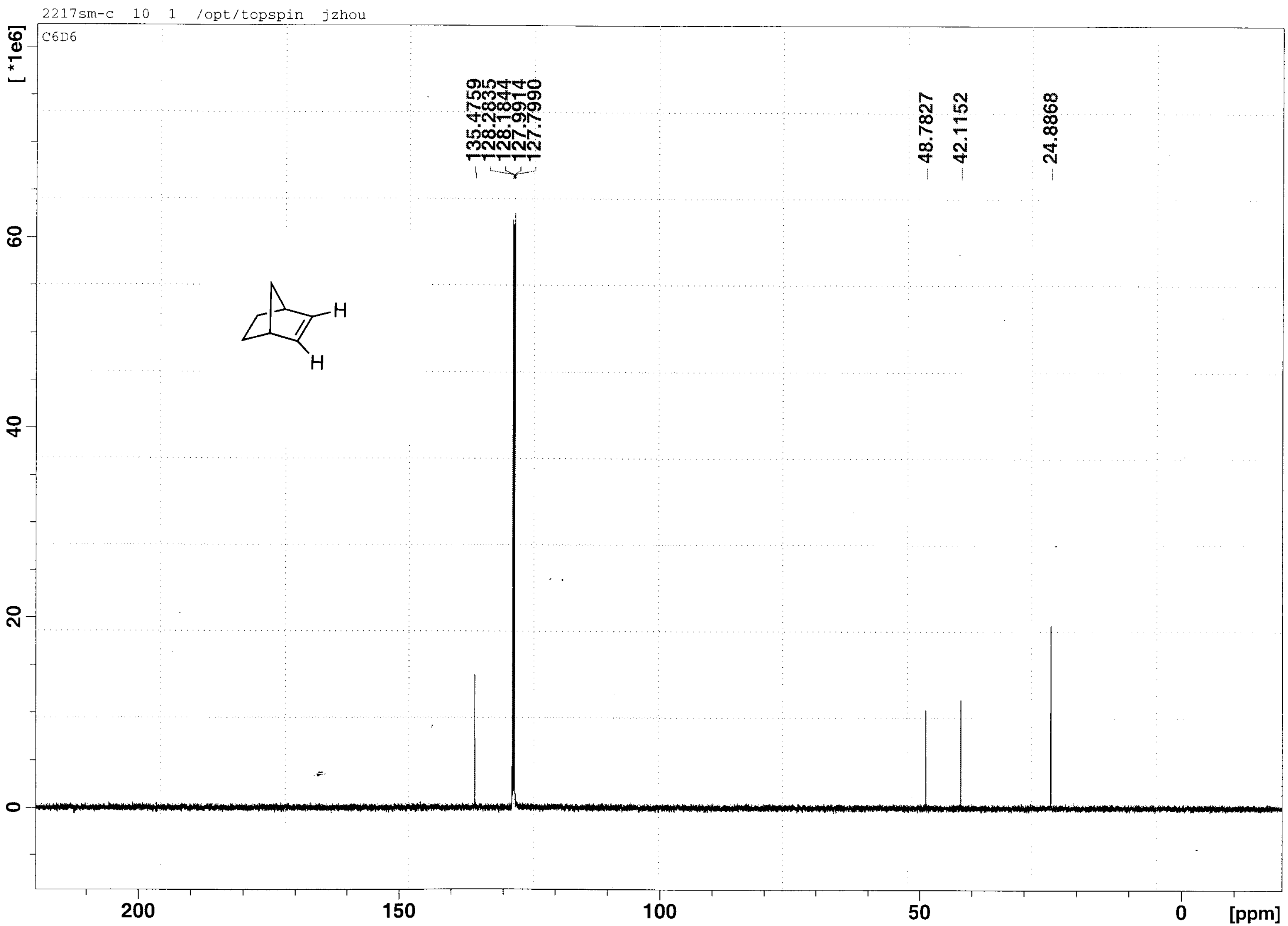


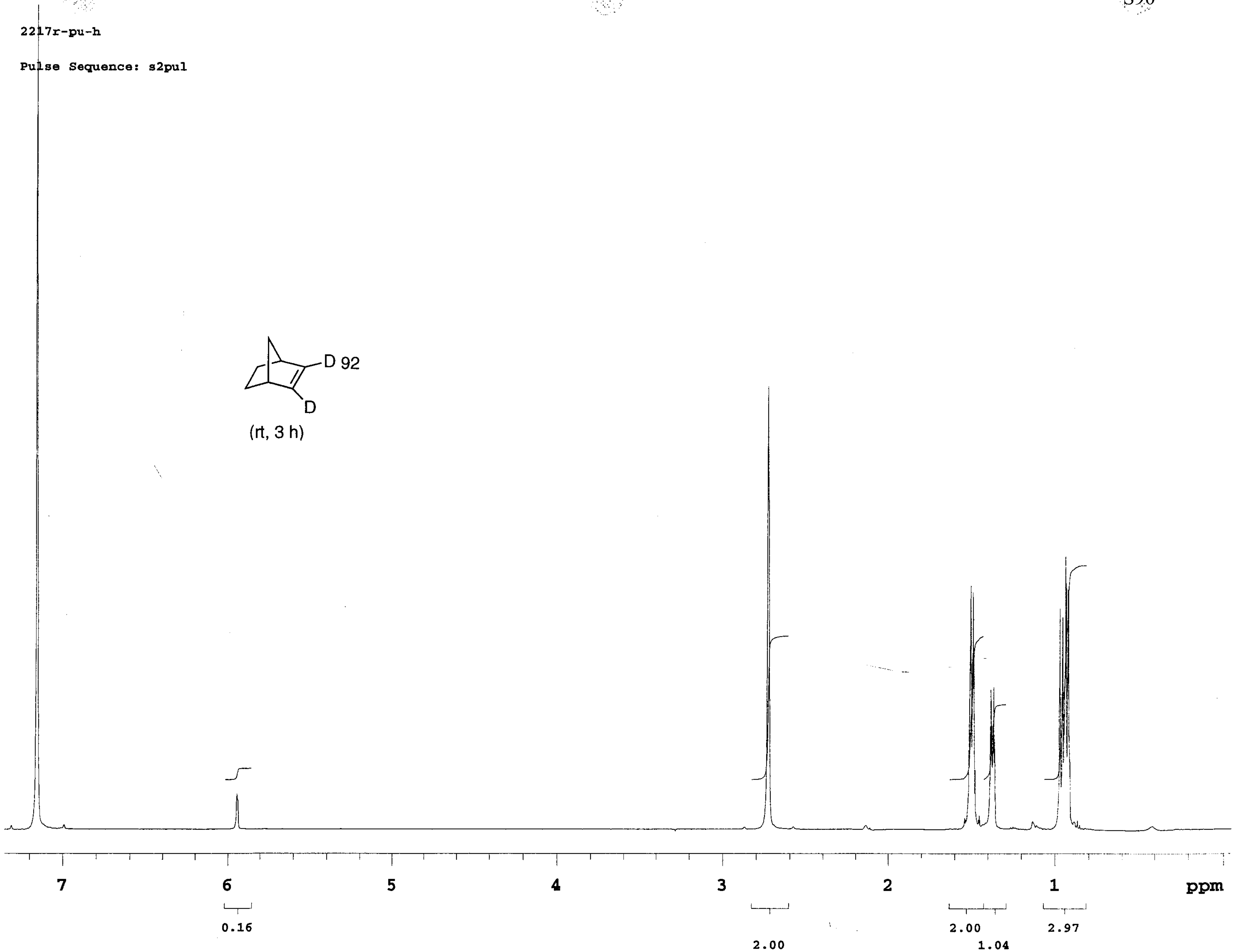
2217sm-h

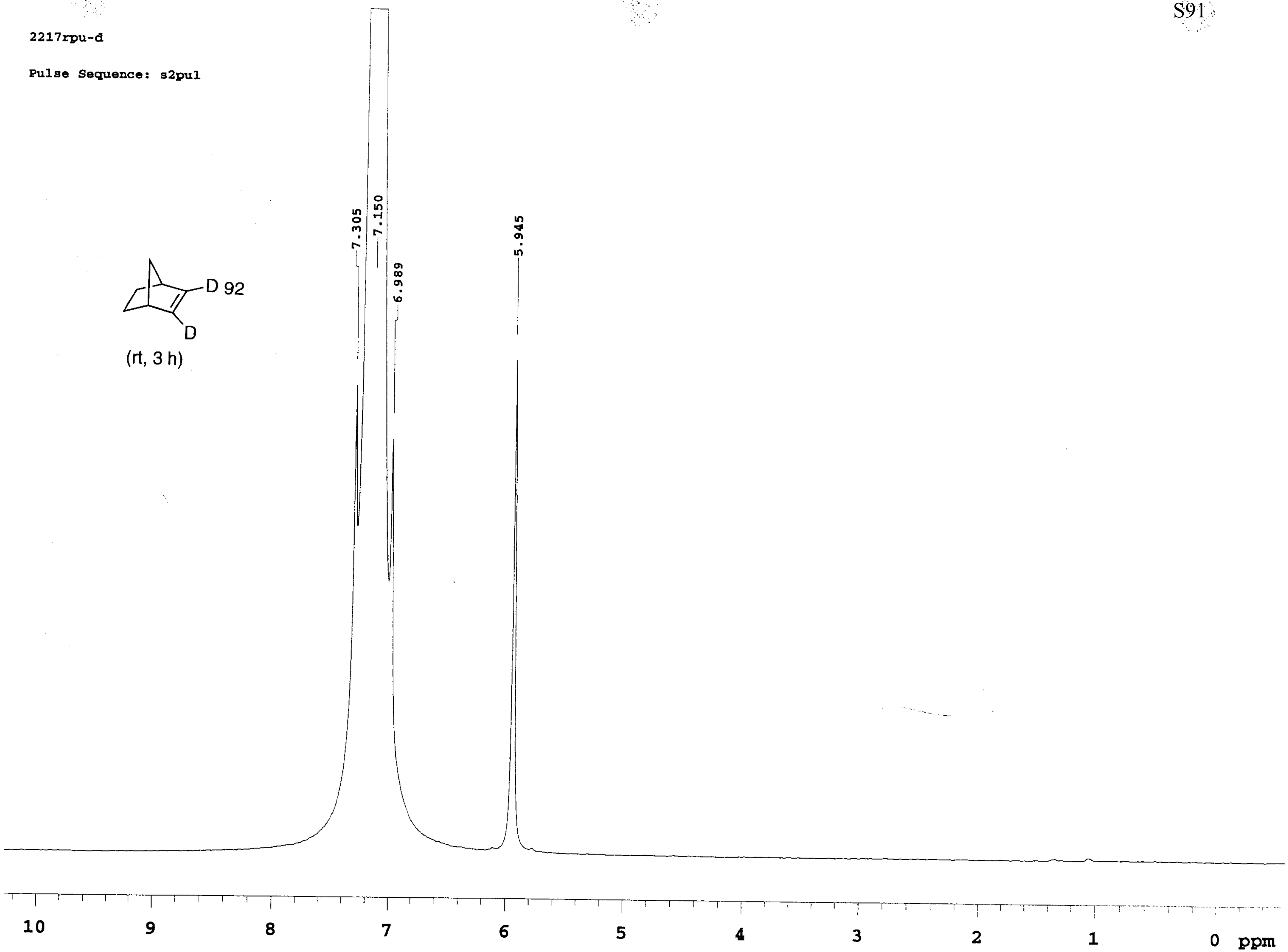
Pulse Sequence: s2pul



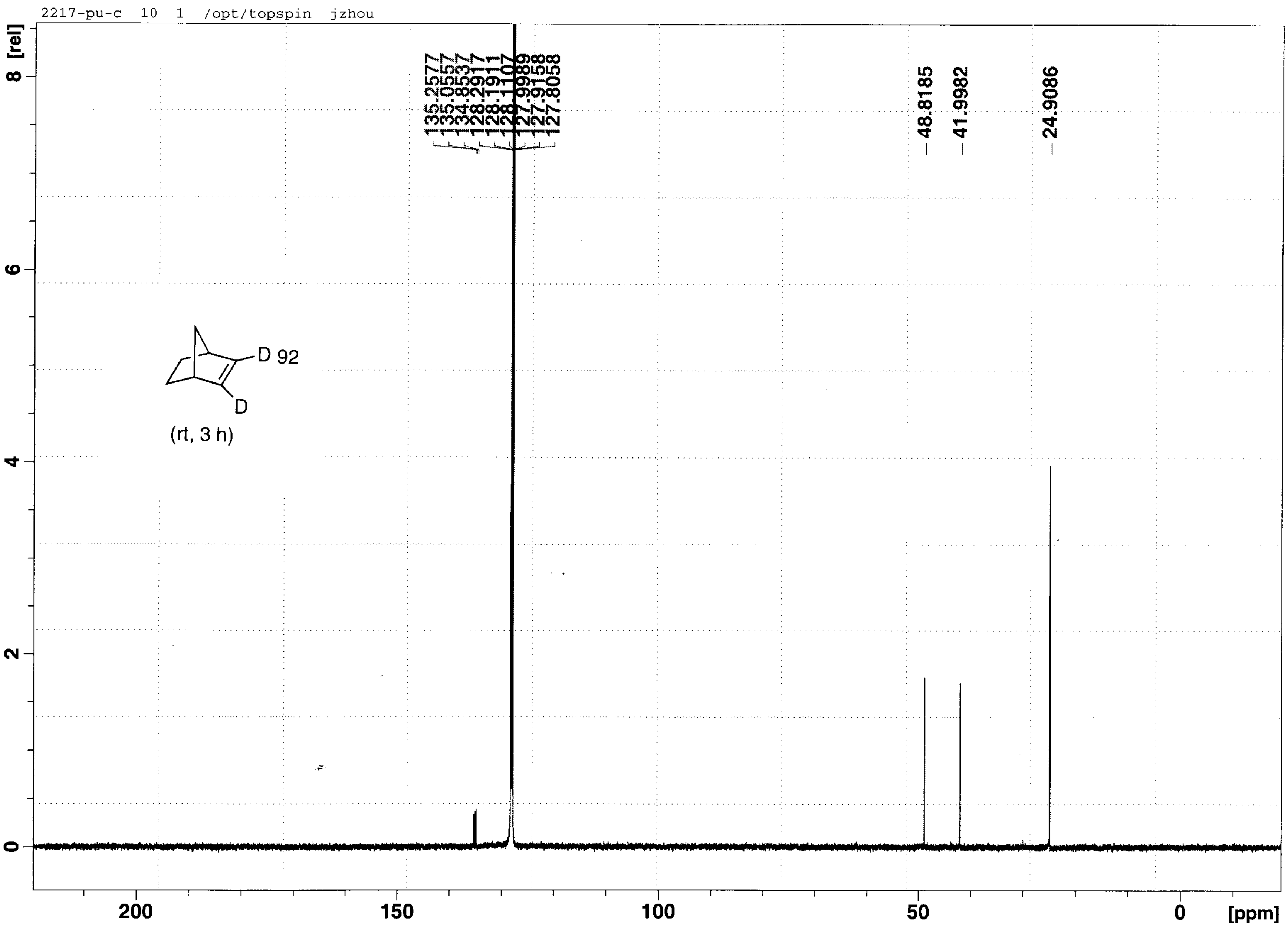



2217sm-c 10 1 /opt/topspin jzhou
C6D6
[*1e6]
135.4759
128.2835
128.1844
127.9914
127.7990
48.7827
42.1152
24.8868
H
H
60
40
20
0
200
150
100
50
0
[ppm]


2217r-pu-h
Pulse Sequence: s2pul
D 92
D
(rt, 3 h)
7
6
5
4
3
2
1
ppm
0.16
2.00
2.00
1.04
2.97

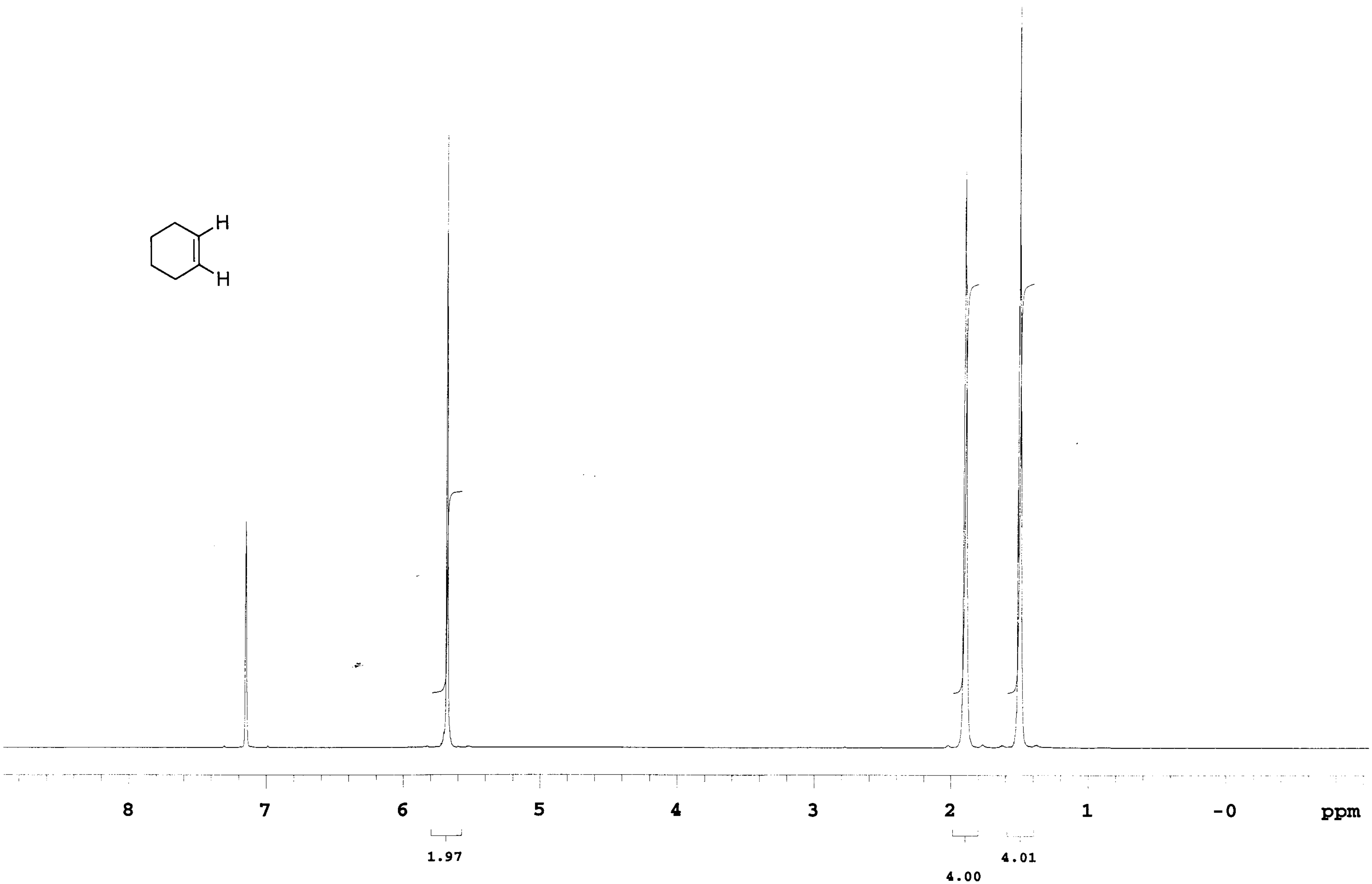


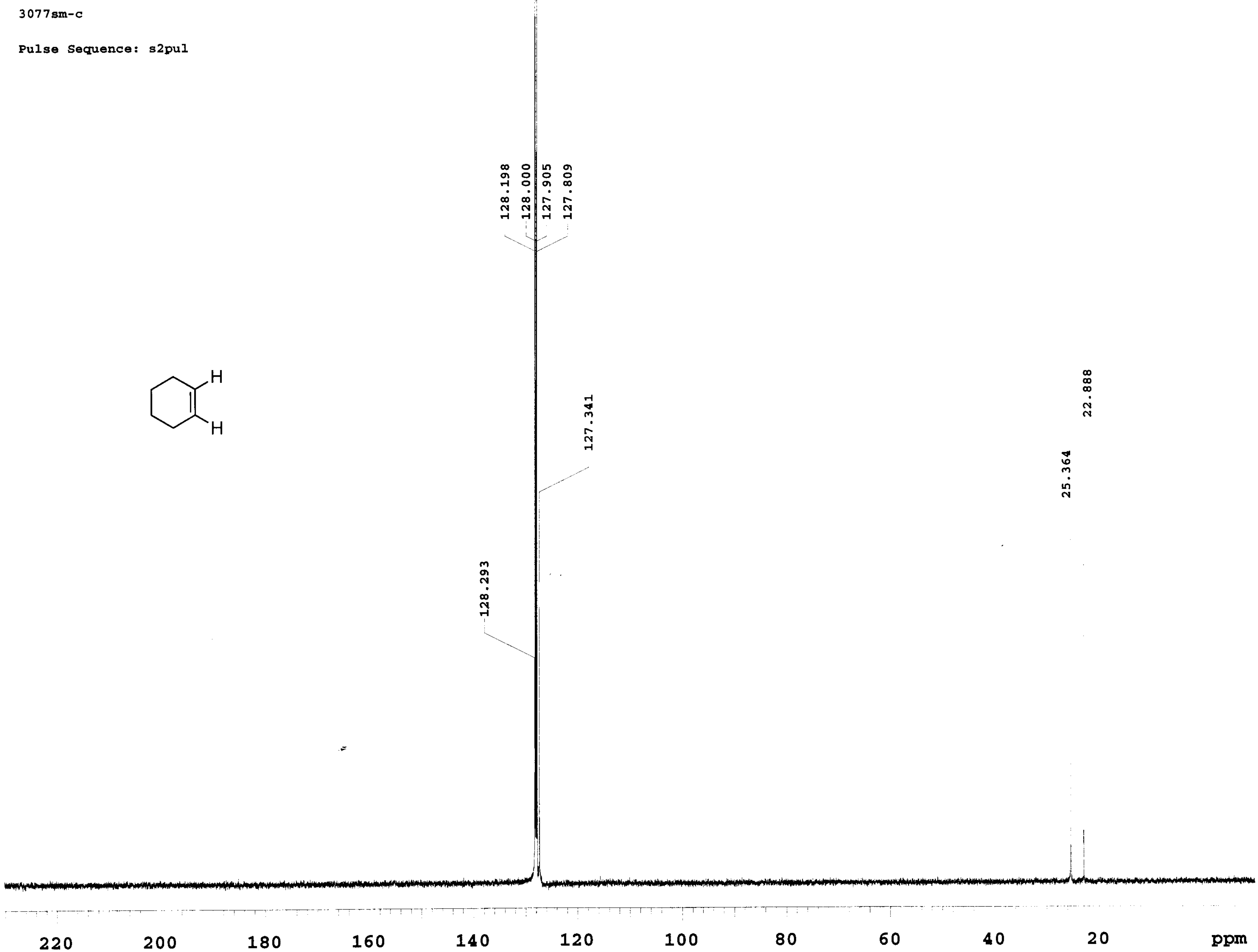
2217rpu-d
Pulse Sequence: s2pul
D
D
92
(rt, 3 h)
7.305
7.150
6.989
5.945
10
9
8
7
6
5
4
3
2
1
0
ppm

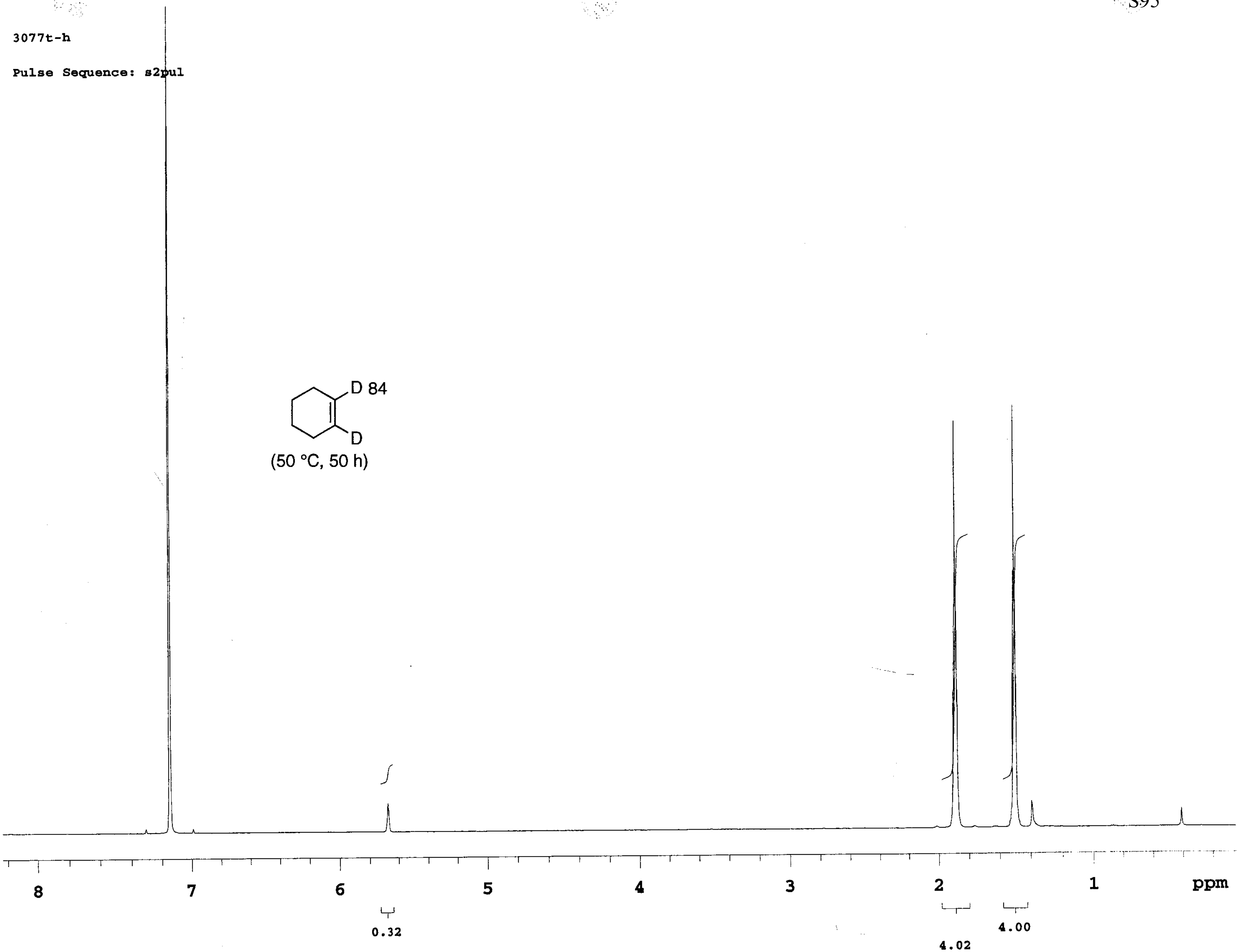

2217-pu-c 10 1 /opt/topspin jzhou
135.2577
135.0557
134.8537
128.2917
128.1911
128.1107
127.9989
127.9158
127.8058
48.8185
41.9982
24.9086
D 92
D
(rt, 3 h)
8 [rel]
6
4
2
0
200
150
100
50
0
[ppm]

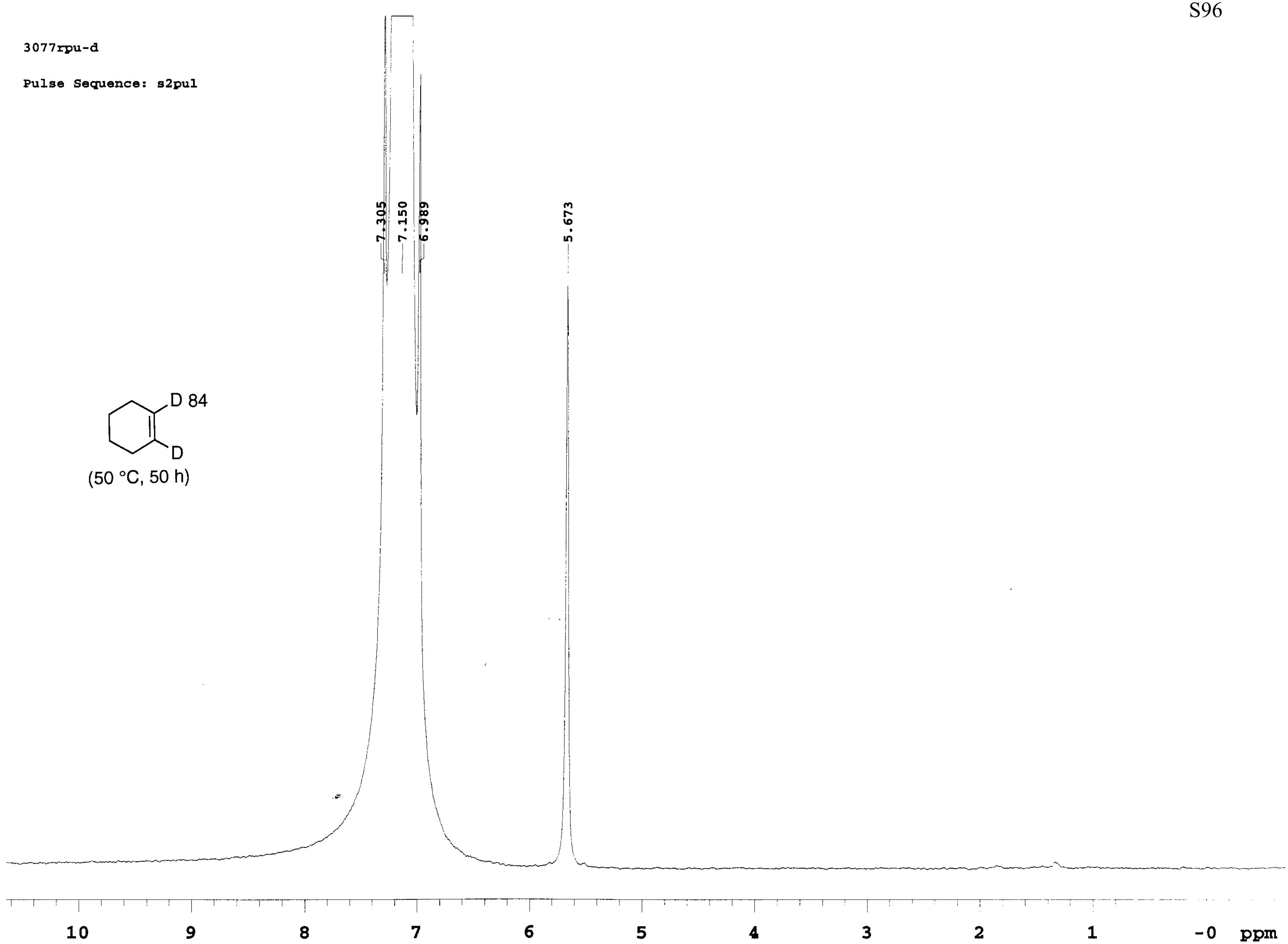
3077sm-h

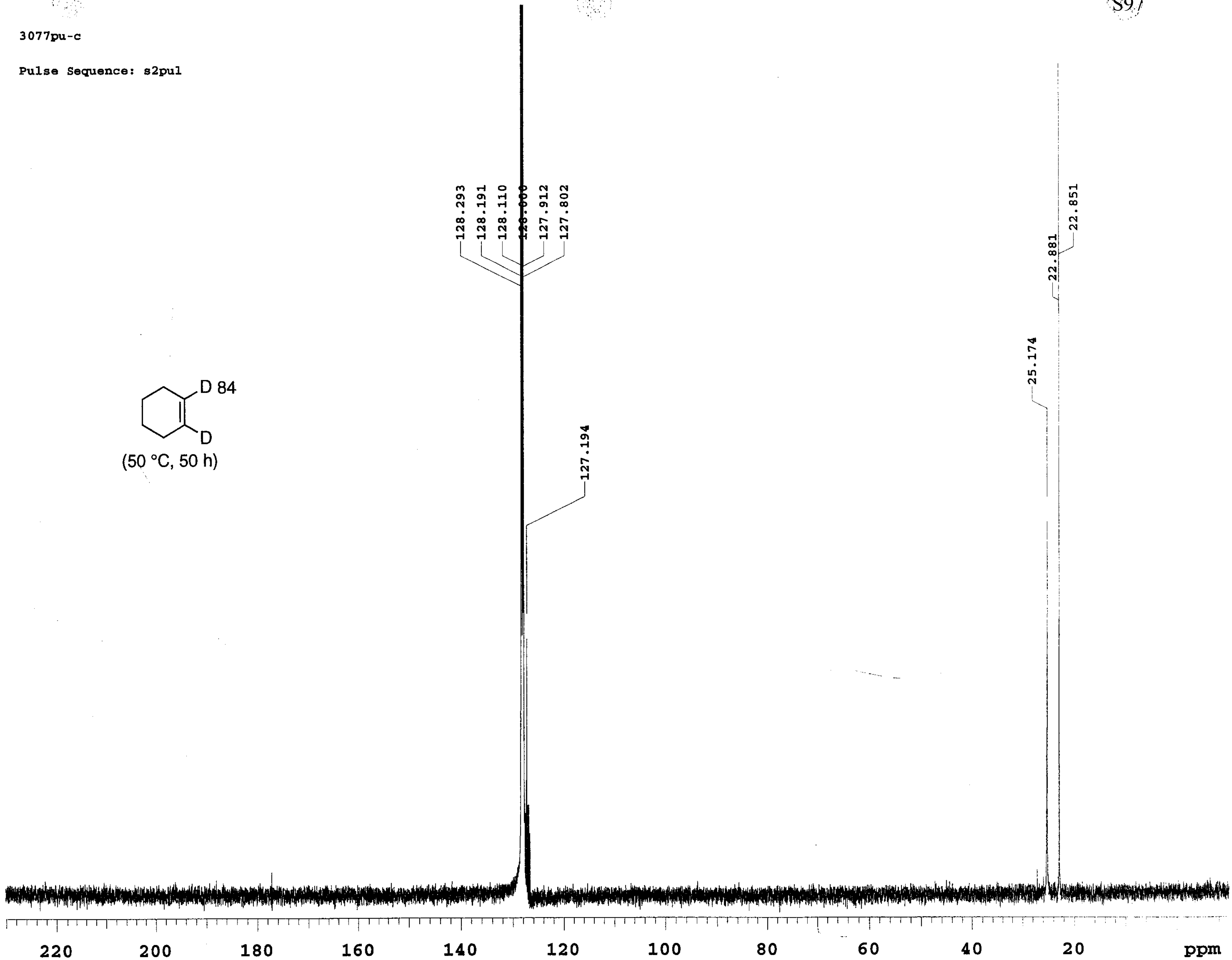
Pulse Sequence: s2pul




3077sm-c
Pulse Sequence: s2pul
128.198
128.000
127.905
127.809
127.341
128.293
25.364
22.888
220
200
180
160
140
120
100
80
60
40
20
ppm

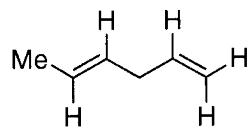

3077t-h
Pulse Sequence: s2pul
D 84
D
(50 °C, 50 h)
8
7
6
5
4
3
2
1
ppm
0.32
4.02
4.00

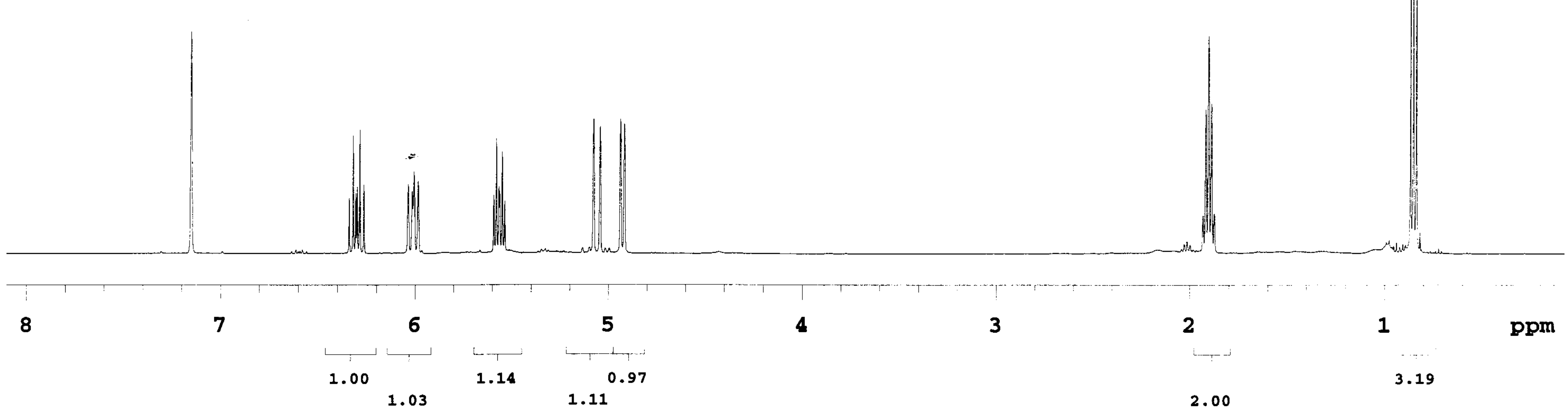

3077rpu-d
Pulse Sequence: s2pul
7.305
7.150
6.989
5.673
10
9
8
7
6
5
4
3
2
1
-0
ppm
D 84
D
(50 °C, 50 h)


3077pu-c
Pulse Sequence: s2pul
D 84
D
(50 °C, 50 h)
128.293
128.191
128.110
127.912
127.802
127.194
25.174
22.881
22.851
220
200
180
160
140
120
100
80
60
40
20
ppm

3076sm-h

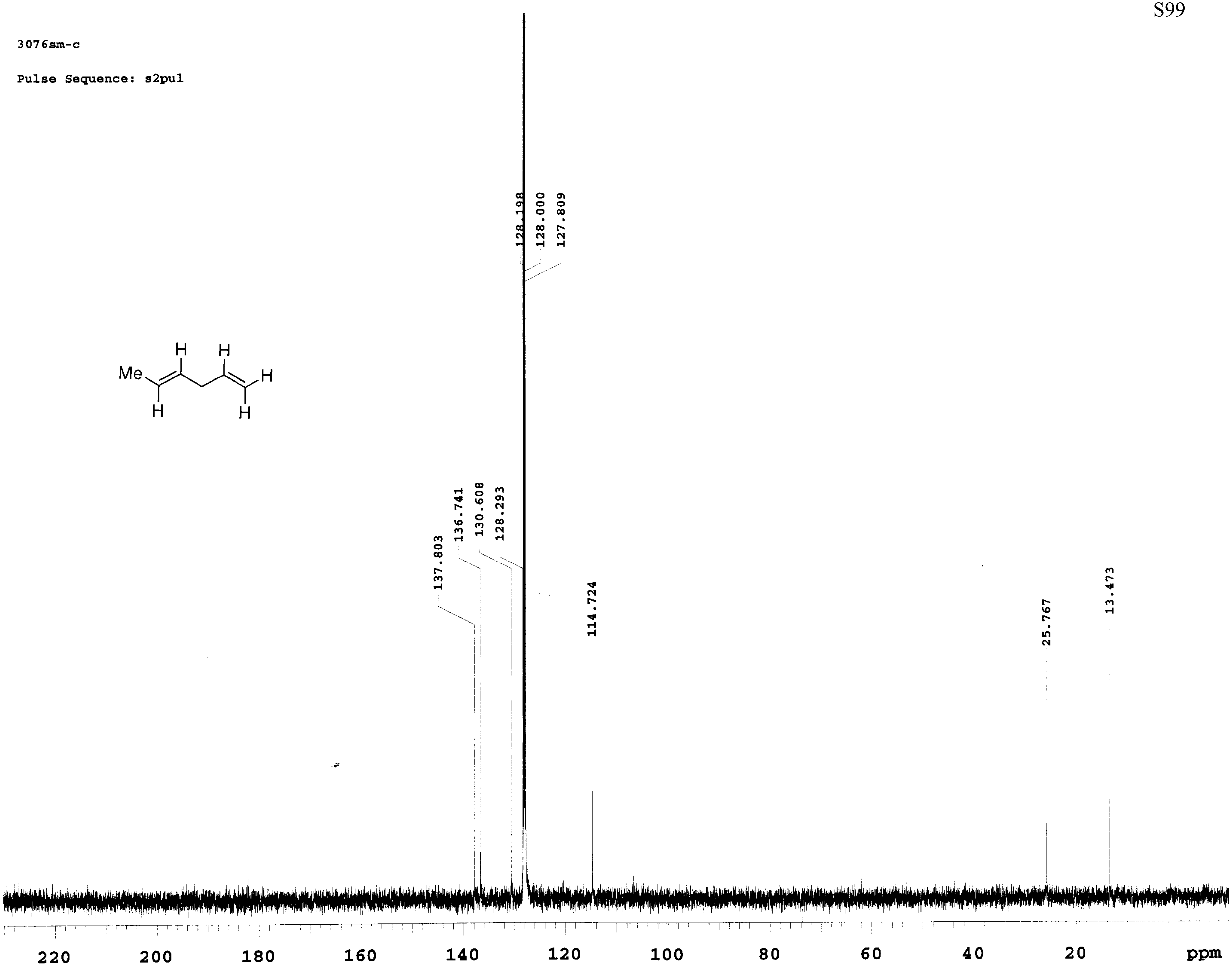
Pulse Sequence: s2pul





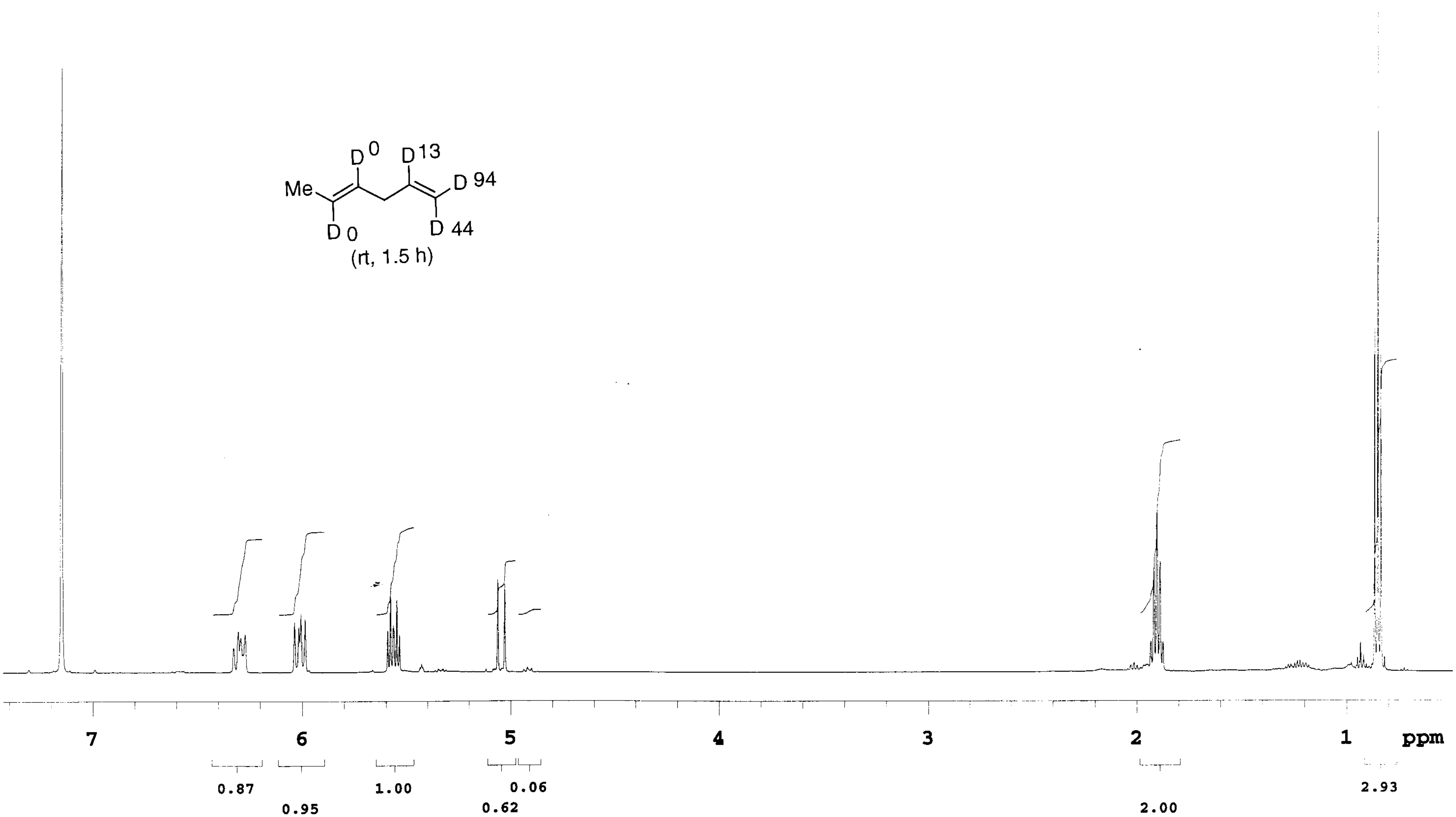
3076sm-c

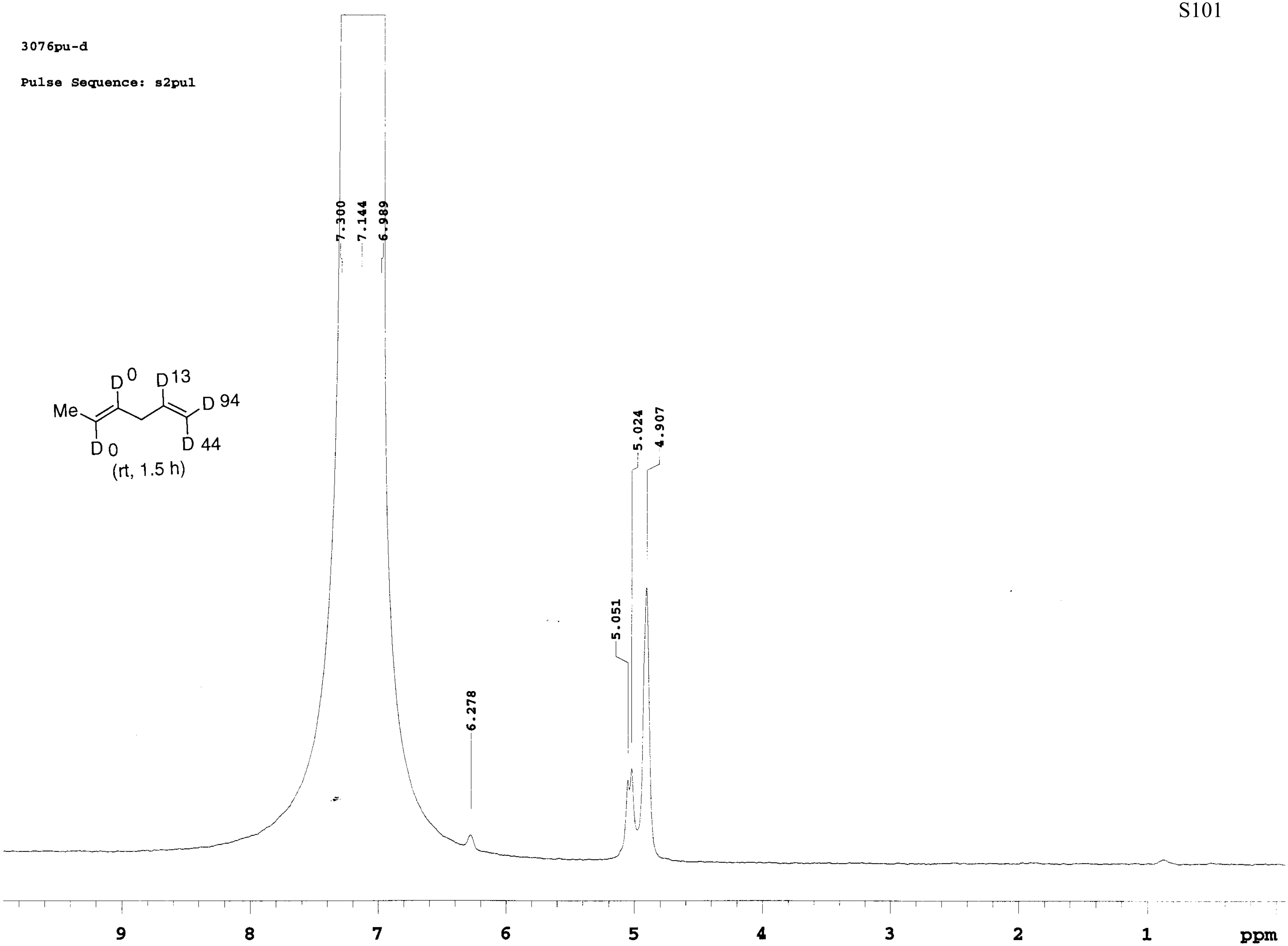
Pulse Sequence: s2pul



3076pu-h

Pulse Sequence: s2pul

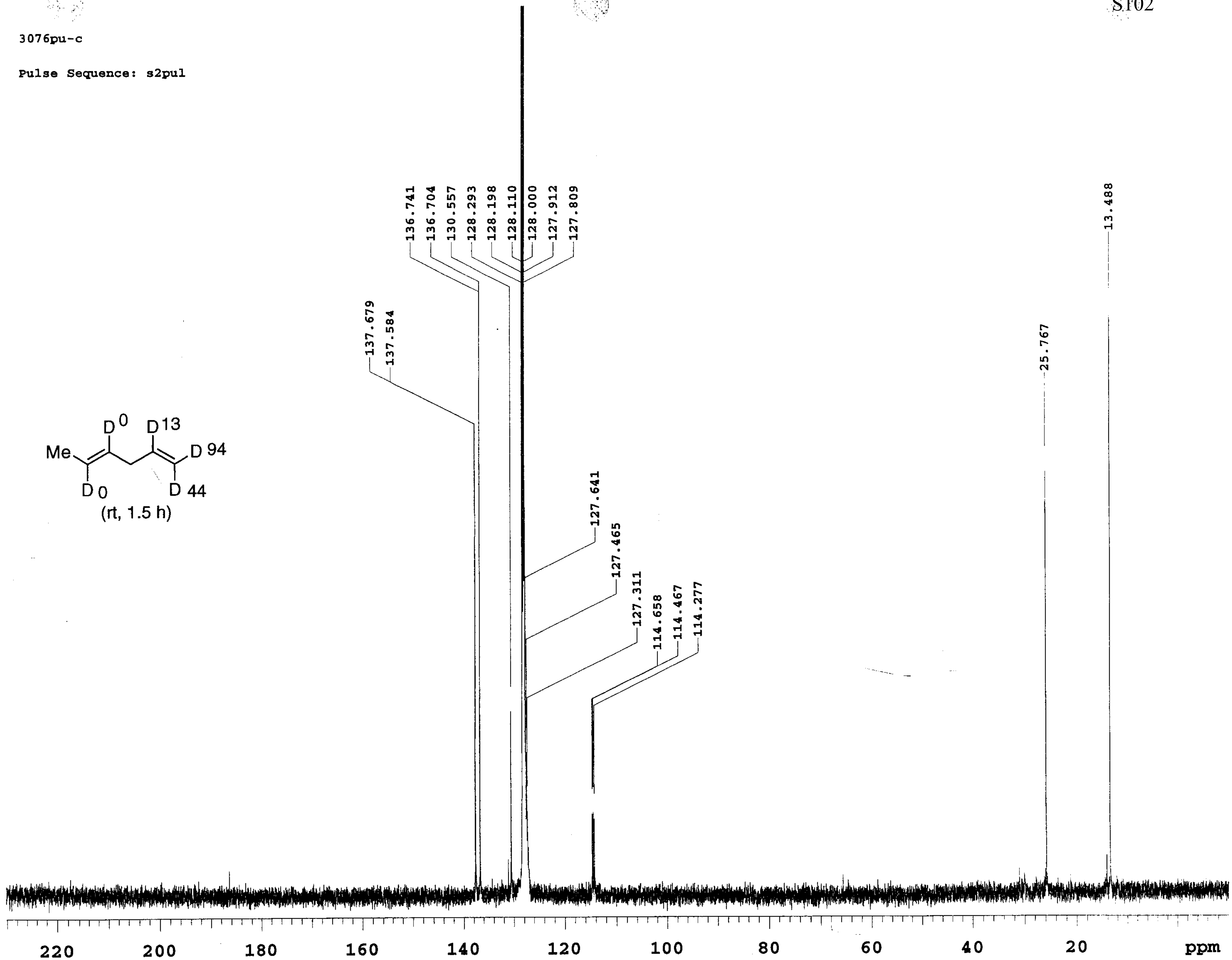




3076pu-d
Pulse Sequence: s2pul
7.300
7.144
6.989
6.278
5.051
5.024
4.907
Me
D 0
D 13
D 94
D 0
D 44
(rt, 1.5 h)
9
8
7
6
5
4
3
2
1
ppm

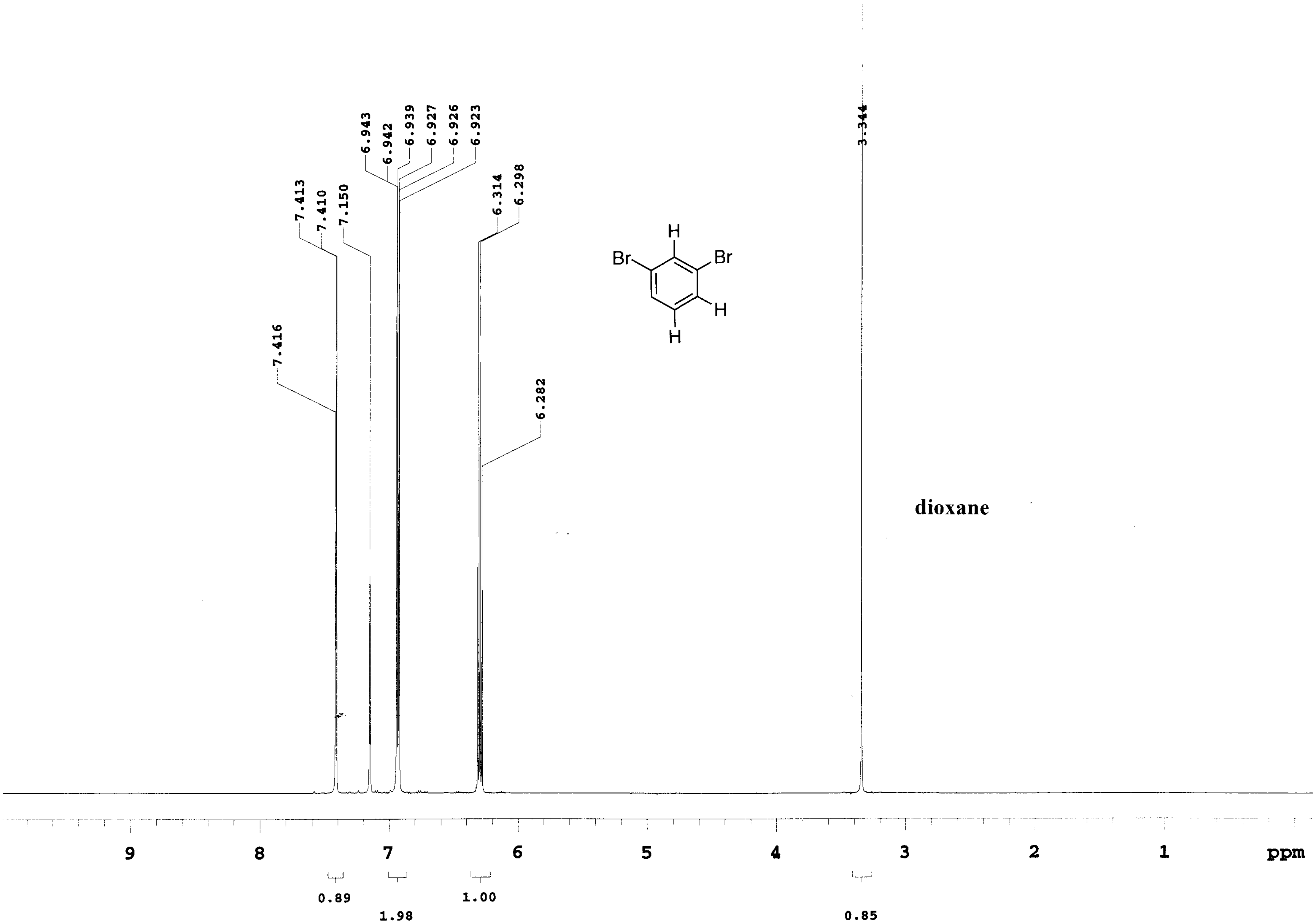
3076pu-c

Pulse Sequence: s2pul



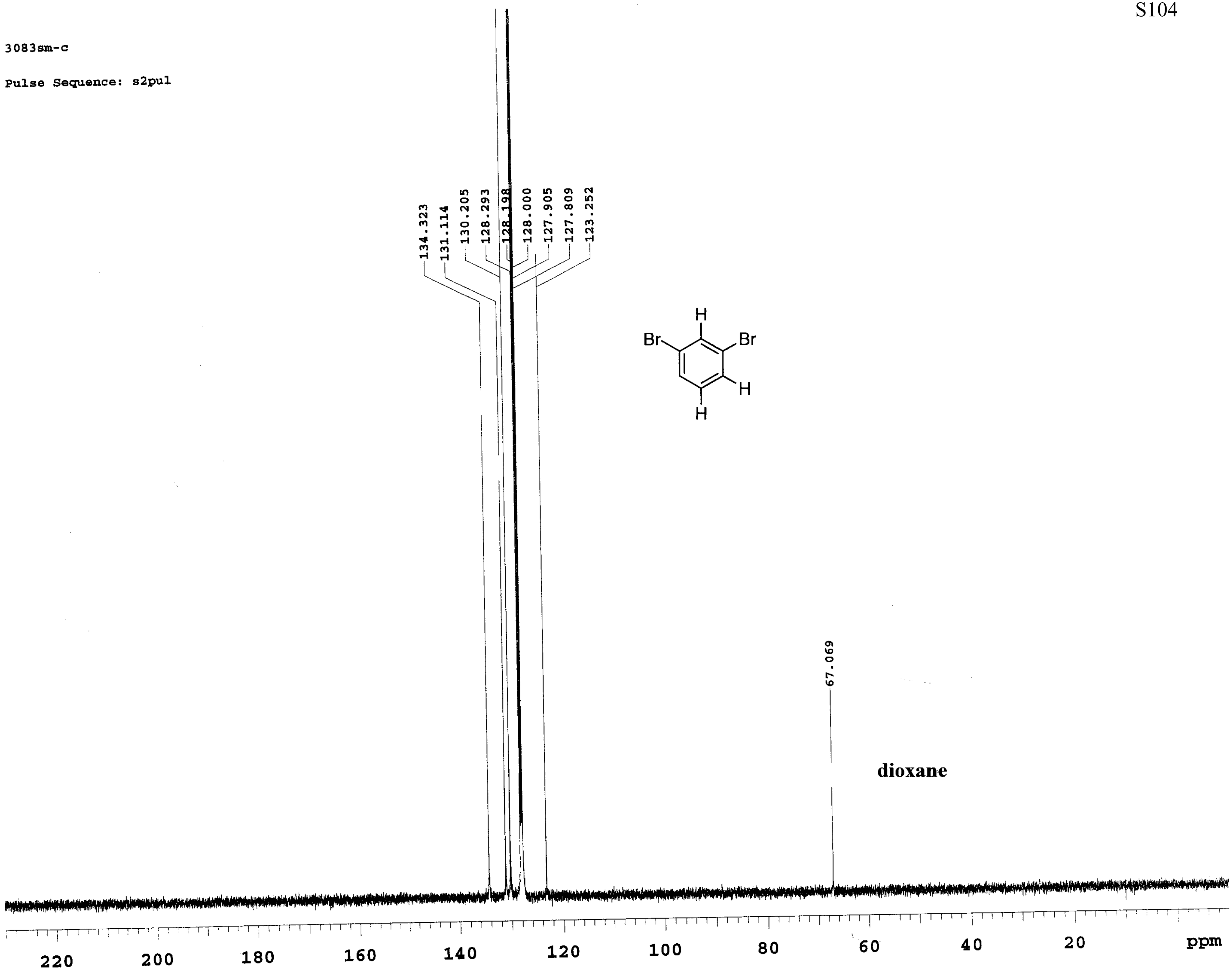
3083sm-h

Pulse Sequence: s2pul



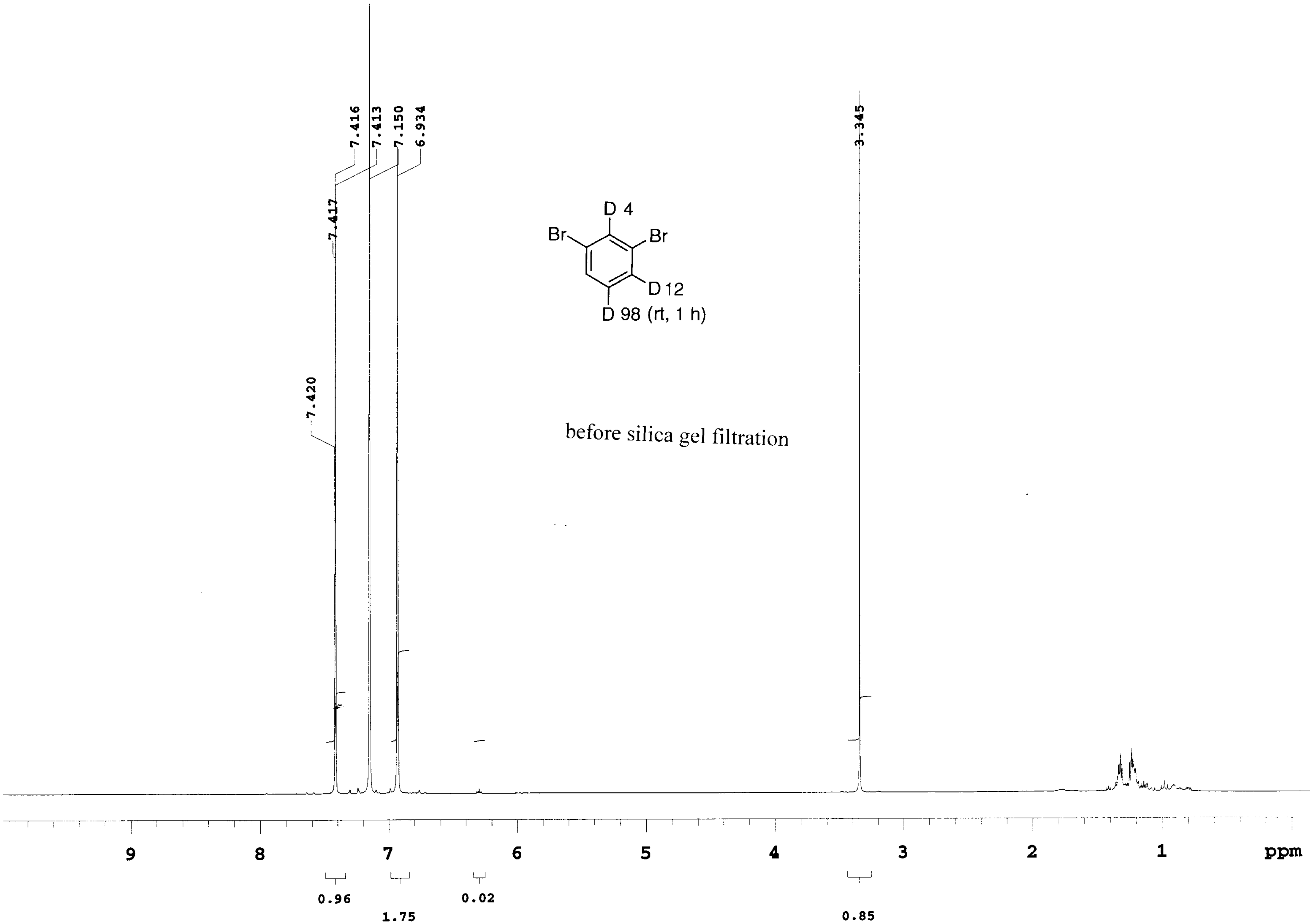
3083sm-c

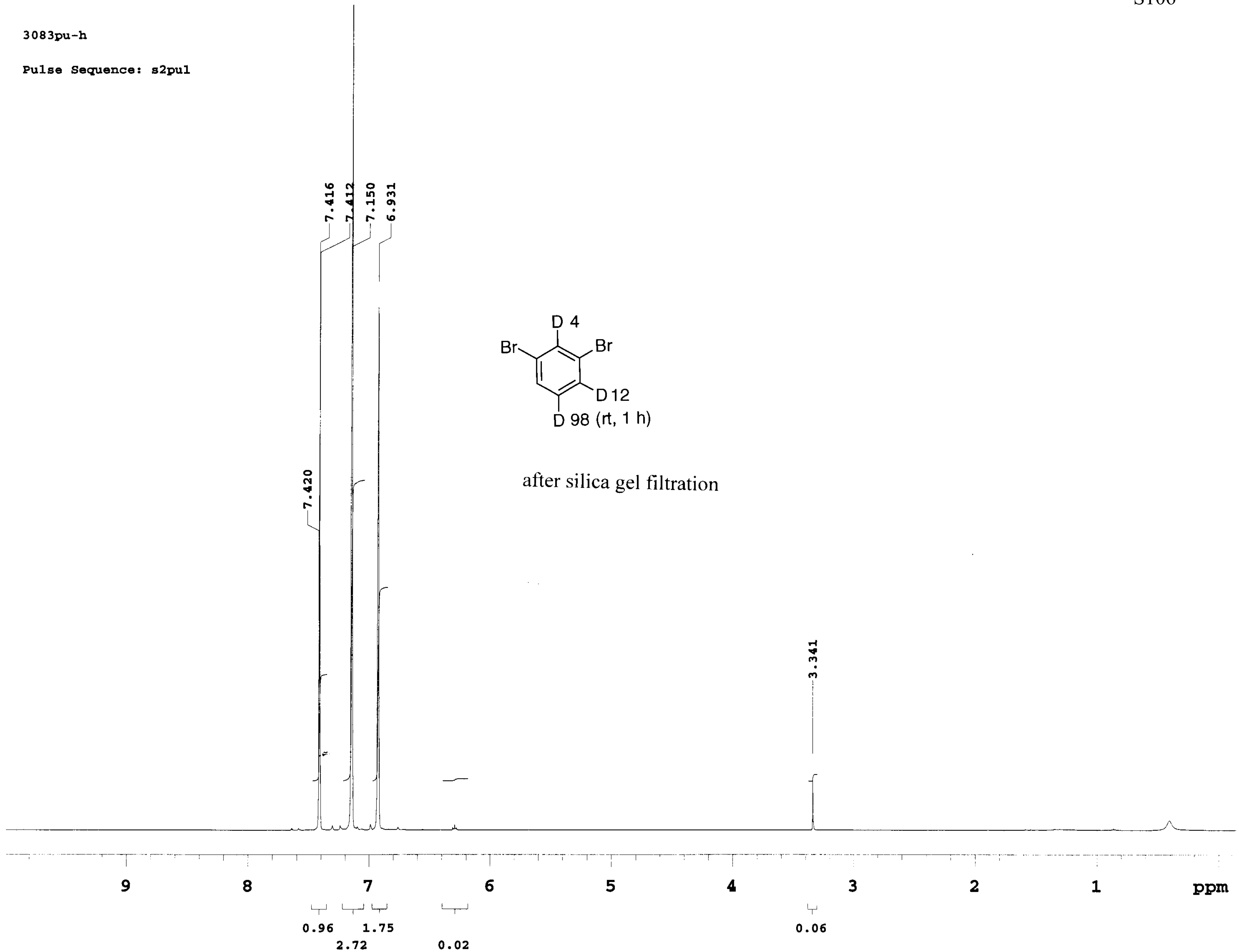
Pulse Sequence: s2pul

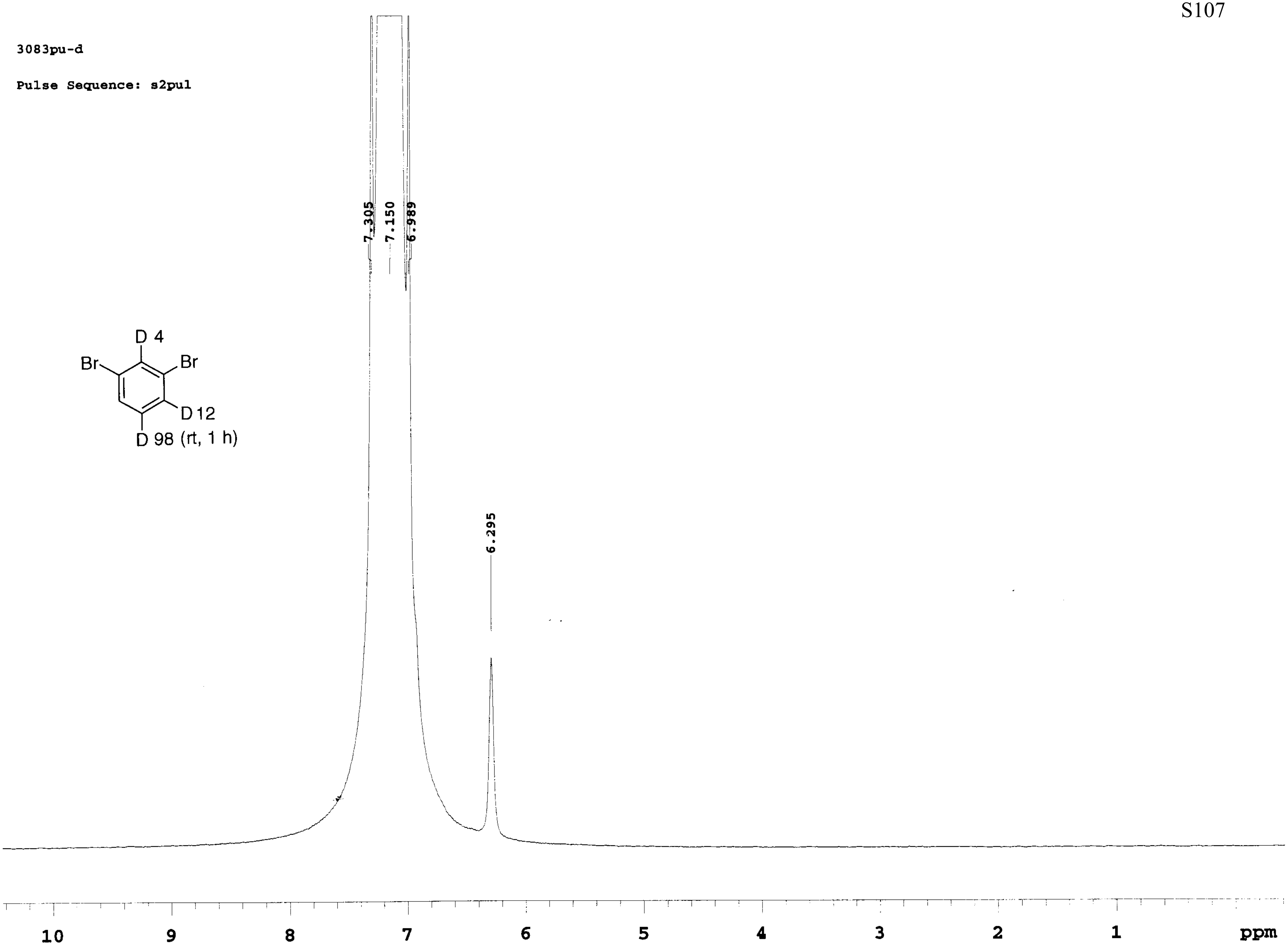


3083-1h

Pulse Sequence: s2pul

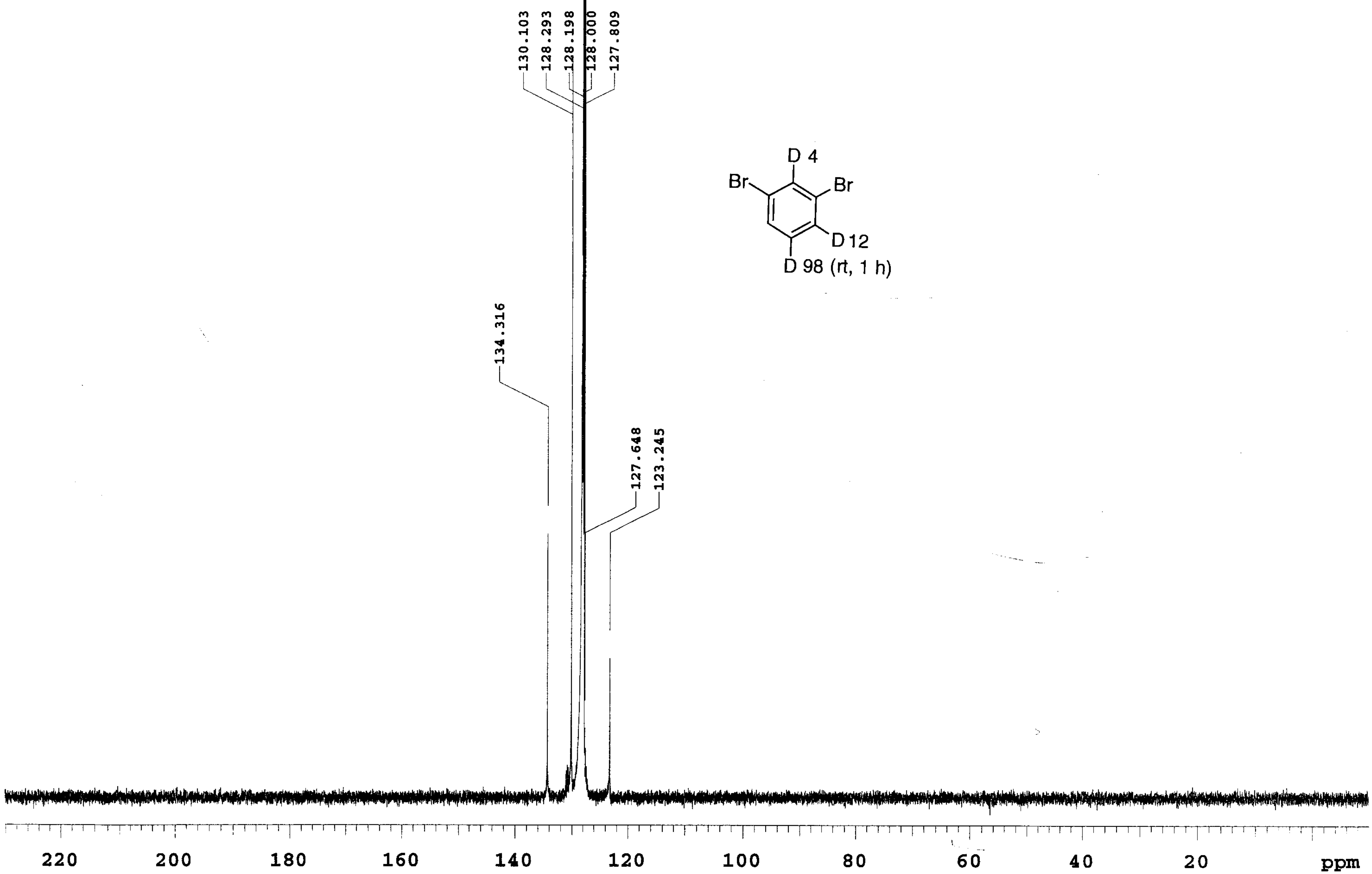


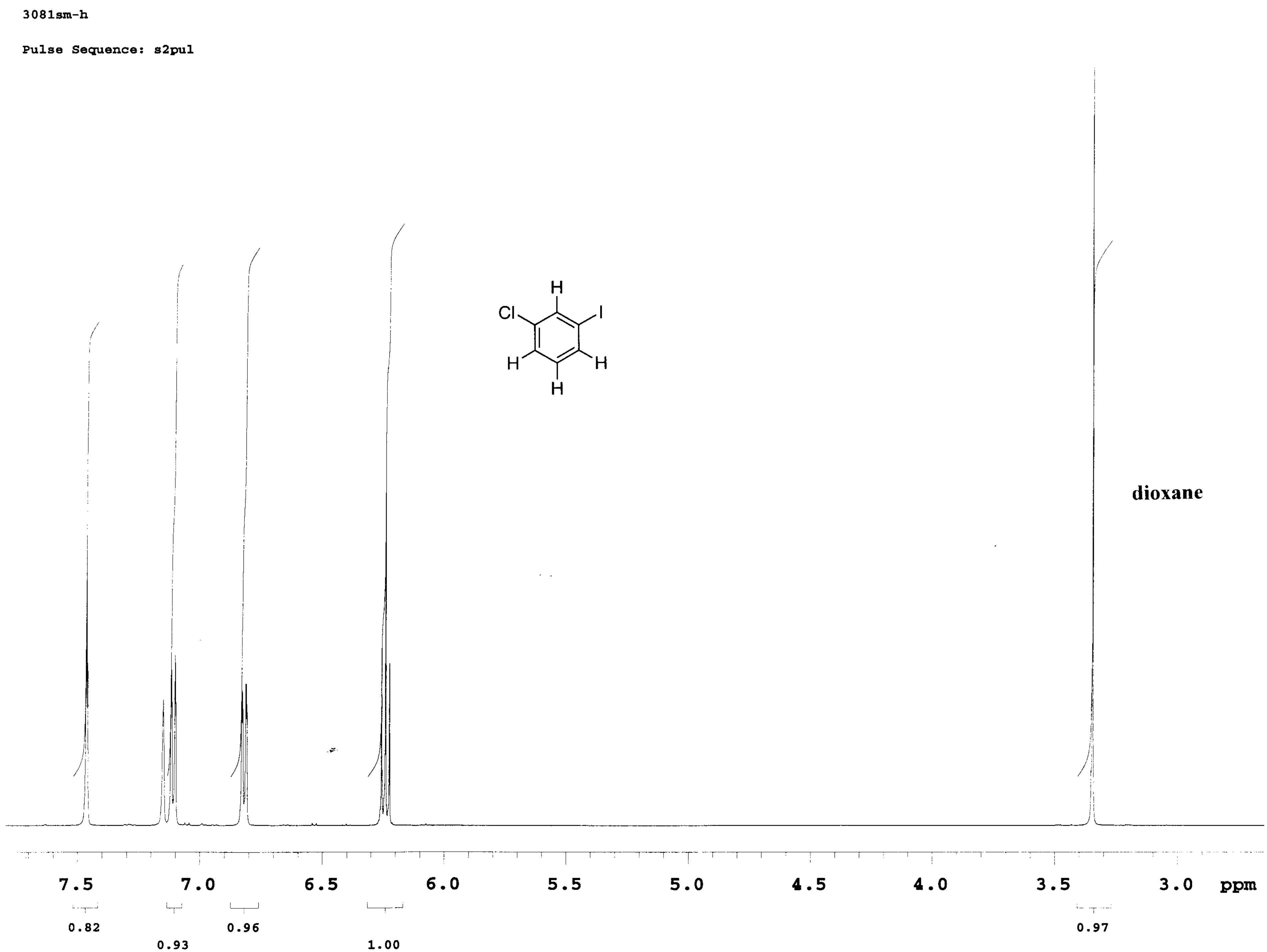

3083pu-h
Pulse Sequence: s2pul
7.416
7.412
7.150
6.931
7.420
3.341
D 4
Br
Br
D 12
D 98 (rt, 1 h)
after silica gel filtration
9
8
7
6
5
4
3
2
1
ppm
0.96
2.72
1.75
0.02
0.06


3083pu-d
Pulse Sequence: s2pul
7.305
7.150
6.989
6.295
D 4
Br
Br
D 12
D 98 (rt, 1 h)
10
9
8
7
6
5
4
3
2
1
ppm

3083pu-c

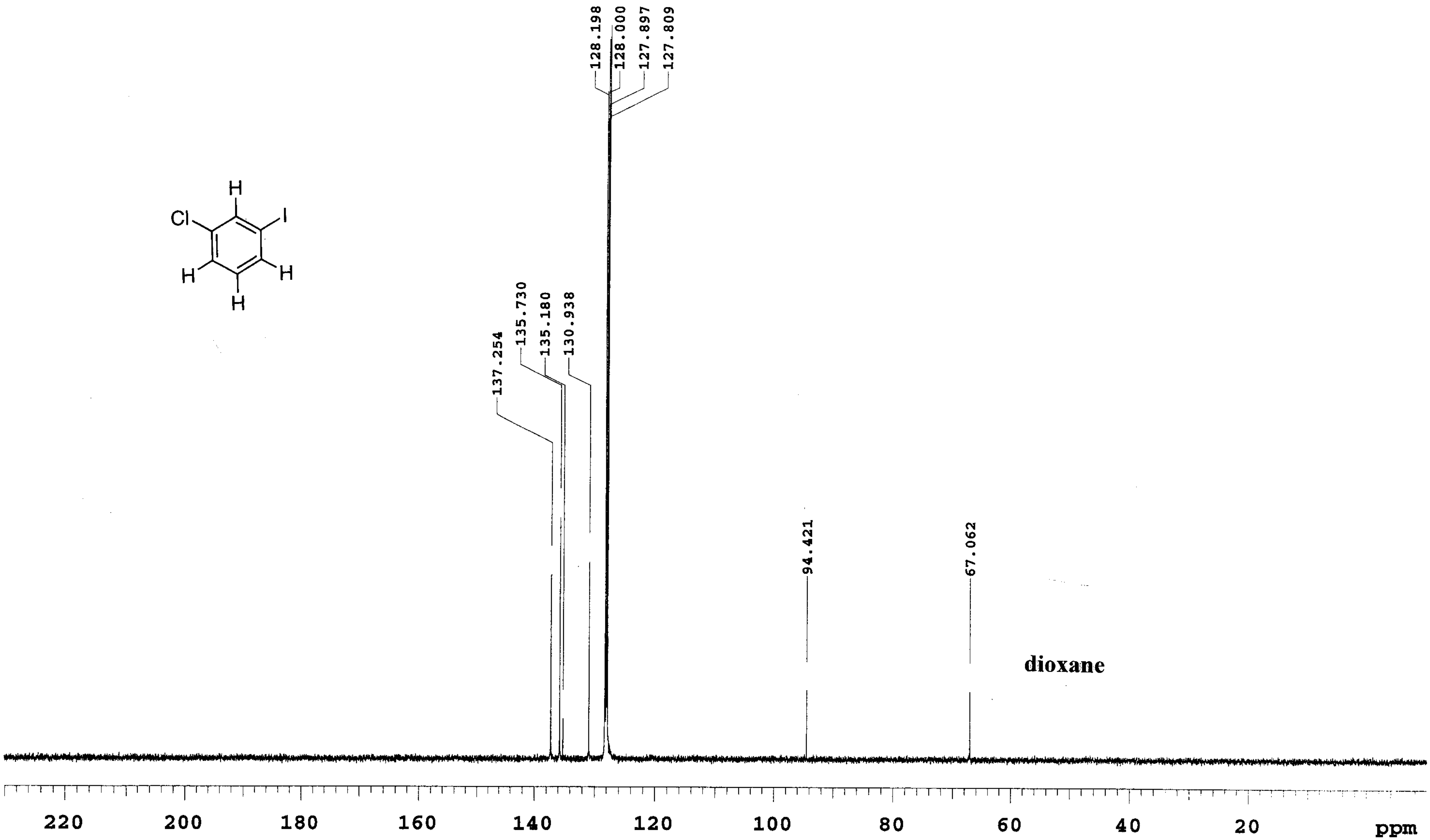
Pulse Sequence: s2pul




3081sm-h
Pulse Sequence: s2pul
Cl
I
H
dioxane
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.82
0.93
0.96
1.00
0.97

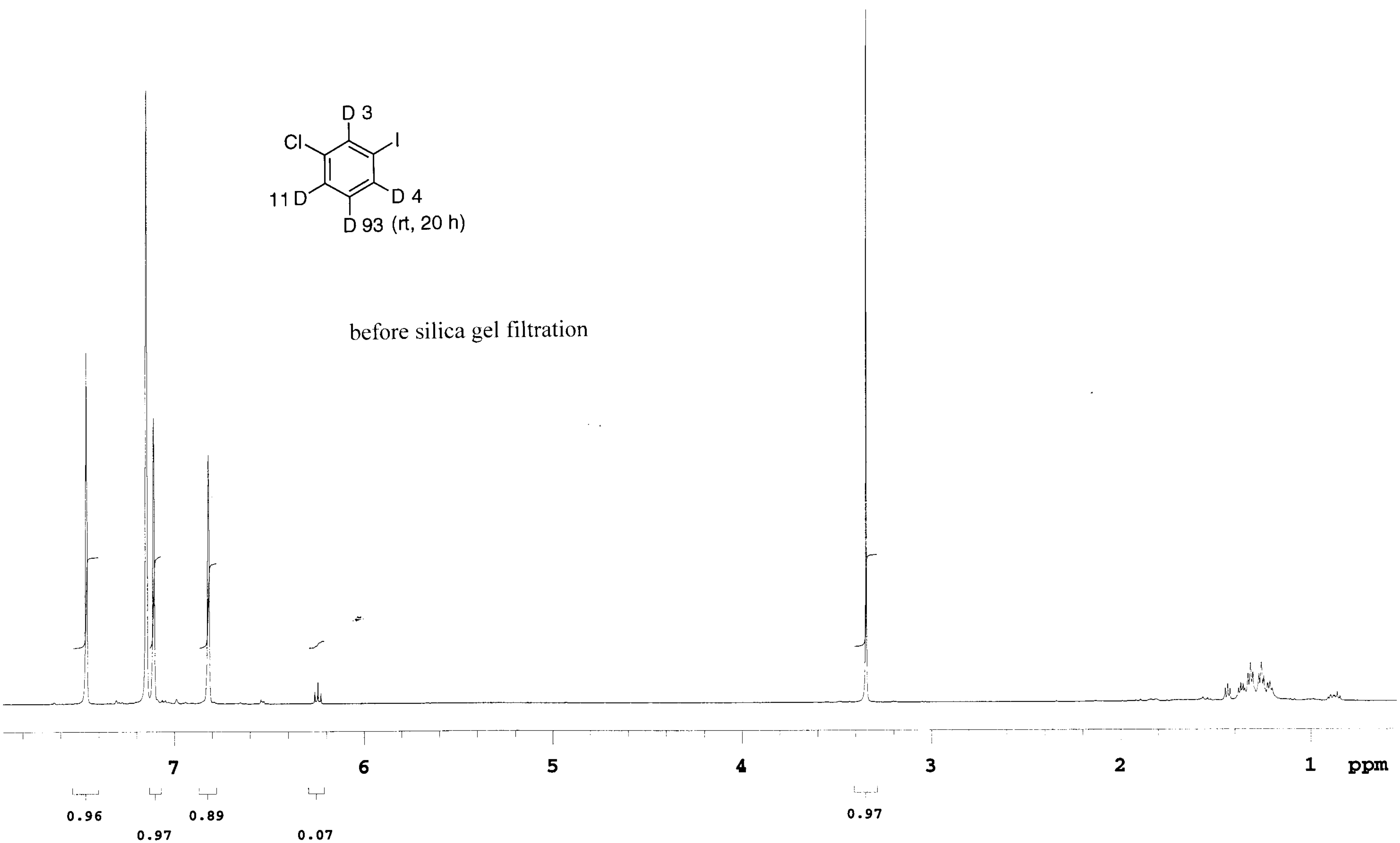
3081sm-c

Pulse Sequence: s2pul



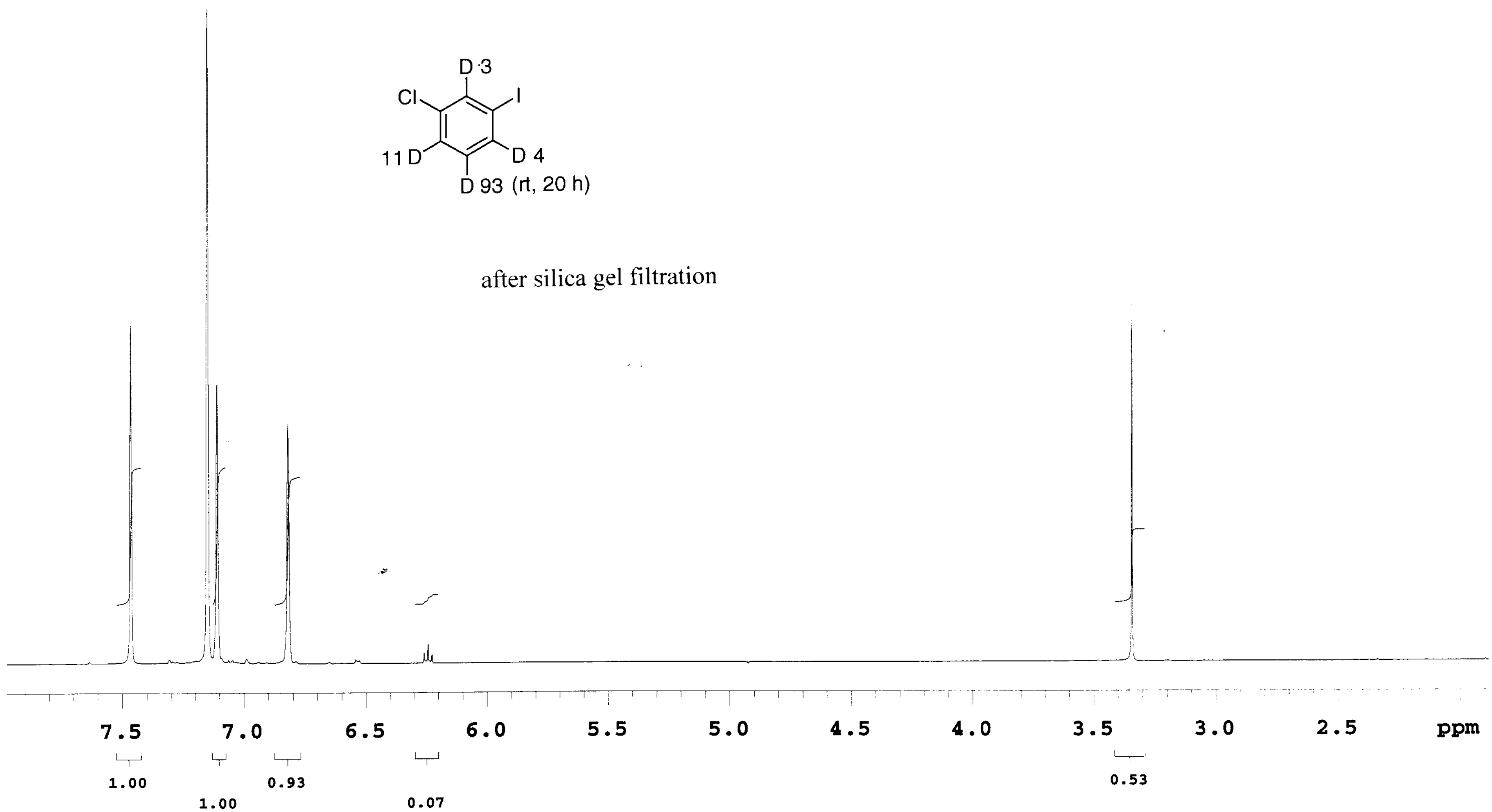
3081-20h

Pulse Sequence: s2pul



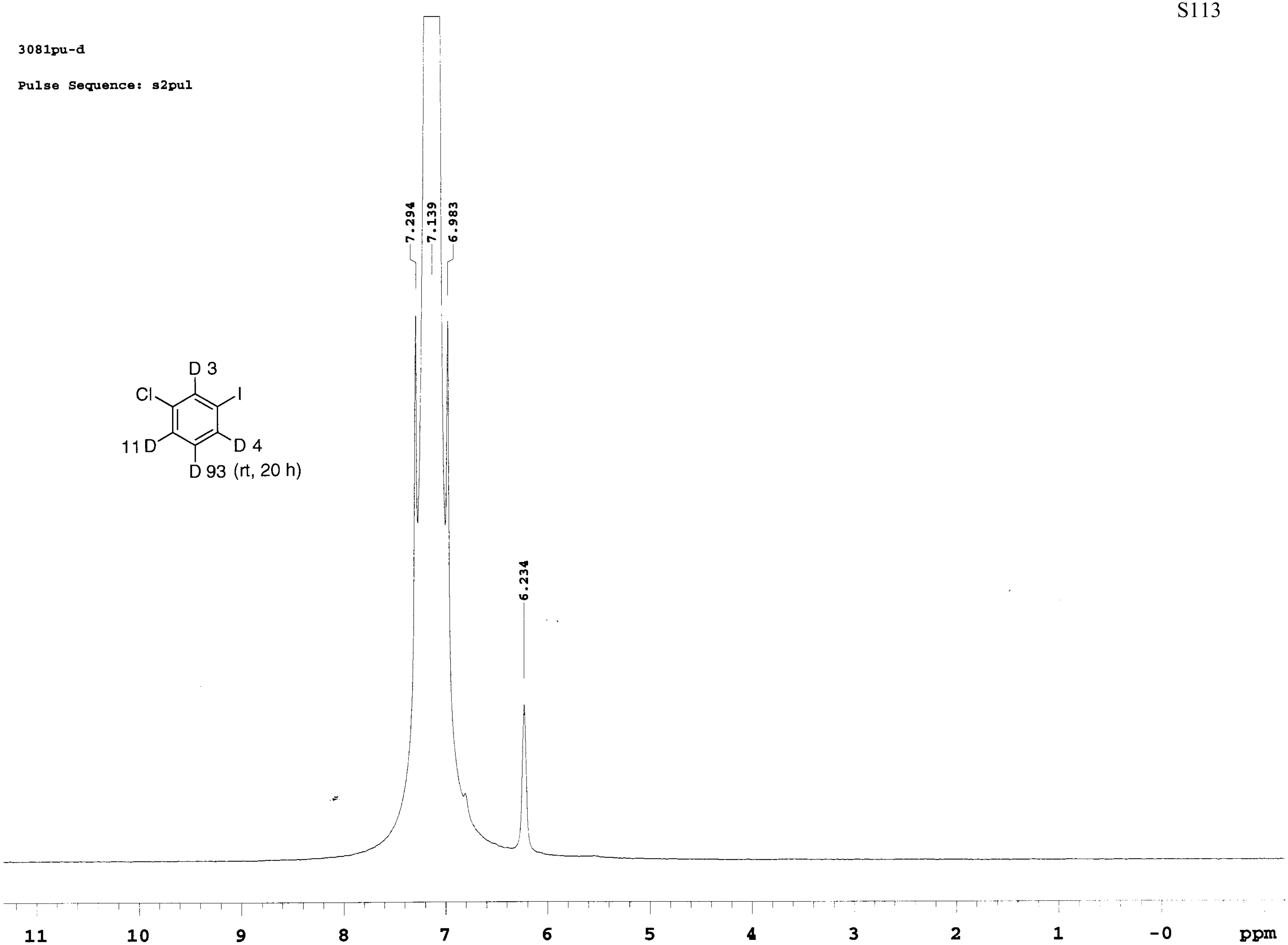
3081pu-h

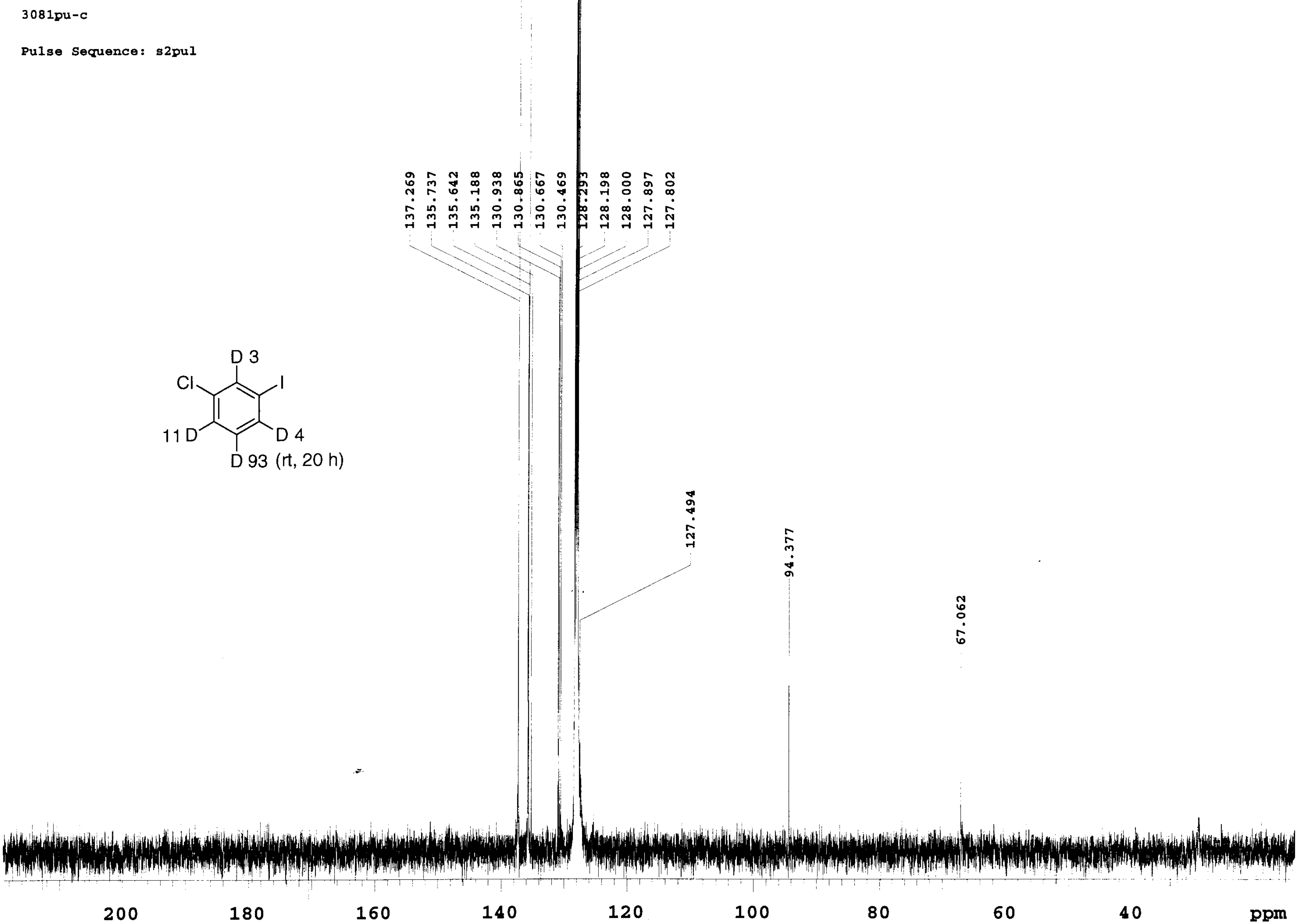
Pulse Sequence: s2pul



3081pu-d

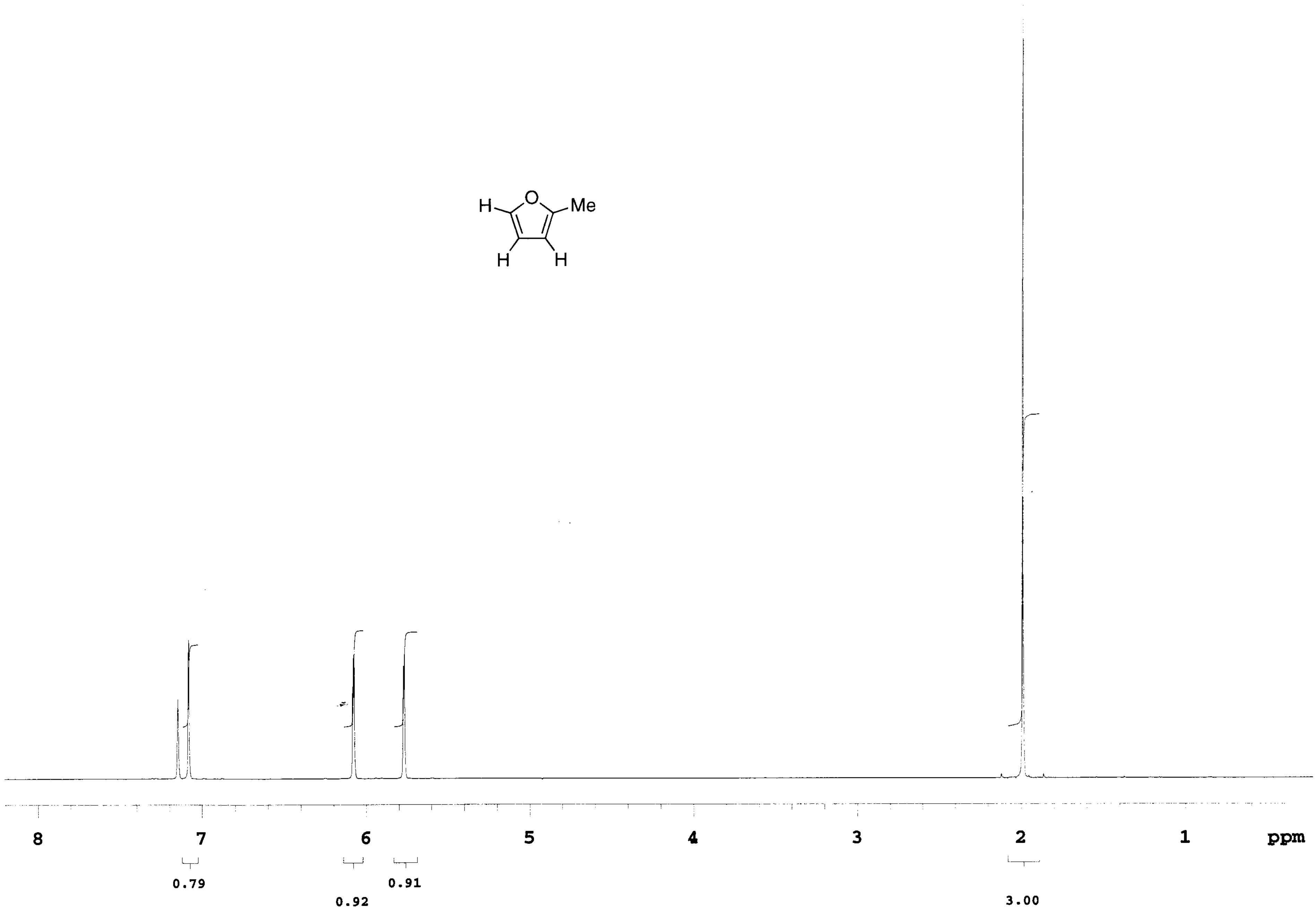
Pulse Sequence: s2pul




3081pu-c
Pulse Sequence: s2pul
137.269
135.737
135.642
135.188
130.938
130.865
130.667
130.469
128.293
128.198
128.000
127.897
127.802
127.494
94.377
67.062
D 3
Cl
I
11 D
D 4
D 93 (rt, 20 h)
200
180
160
140
120
100
80
60
40
ppm

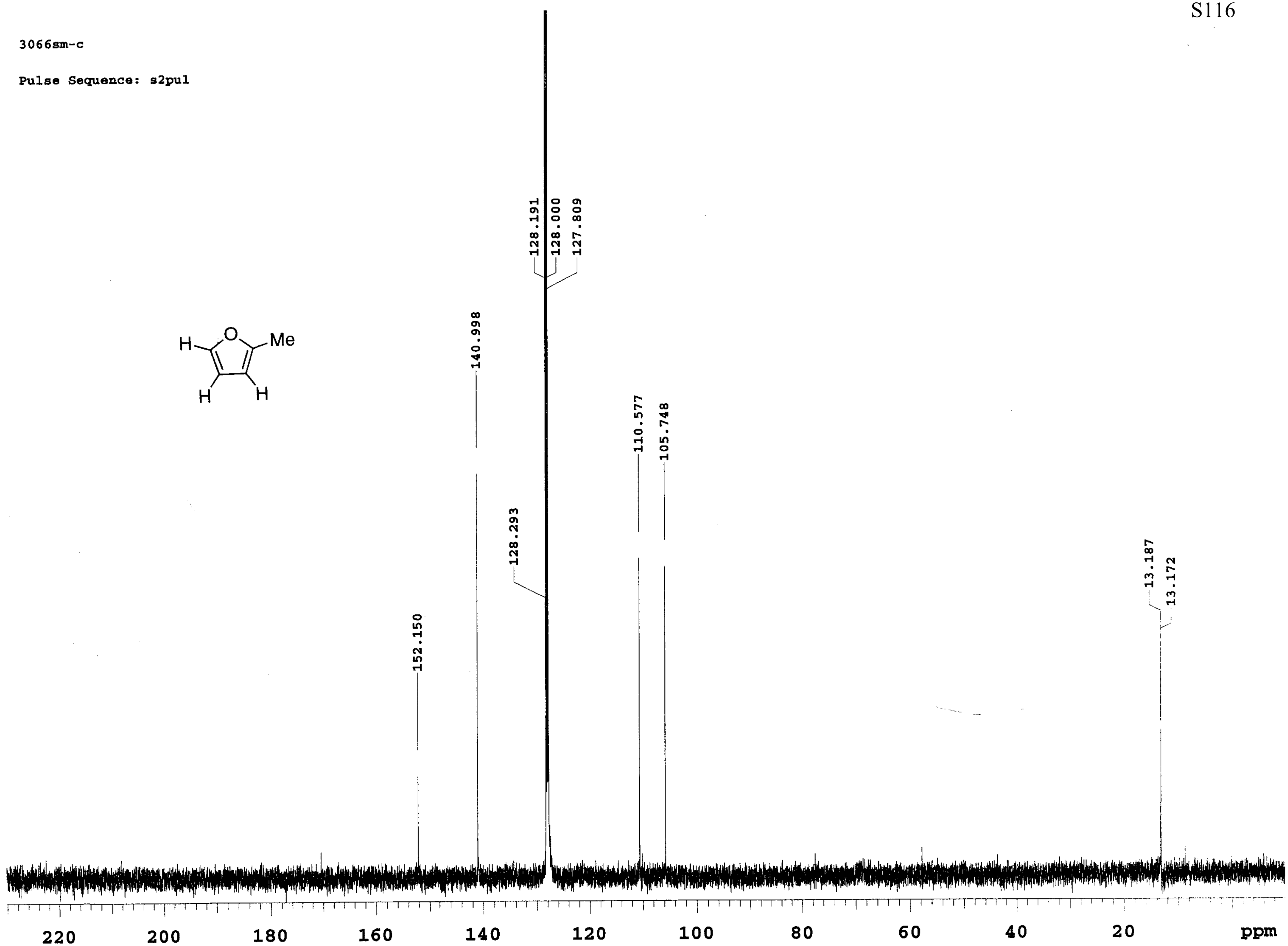
3066sm-h

Pulse Sequence: s2pul



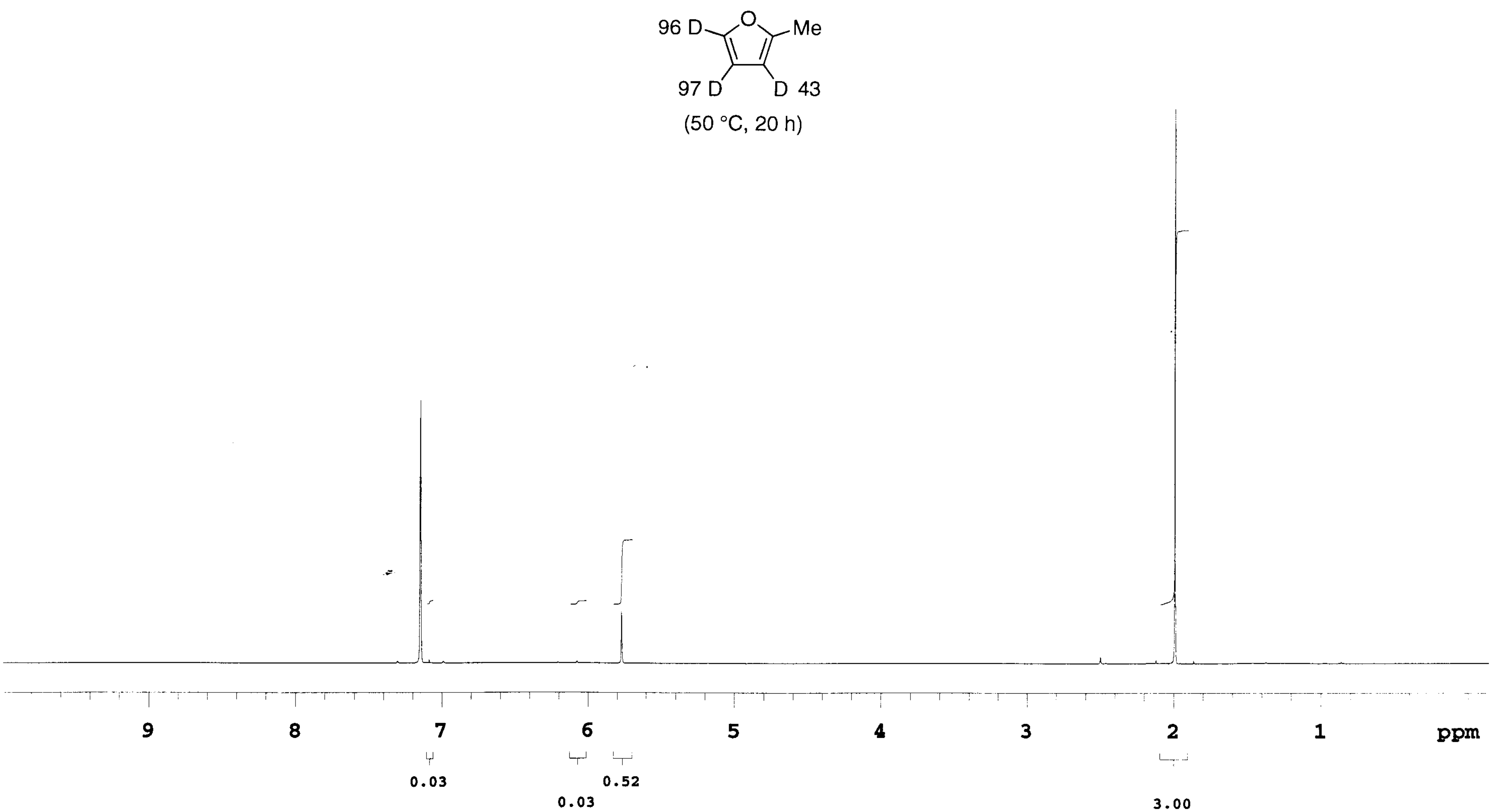
3066sm-c

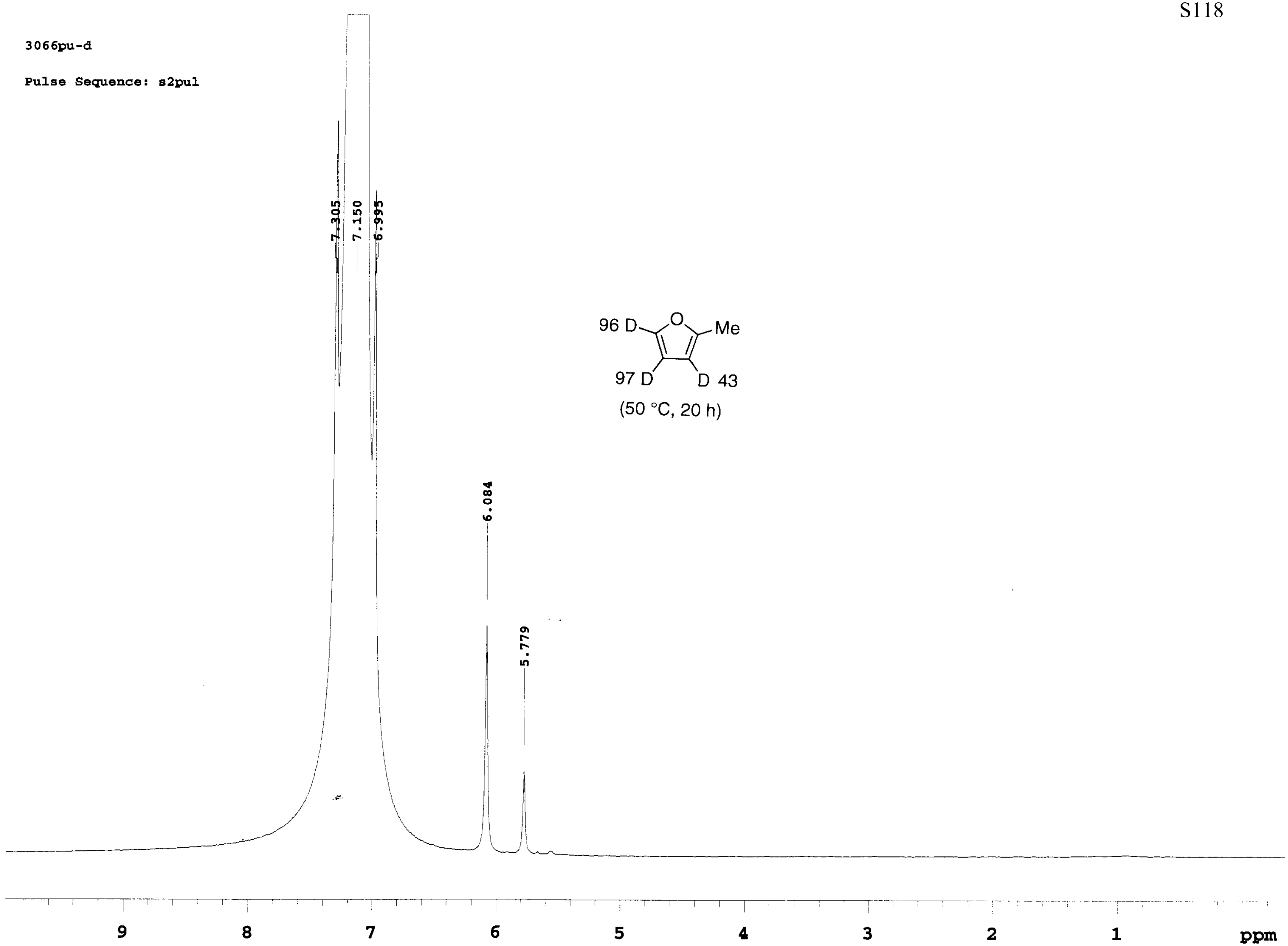
Pulse Sequence: s2pul



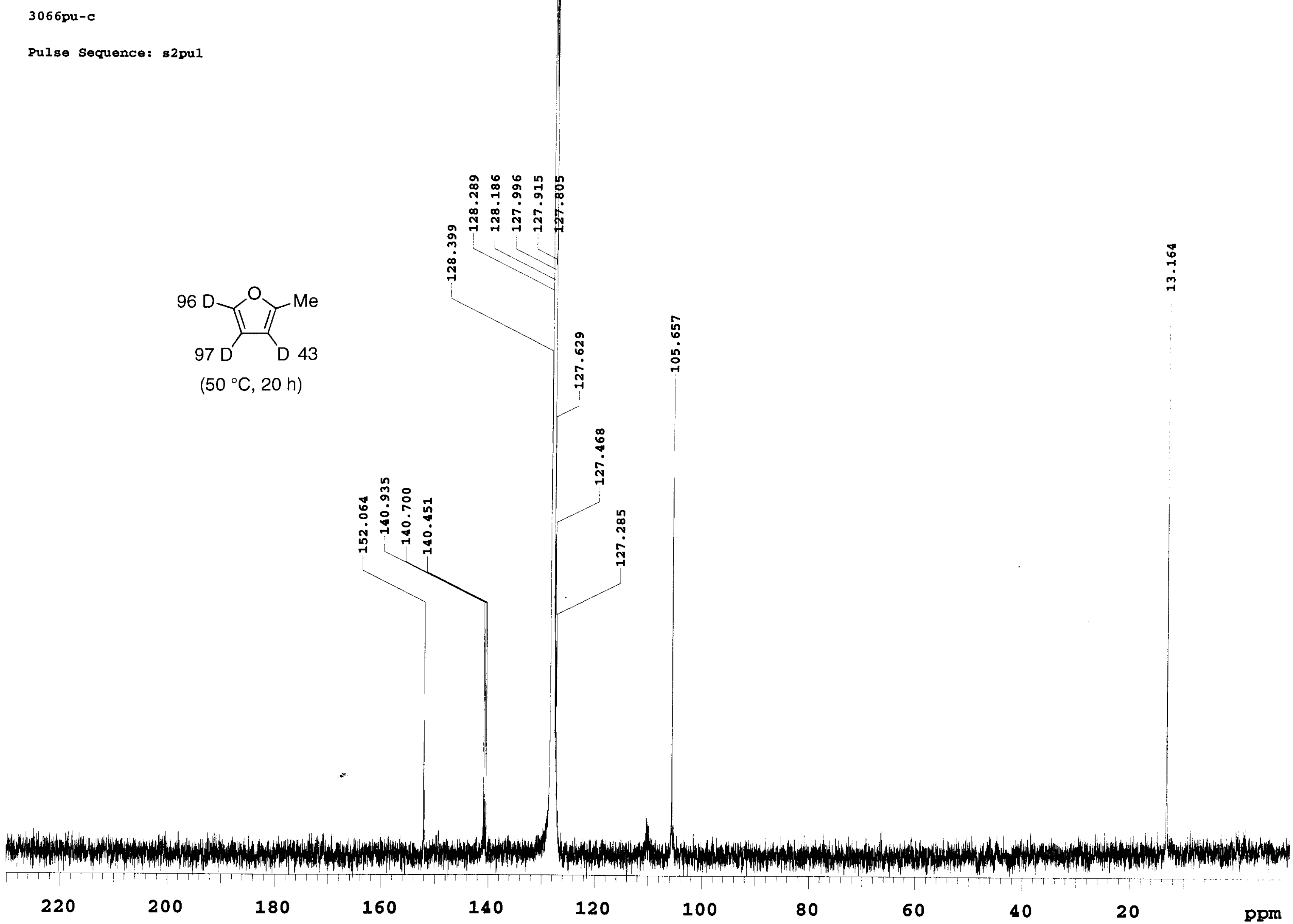
3066.

Pulse Sequence: s2pul



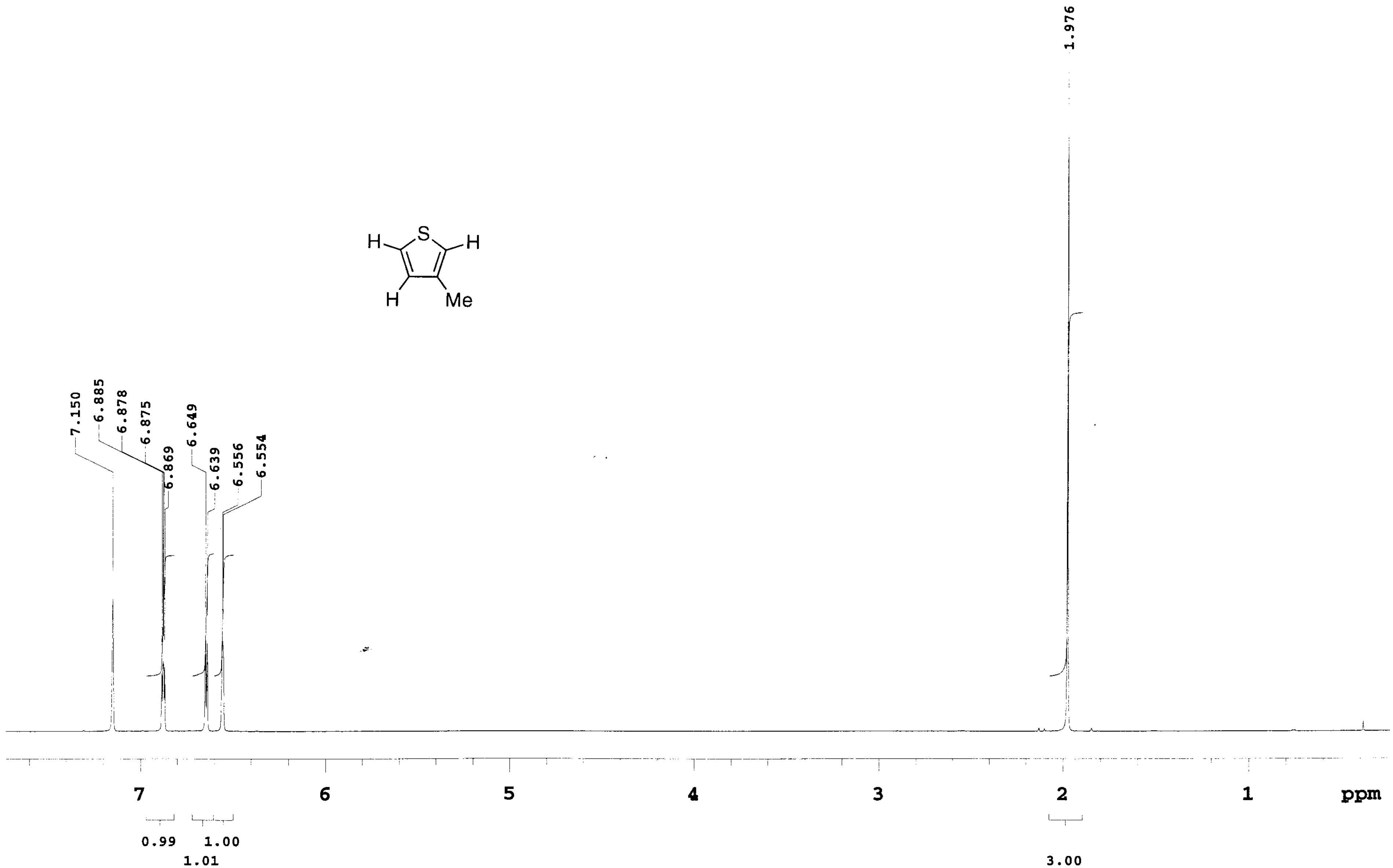


3066pu-d
Pulse Sequence: s2pul
7.305
7.150
6.995
6.084
5.779
96 D
O
Me
97 D
D 43
(50 °C, 20 h)
9
8
7
6
5
4
3
2
1
ppm


3066pu-c
Pulse Sequence: s2pul
96 D
Me
97 D
D 43
(50 °C, 20 h)
152.064
140.935
140.700
140.451
128.399
128.289
128.186
127.996
127.915
127.805
127.629
127.468
127.285
105.657
13.164
220
200
180
160
140
120
100
80
60
40
20
ppm

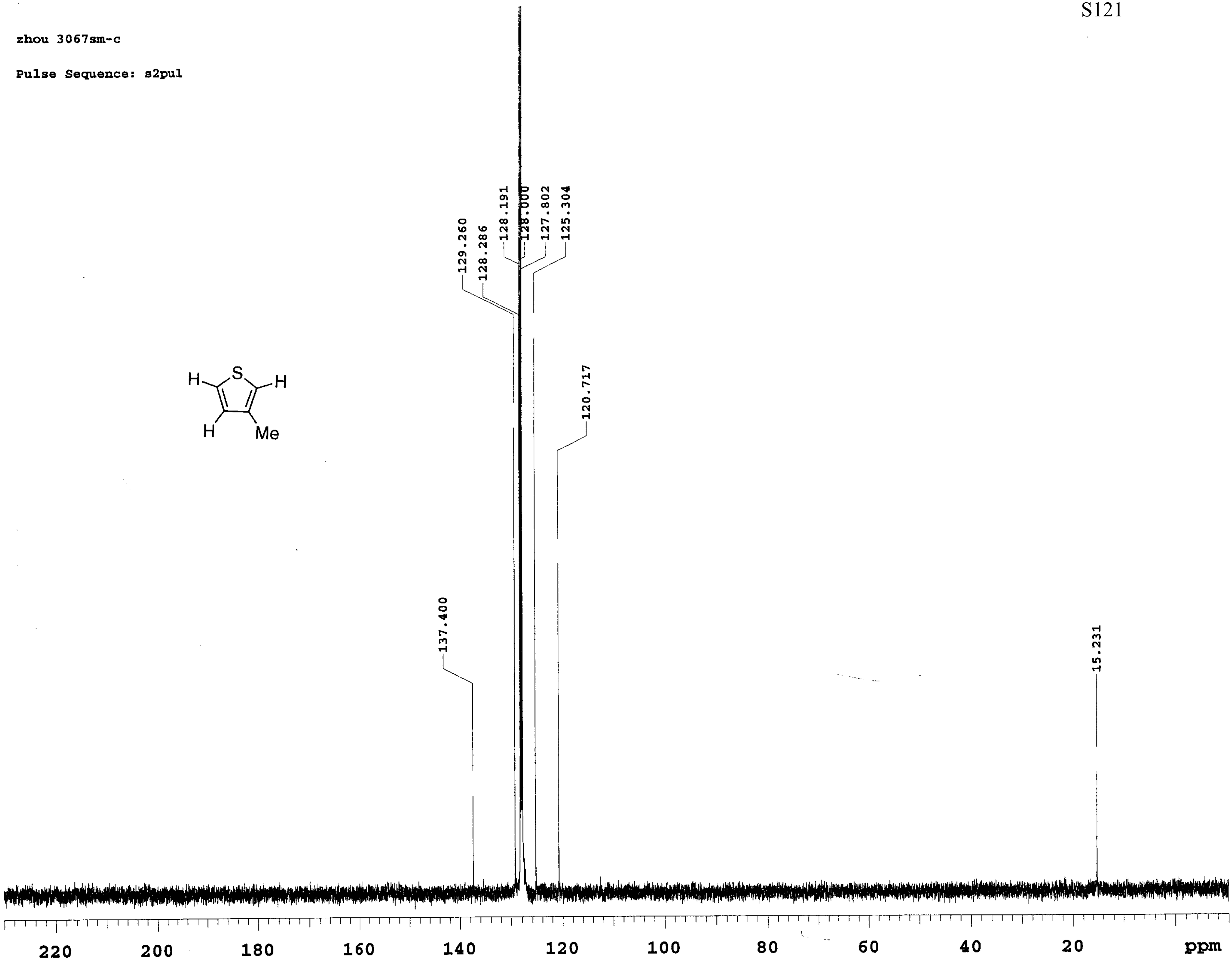
3067sm-h

Pulse Sequence: s2pul



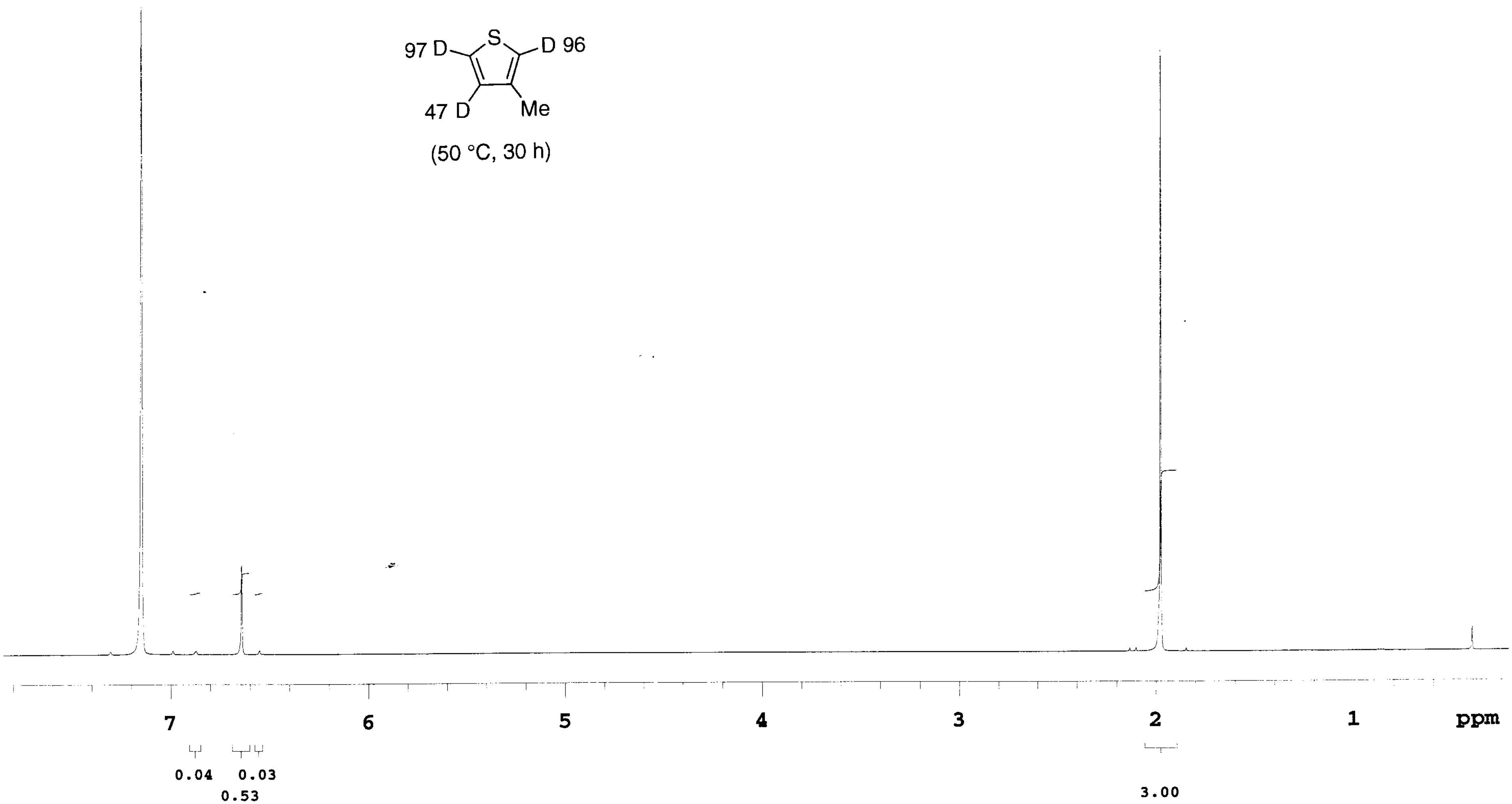
zhou 3067sm-c

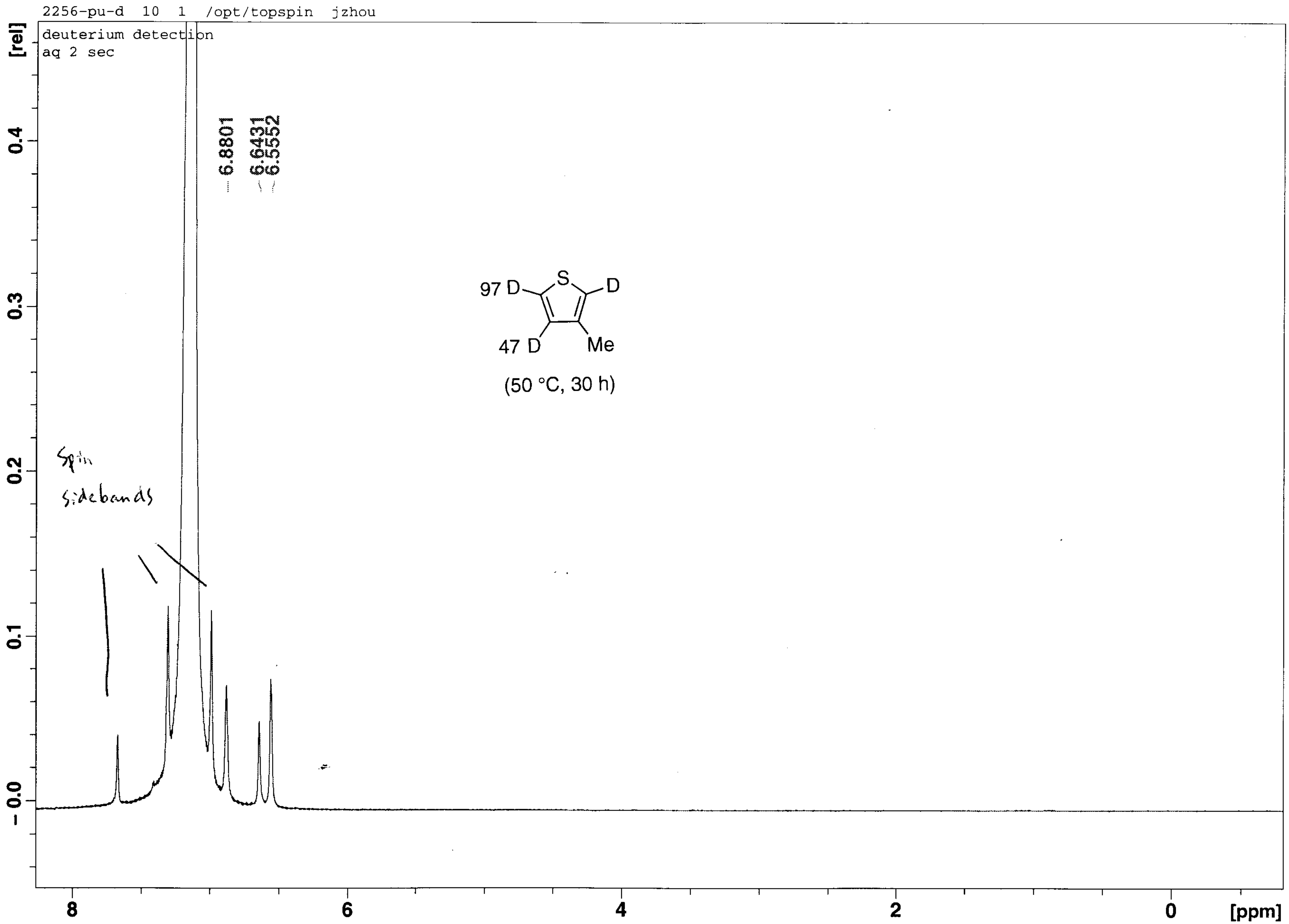
Pulse Sequence: s2pul

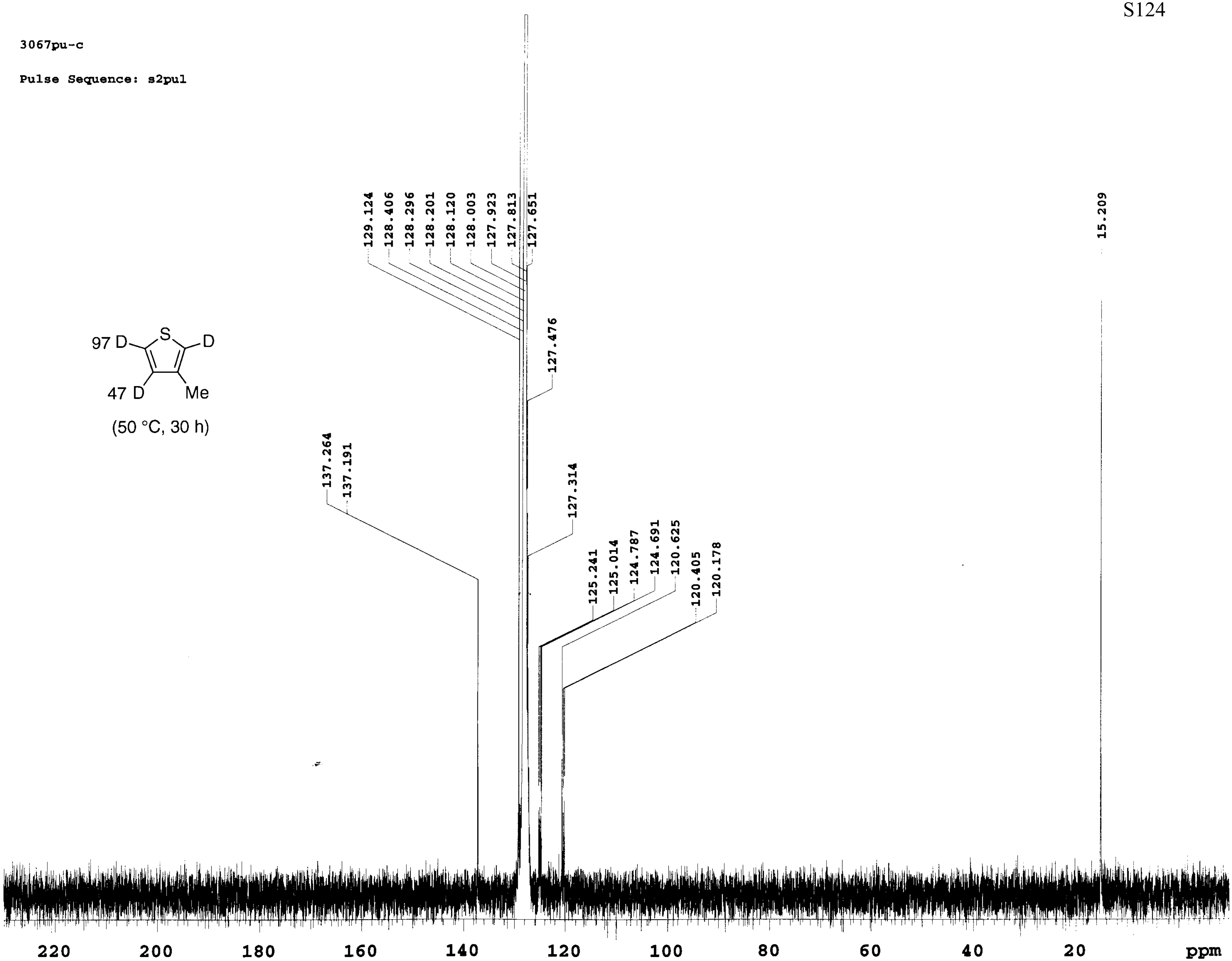


3067pu-h

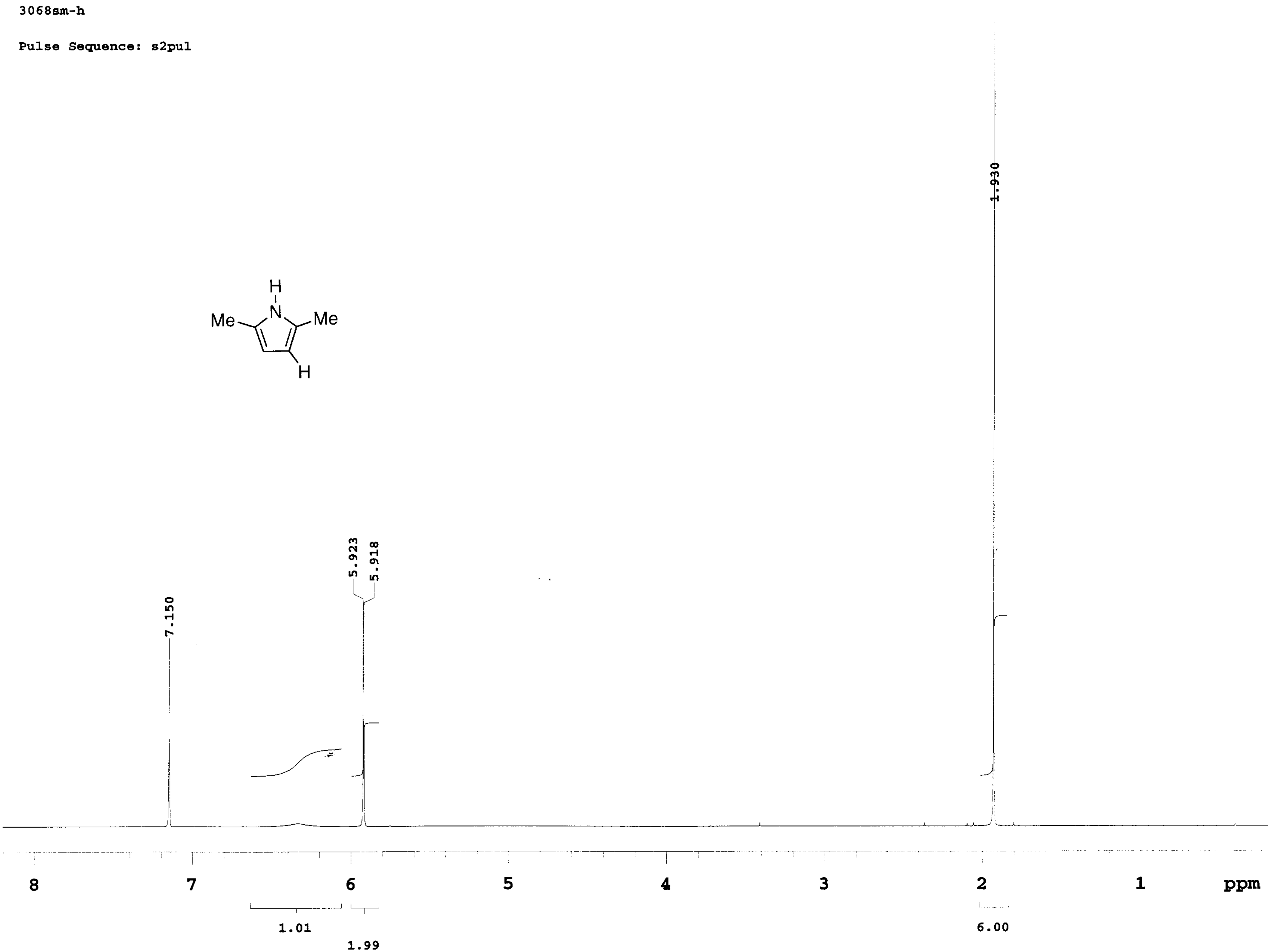
Pulse Sequence: s2pul

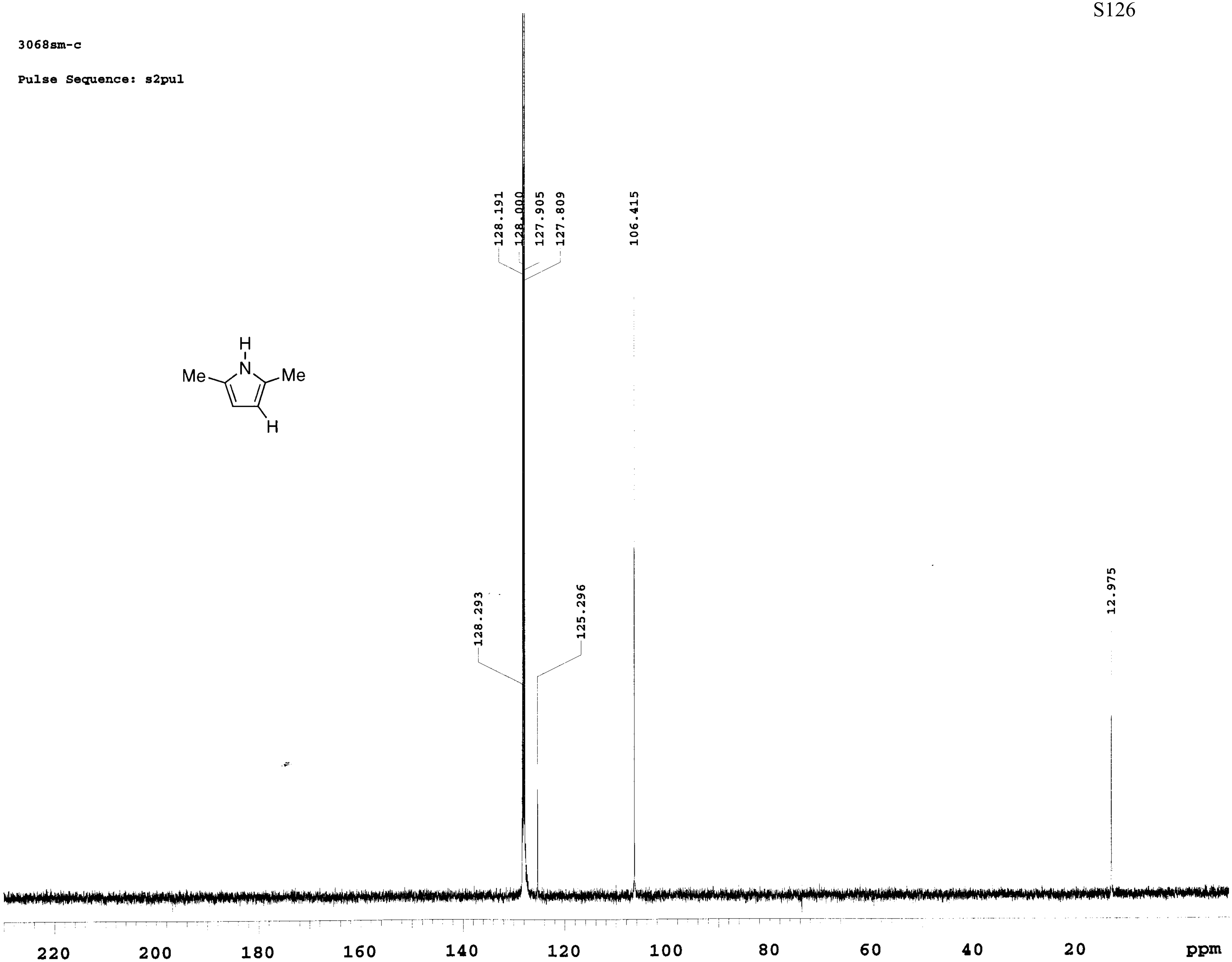



2256-pu-d 10 1 /opt/topspin jzhou
deuterium detection
aq 2 sec
[rel]
6.8801
6.6431
6.5552
97 D
S
D
47 D
Me
(50 °C, 30 h)
Spin
sidebands
[ppm]



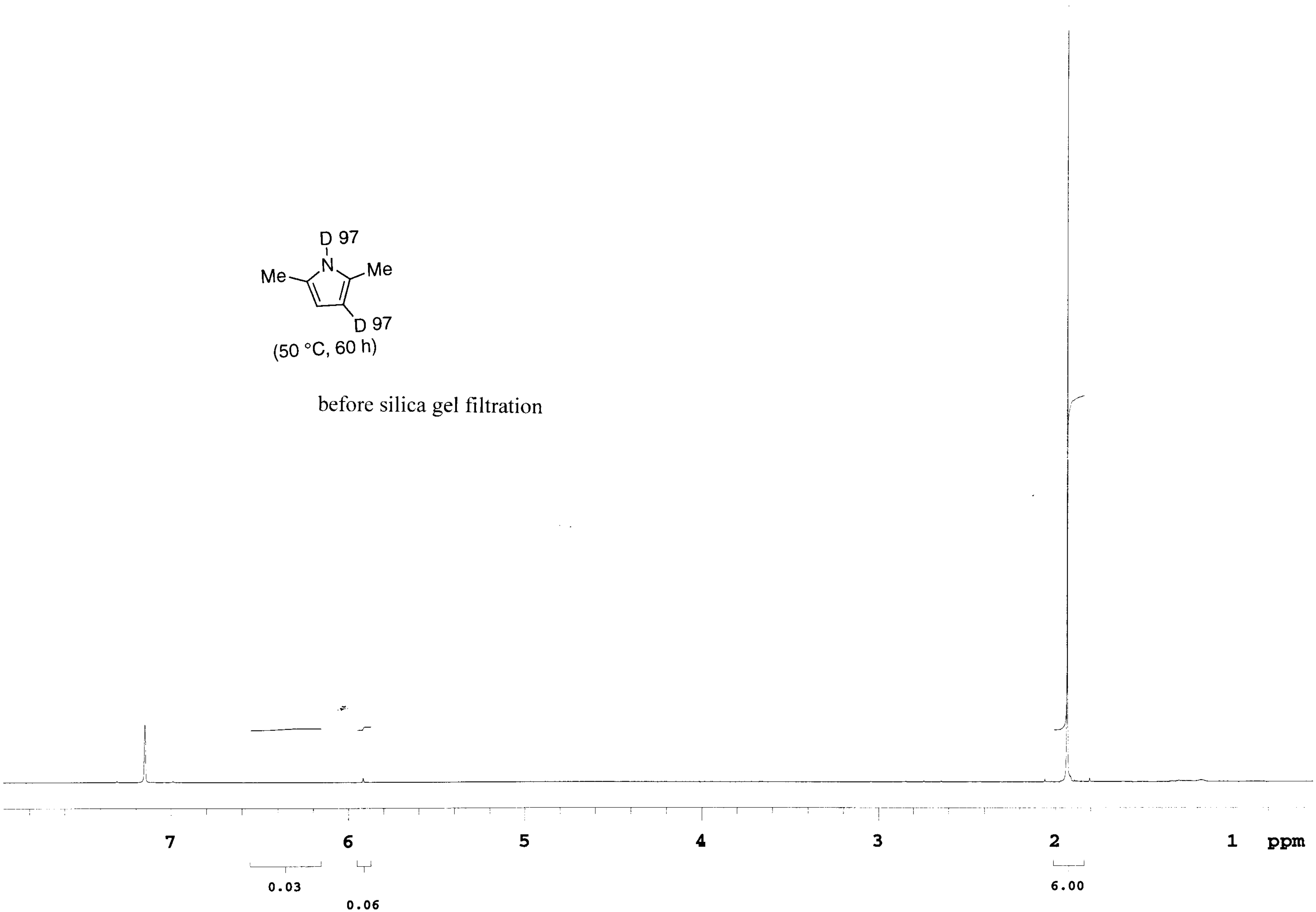
3067pu-c
Pulse Sequence: s2pul
97 D
S
D
47 D
Me
(50 °C, 30 h)
129.124
128.406
128.296
128.201
128.120
128.003
127.923
127.813
127.651
127.476
127.314
137.264
137.191
125.241
125.014
124.787
124.691
120.625
120.405
120.178
15.209
220
200
180
160
140
120
100
80
60
40
20
ppm


3068sm-h
Pulse Sequence: s2pul
H
N
Me
Me
H
7.150
5.923
5.918
1.930
8
7
6
5
4
3
2
1
ppm
1.01
1.99
6.00


3068sm-c
Pulse Sequence: s2pul
128.191
128.000
127.905
127.809
106.415
128.293
125.296
12.975
Me
Me
H
N
H
220
200
180
160
140
120
100
80
60
40
20
ppm

3068-60h

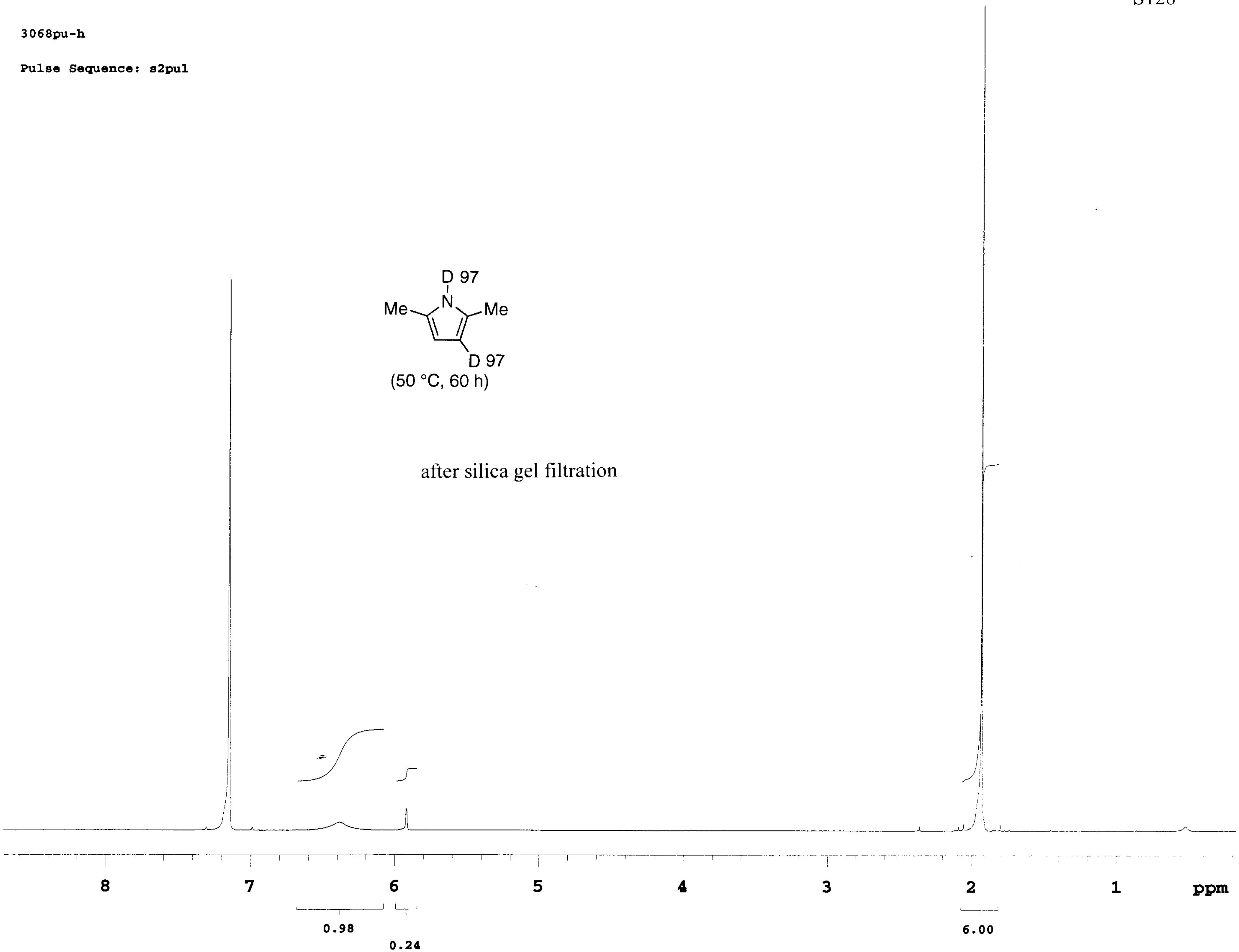
Pulse Sequence: s2pul

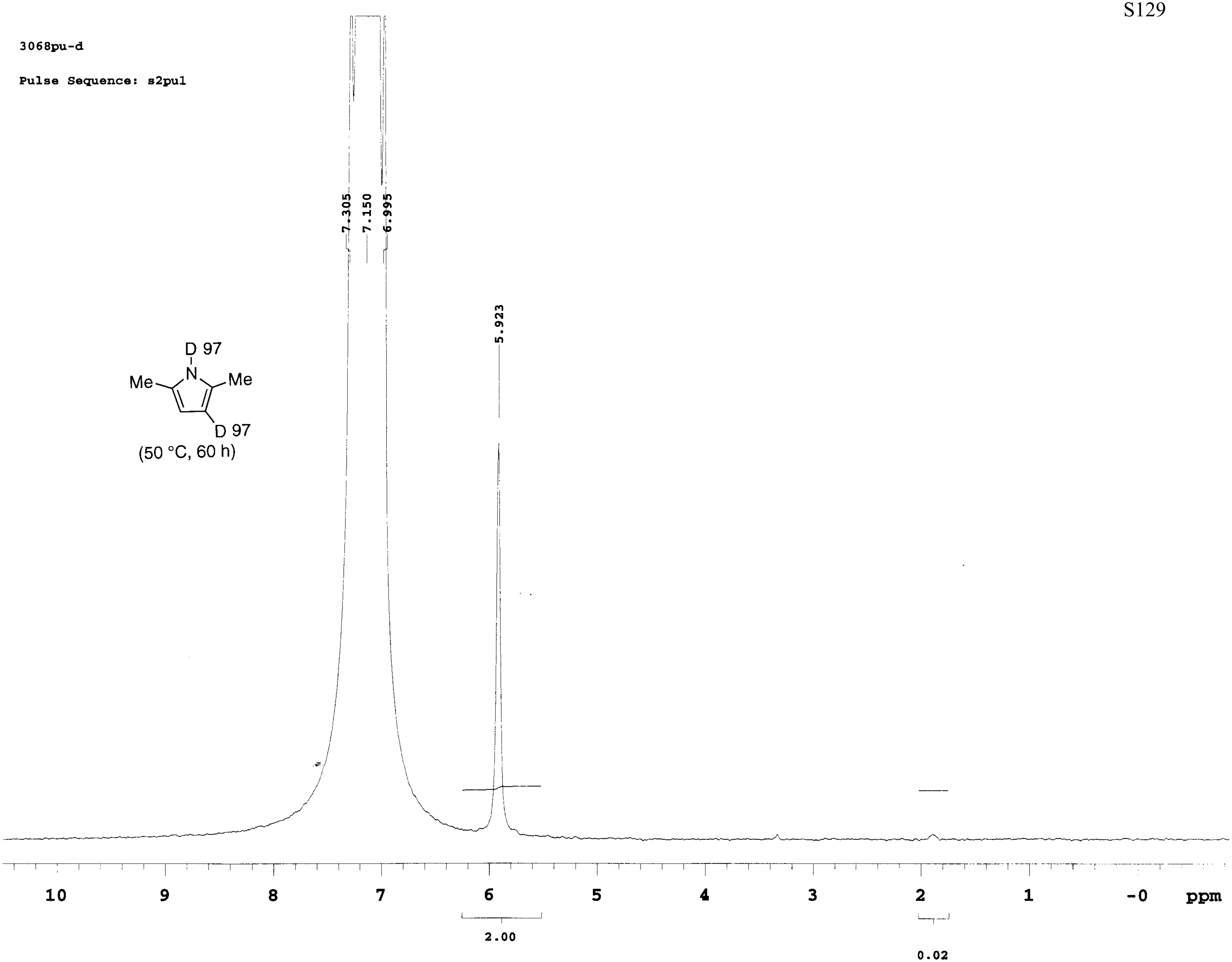


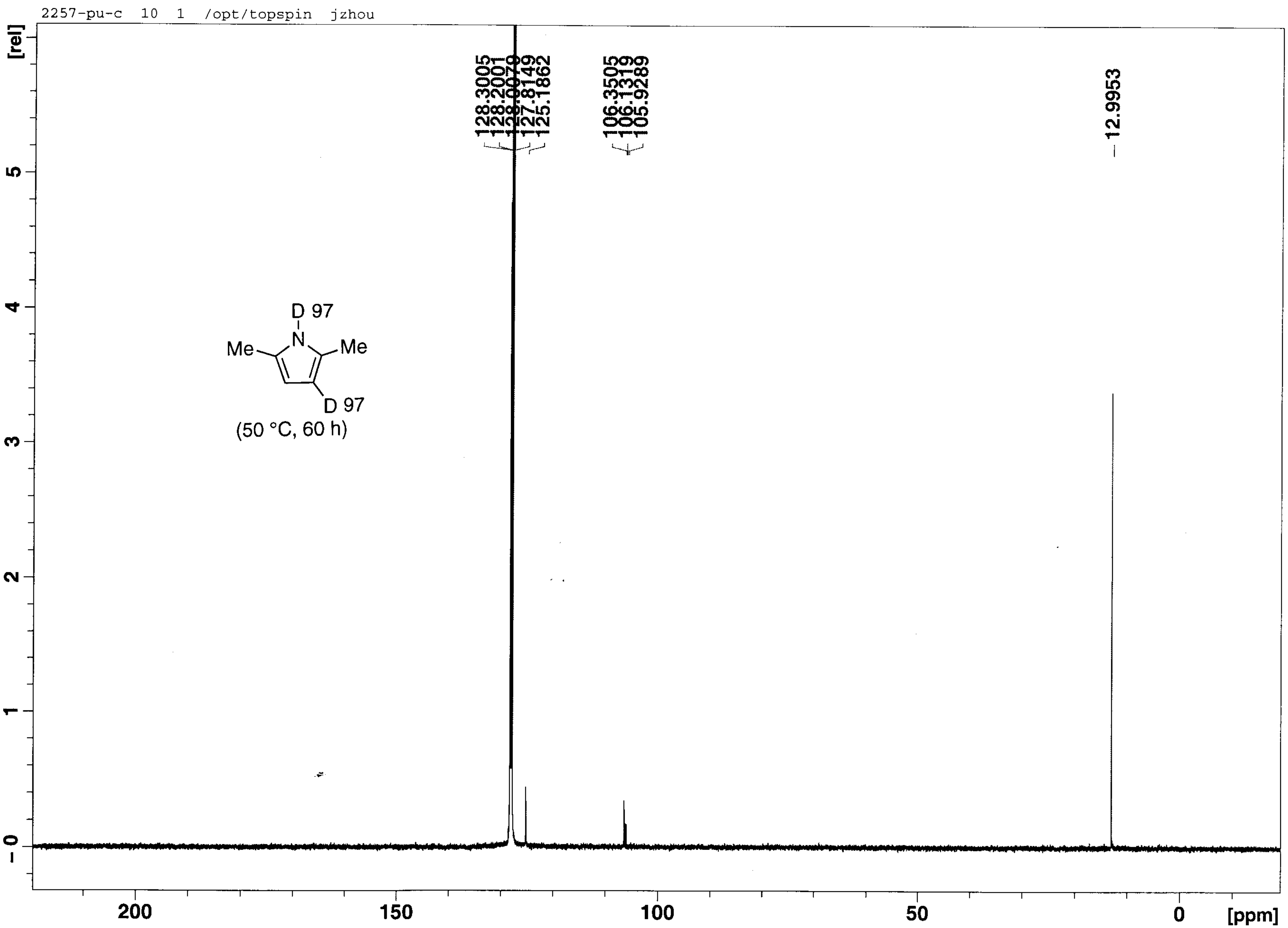
before silica gel filtration

3068pu-h

Pulse Sequence: s2pul

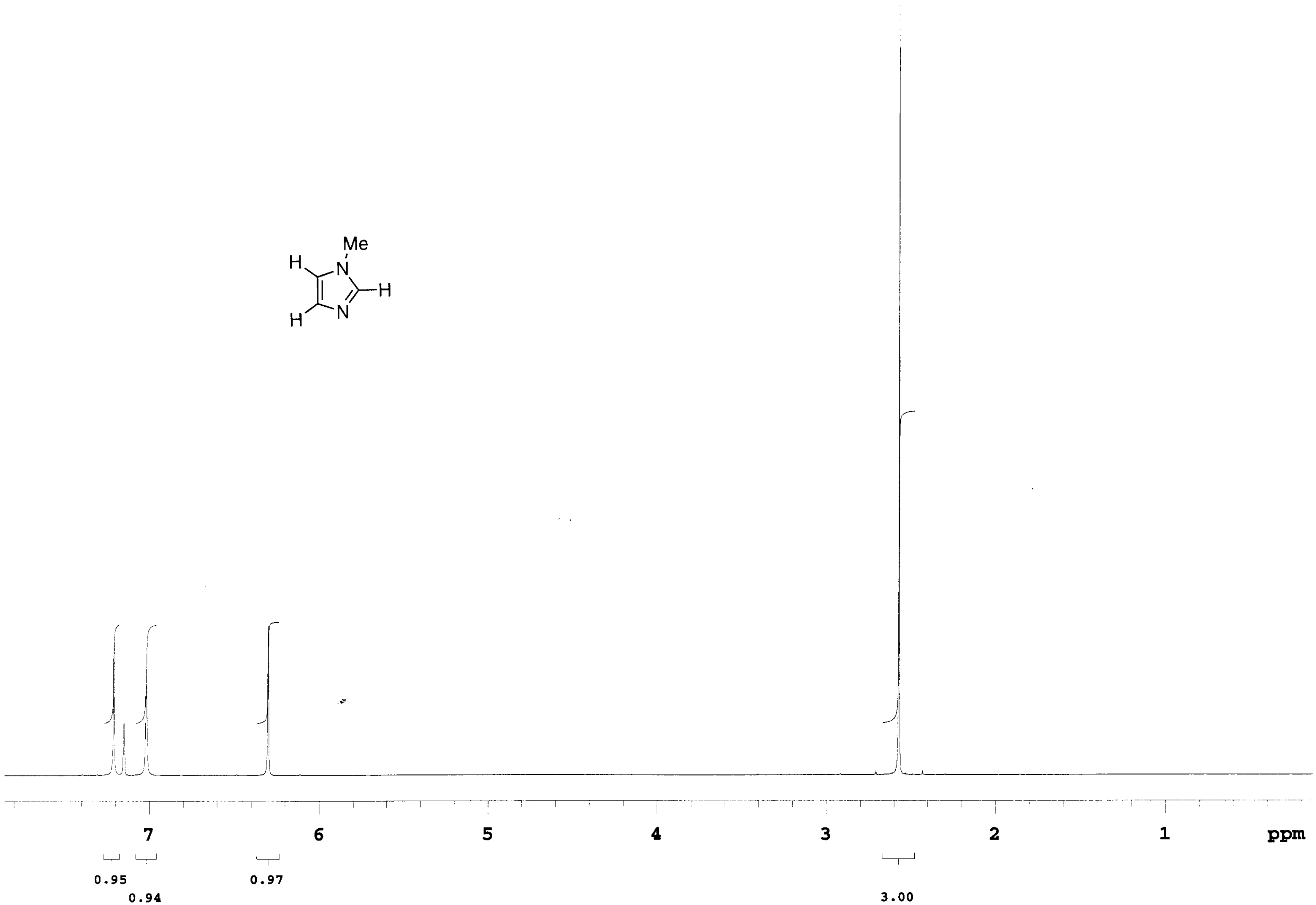



3068pu-d
Pulse Sequence: s2pul
7.305
7.150
6.995
5.923
D 97
N
Me
Me
D 97
(50 °C, 60 h)
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.00
0.02


2257-pu-c 10 1 /opt/topspin jzhou
[rel]
128.3005
128.2001
128.0079
127.8149
125.1862
106.3505
106.1319
105.9289
12.9953
D 97
N
Me
Me
D 97
(50 °C, 60 h)
0
1
2
3
4
5
200
150
100
50
0
[ppm]

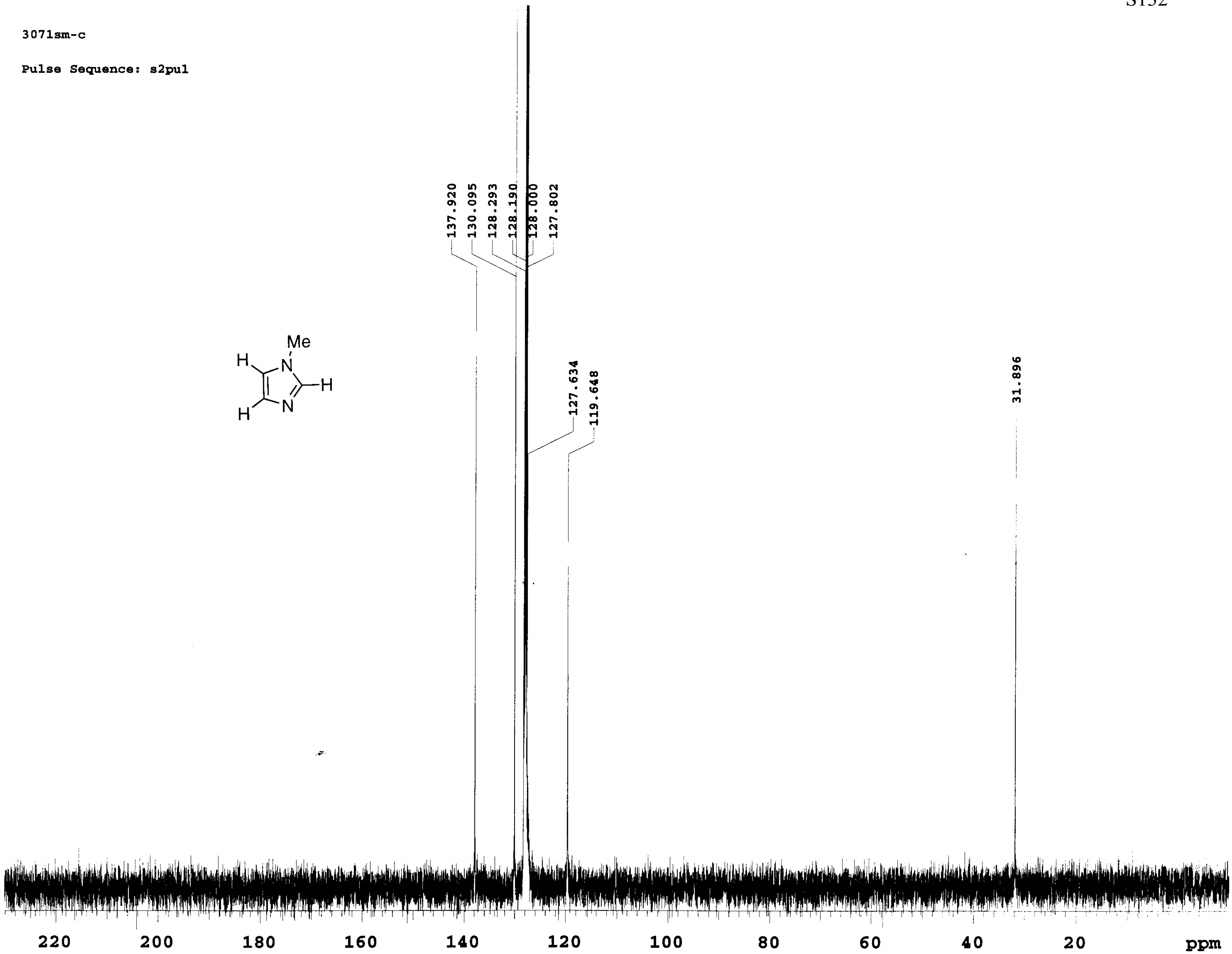
3071sm-h

Pulse Sequence: s2pul



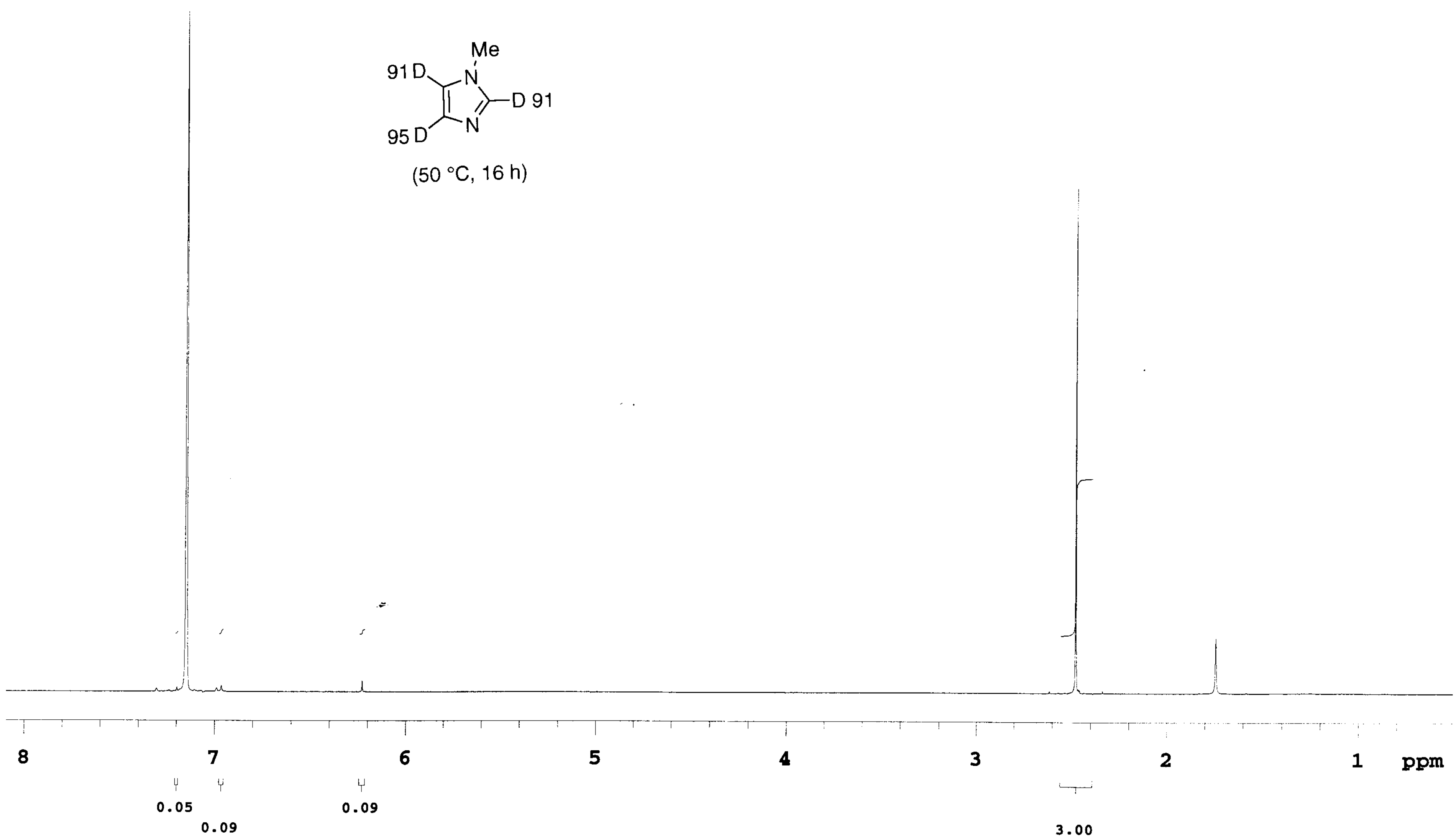
3071sm-c

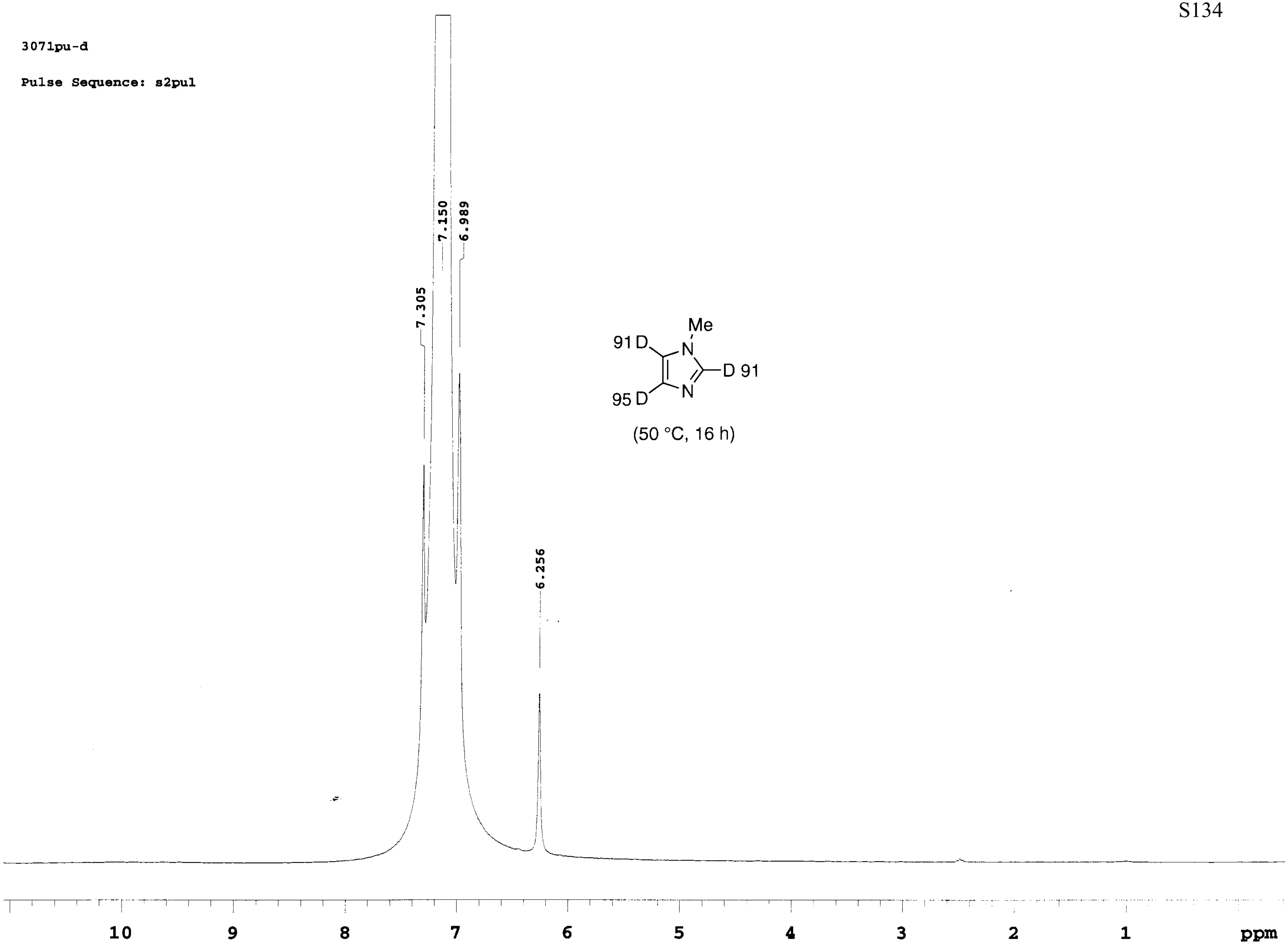
Pulse Sequence: s2pul



3071pu-h

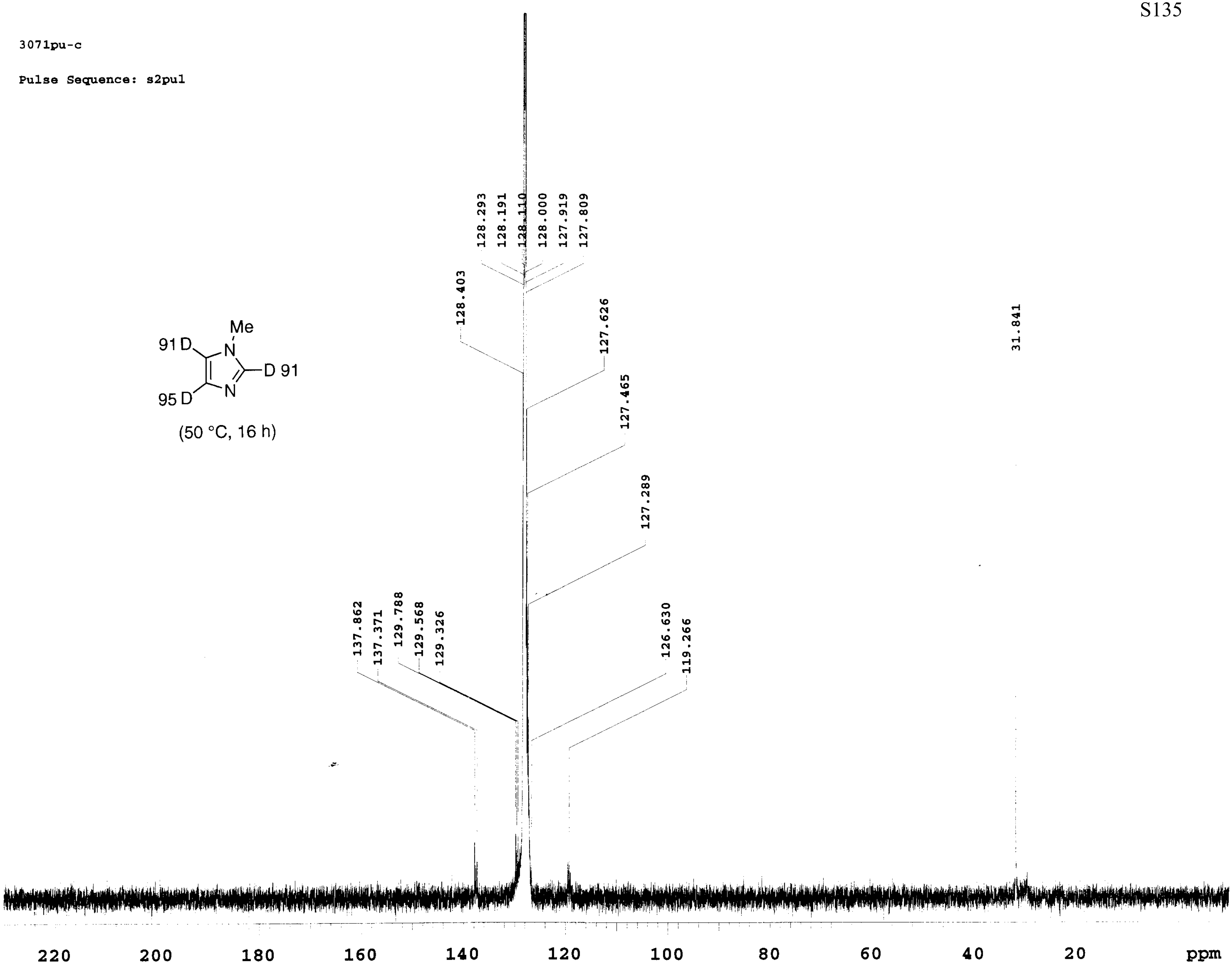
Pulse Sequence: s2pul

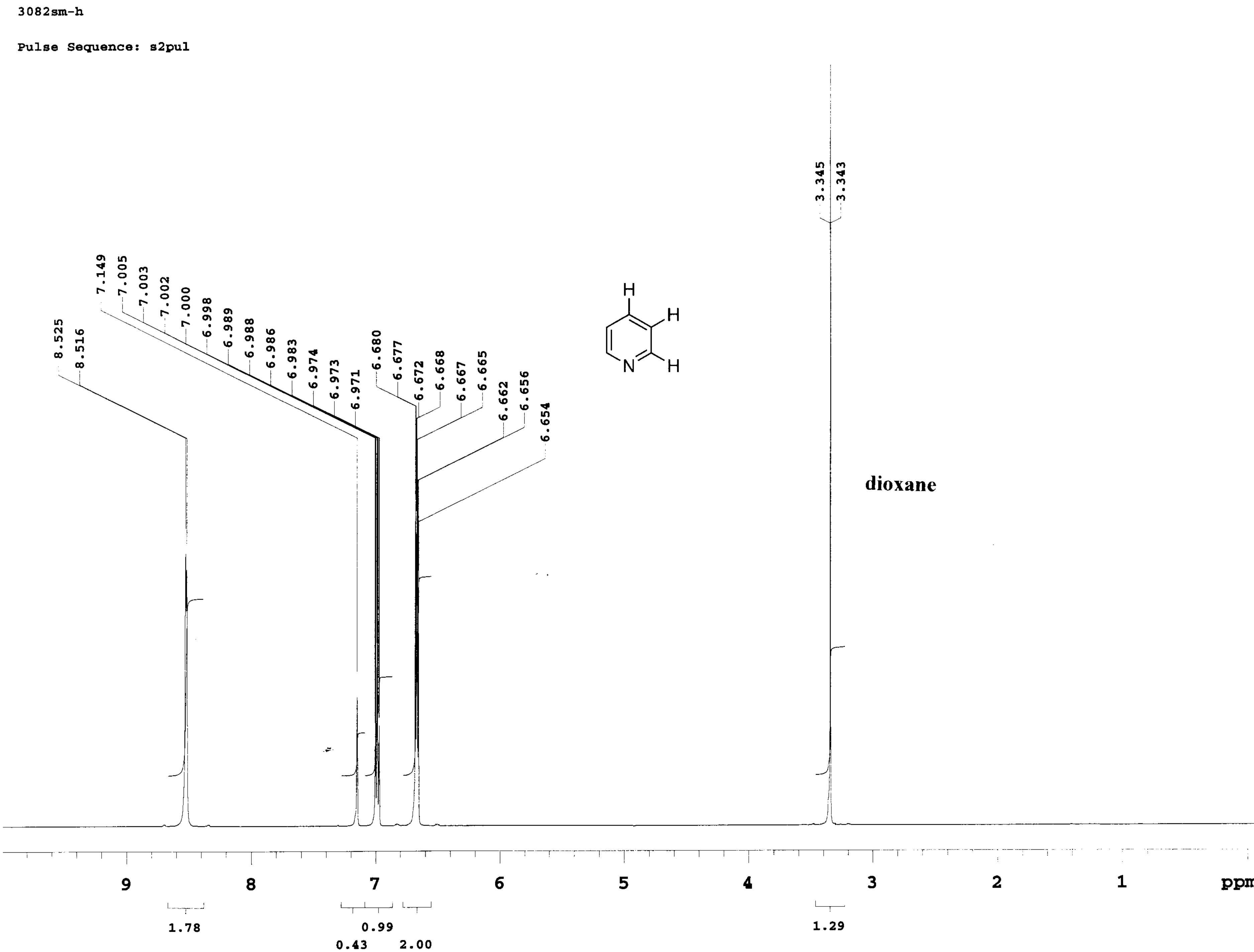



3071pu-d
Pulse Sequence: s2pul
7.305
7.150
6.989
6.256
Me
91 D
D 91
95 D
N
N
(50 °C, 16 h)
10
9
8
7
6
5
4
3
2
1
ppm

3071pu-c

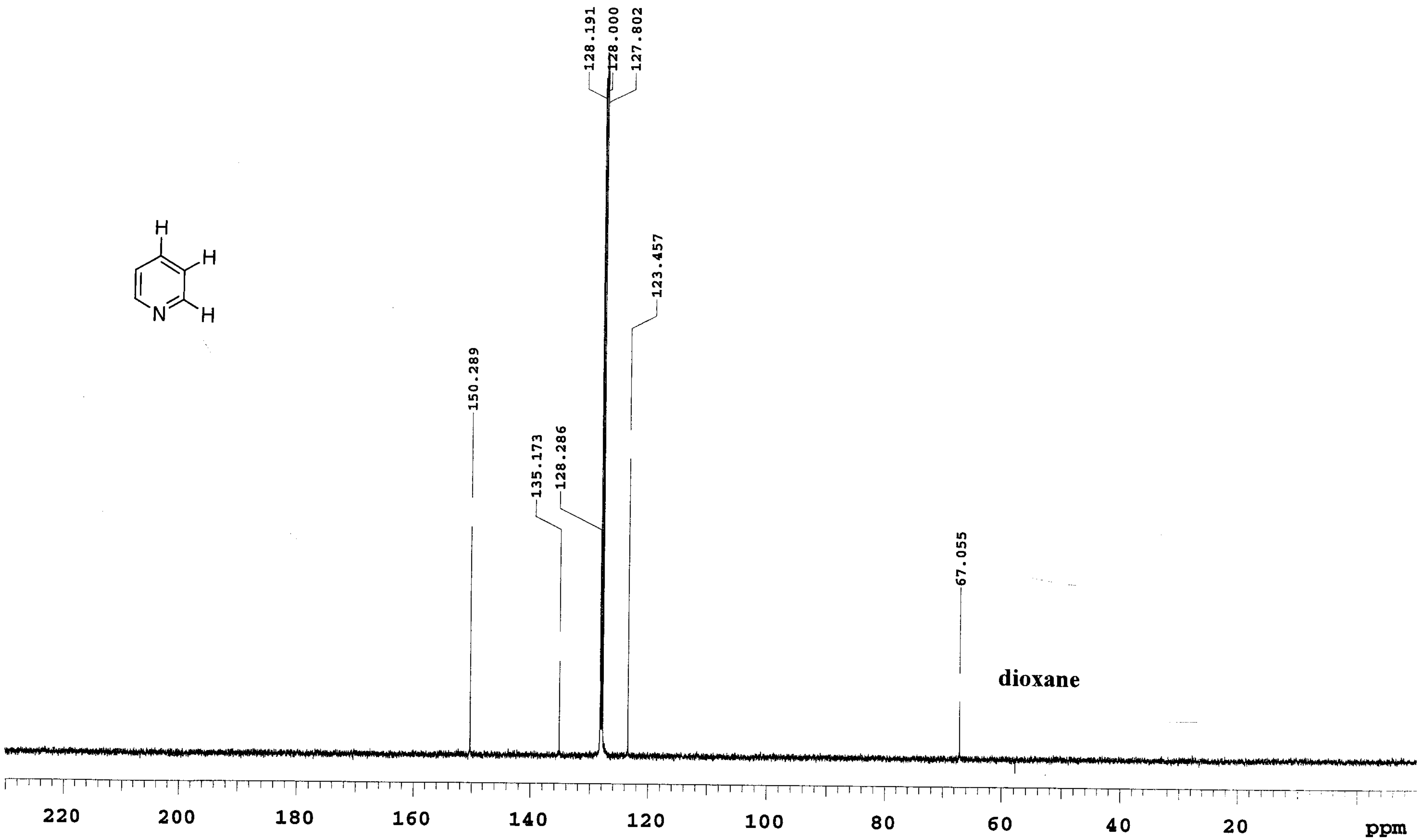
Pulse Sequence: s2pul




3082sm-h
Pulse Sequence: s2pul
8.525
8.516
7.149
7.005
7.003
7.002
7.000
6.998
6.989
6.988
6.986
6.983
6.974
6.973
6.971
6.680
6.677
6.672
6.668
6.667
6.665
6.662
6.656
6.654
3.345
3.343
H
H
H
N
dioxane
9
8
7
6
5
4
3
2
1
ppm
1.78
0.99
0.43
2.00
1.29

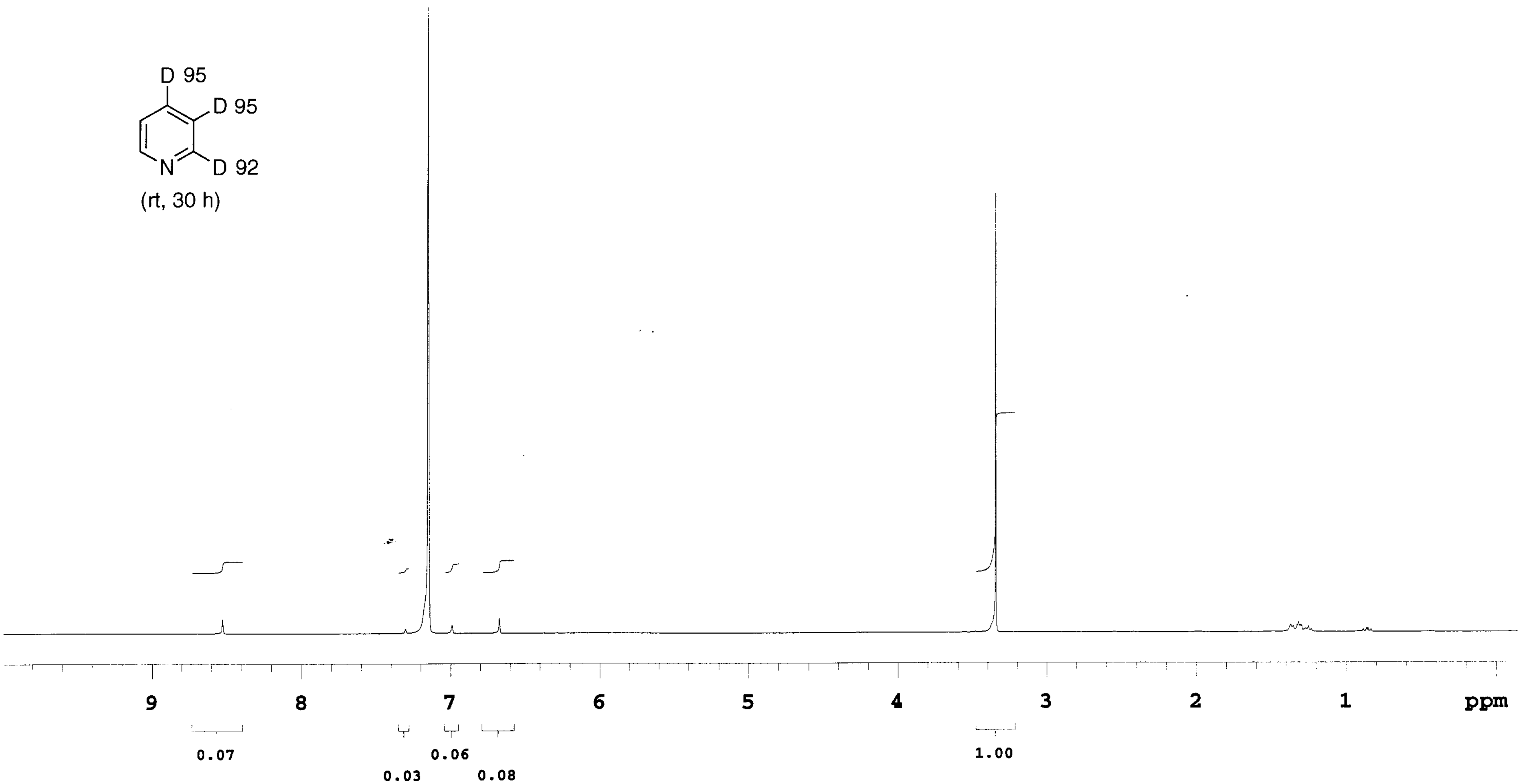
3082sm-c

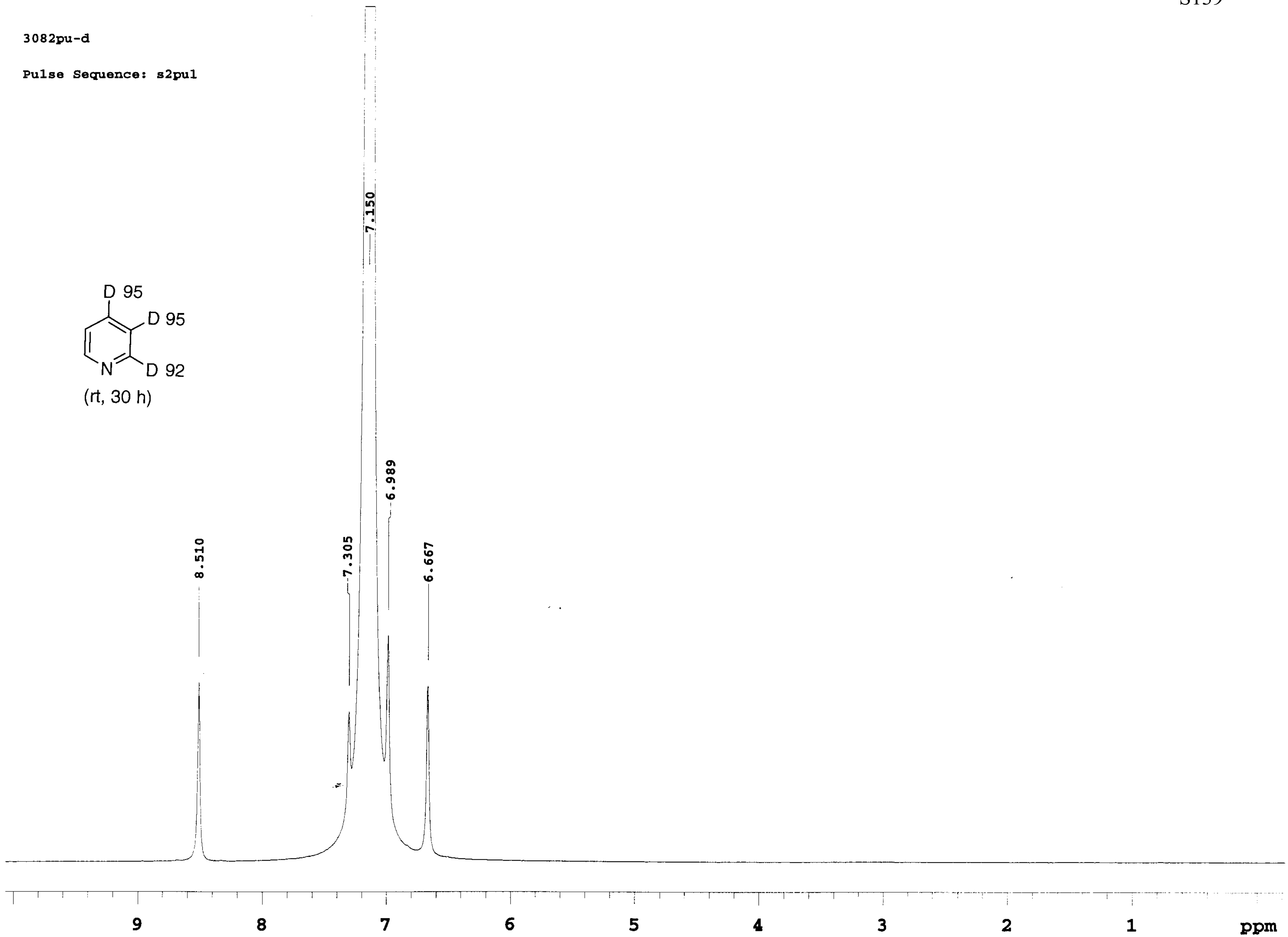
Pulse Sequence: s2pul



3082-30h

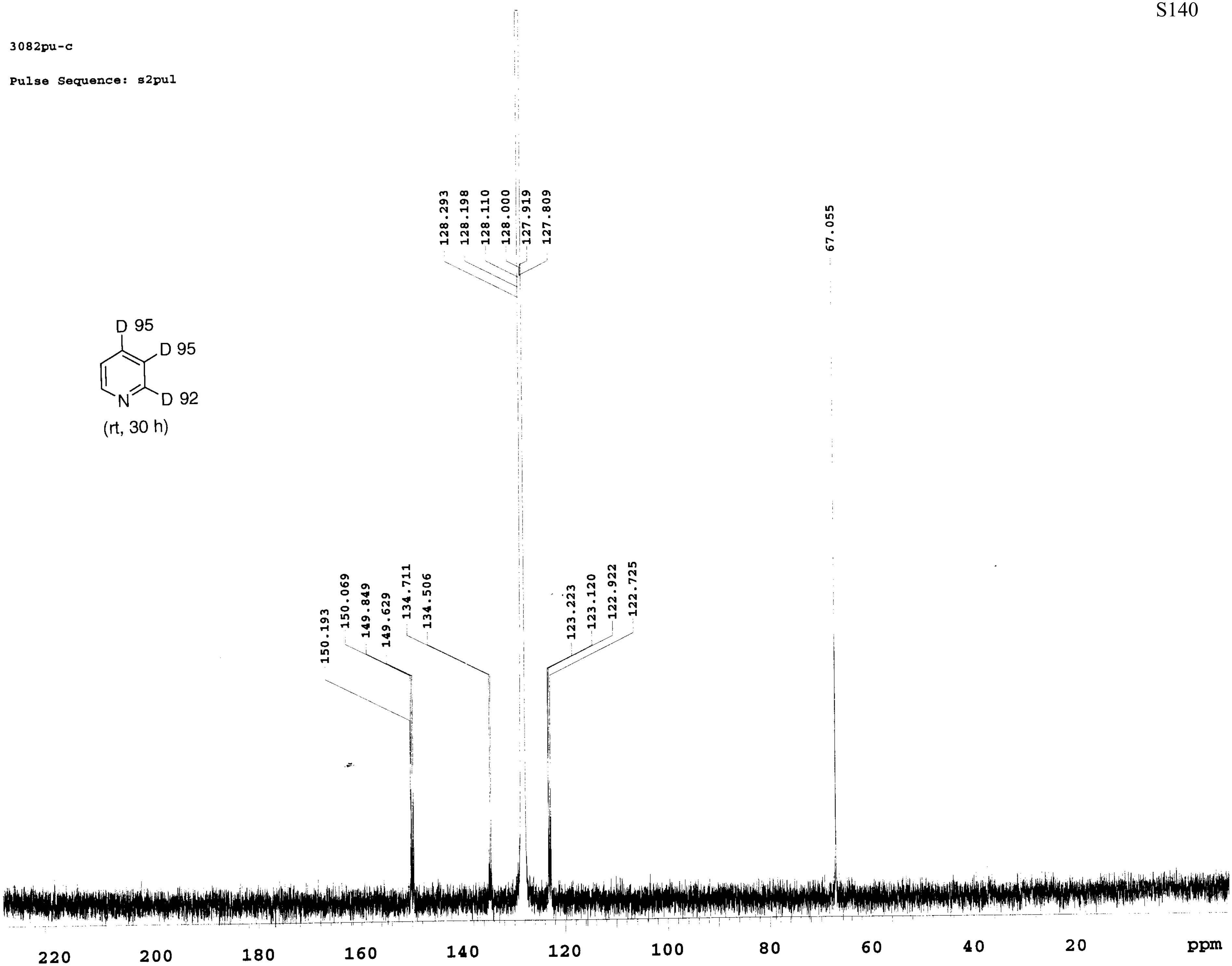
Pulse Sequence: s2pul




3082pu-d
Pulse Sequence: s2pul
D 95
D 95
D 92
N
(rt, 30 h)
8.510
7.305
7.150
6.989
6.667
9
8
7
6
5
4
3
2
1
ppm

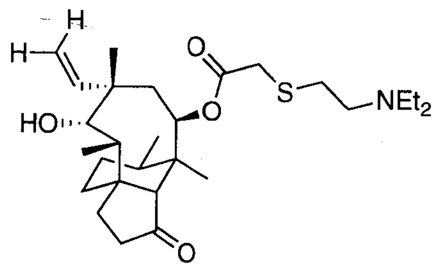
3082pu-c

Pulse Sequence: s2pul

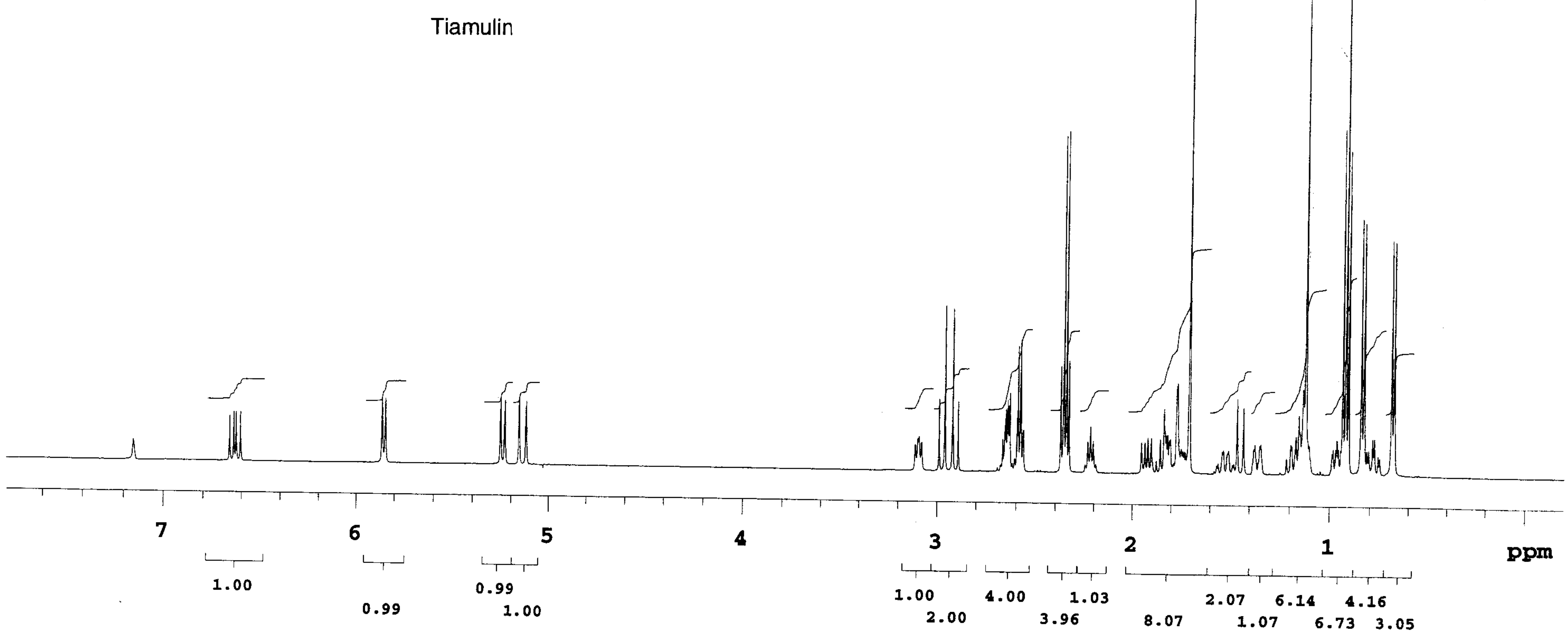


3069sm-h

Pulse Sequence: s2pul

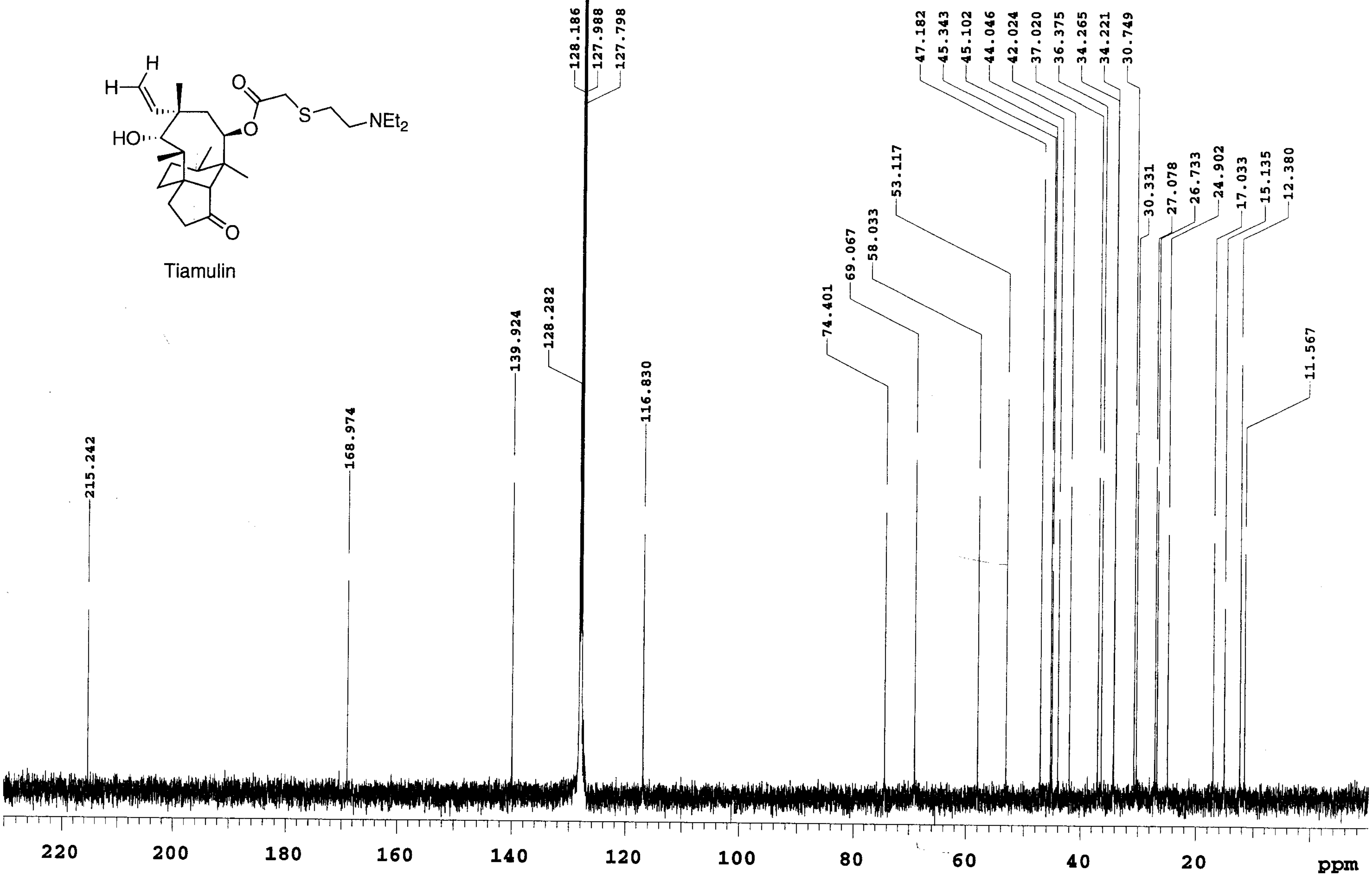


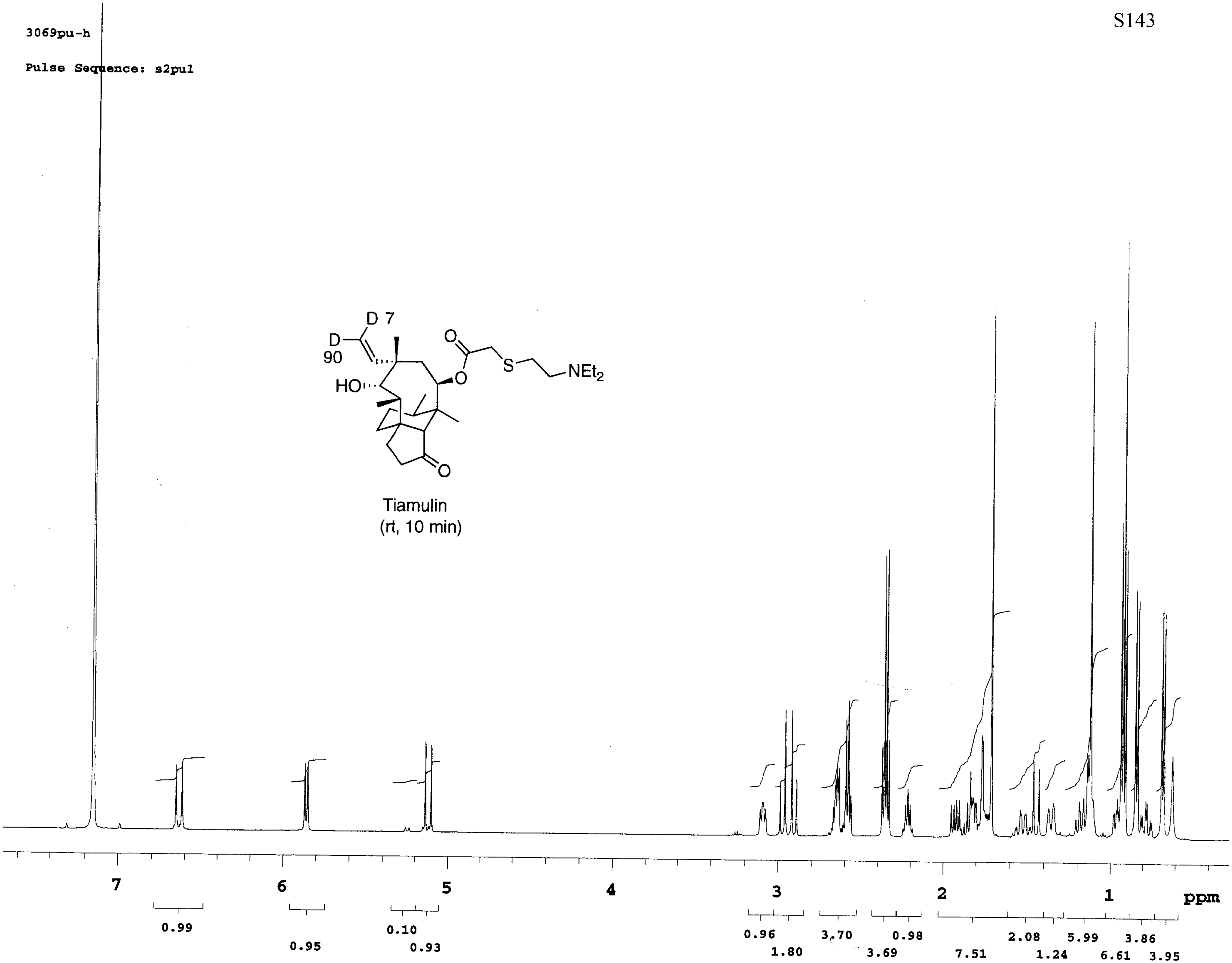
Tiamulin



3069sm-c

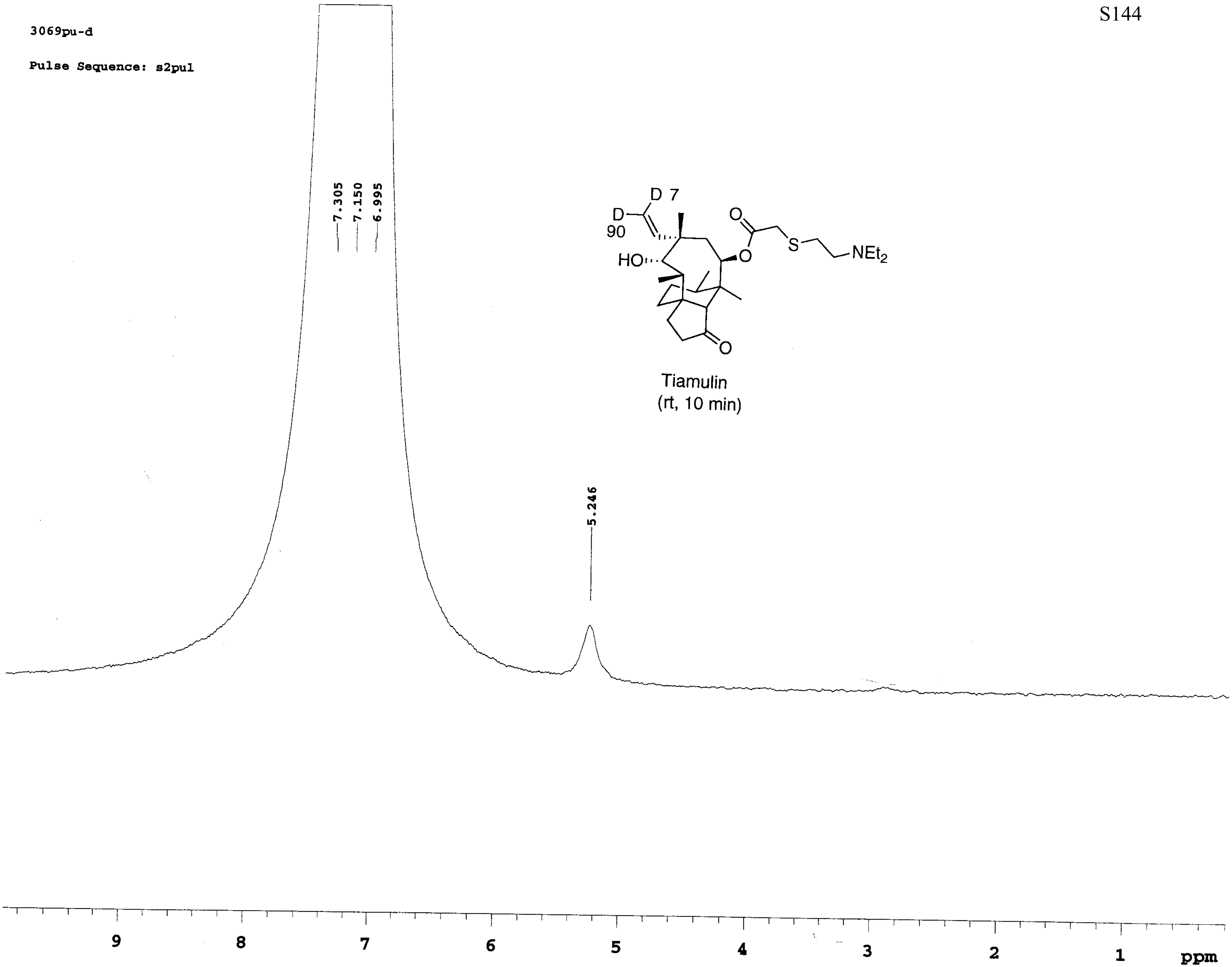
Pulse Sequence: s2pul




3069pu-h
Pulse Sequence: s2pul
D 7
D
90
HO
O
O
S
NEt_2
O
Tiamulin
(rt, 10 min)
7
6
5
4
3
2
1
ppm
0.99
0.95
0.10
0.93
0.96
1.80
3.70
3.69
0.98
7.51
2.08
1.24
5.99
6.61
3.86
3.95

3069pu-d

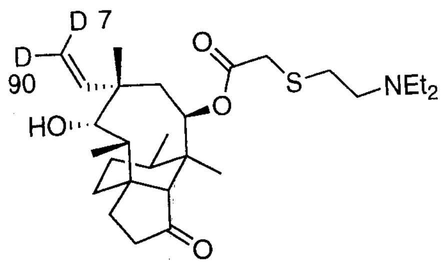
Pulse Sequence: s2pul



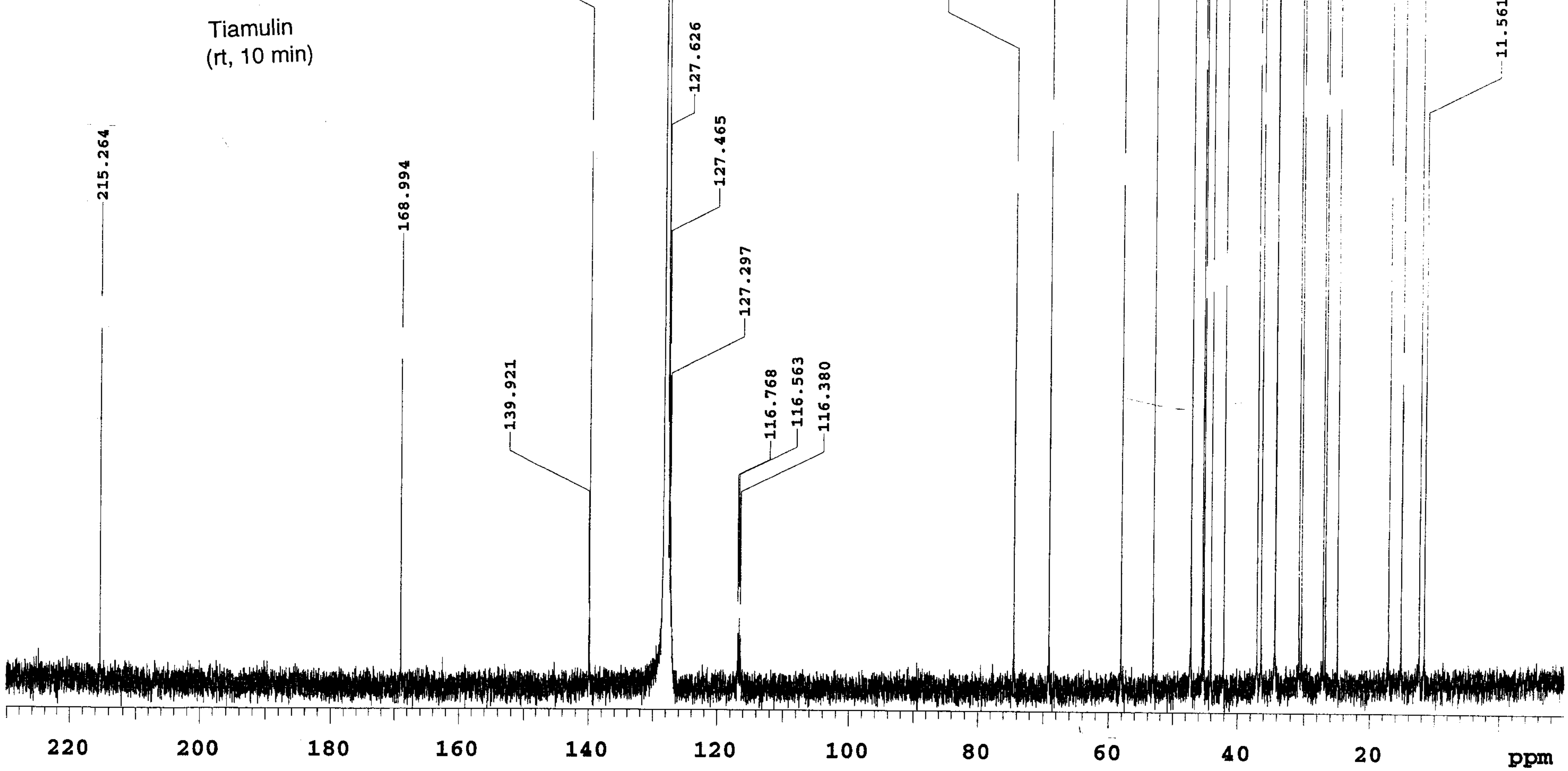
Tiamulin
(rt, 10 min)

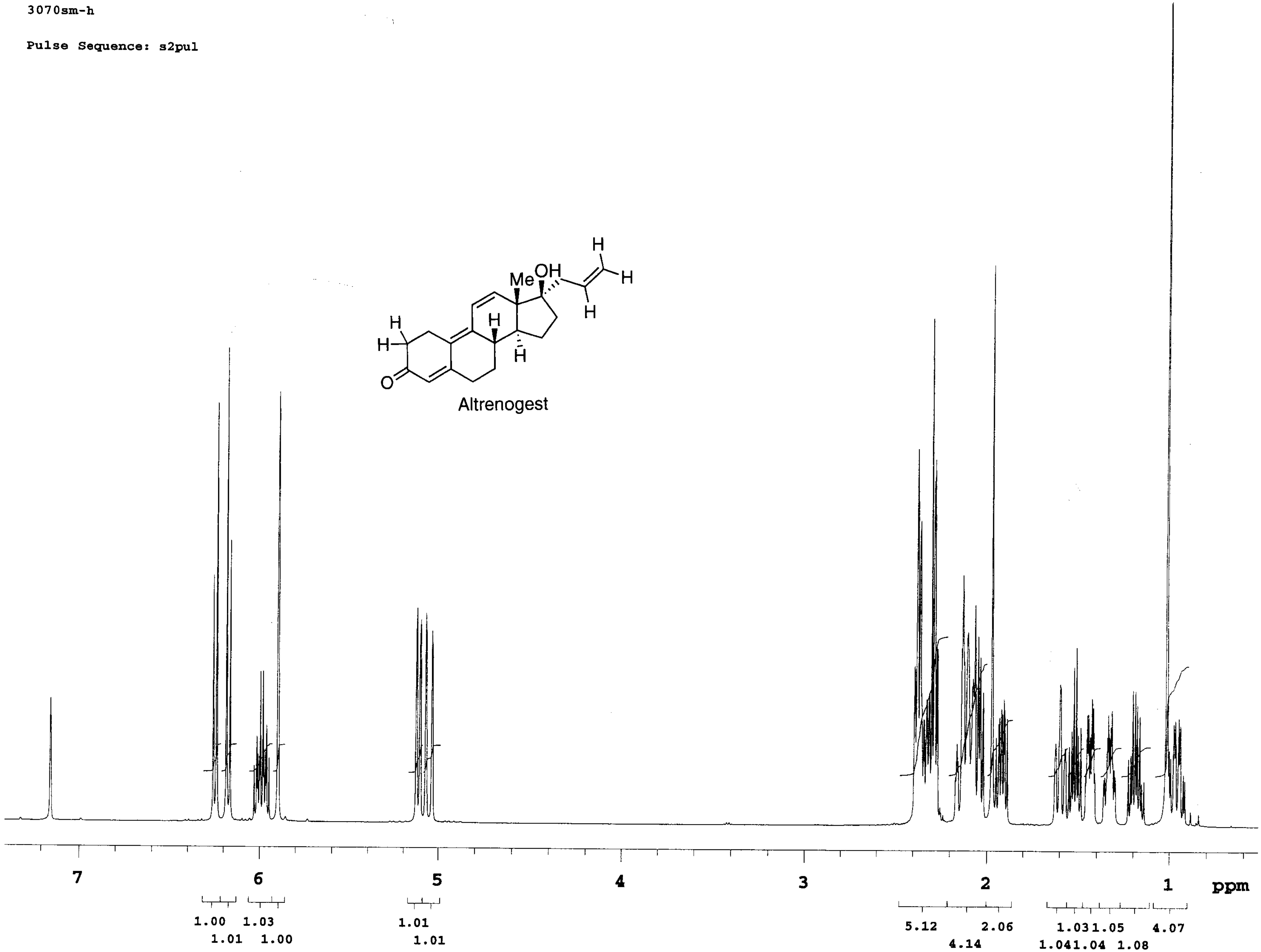
3069pu-c

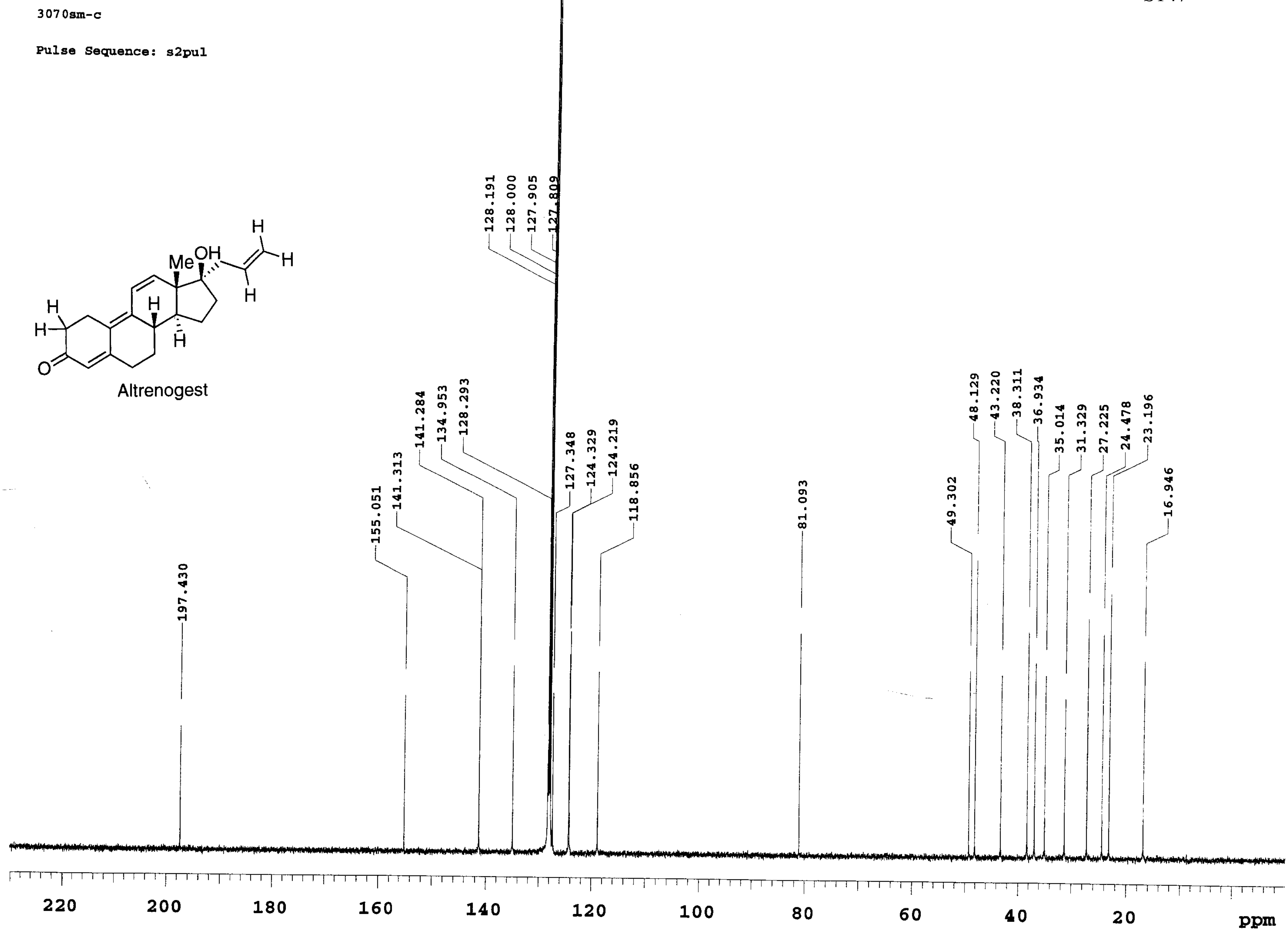
Pulse Sequence: s2pul

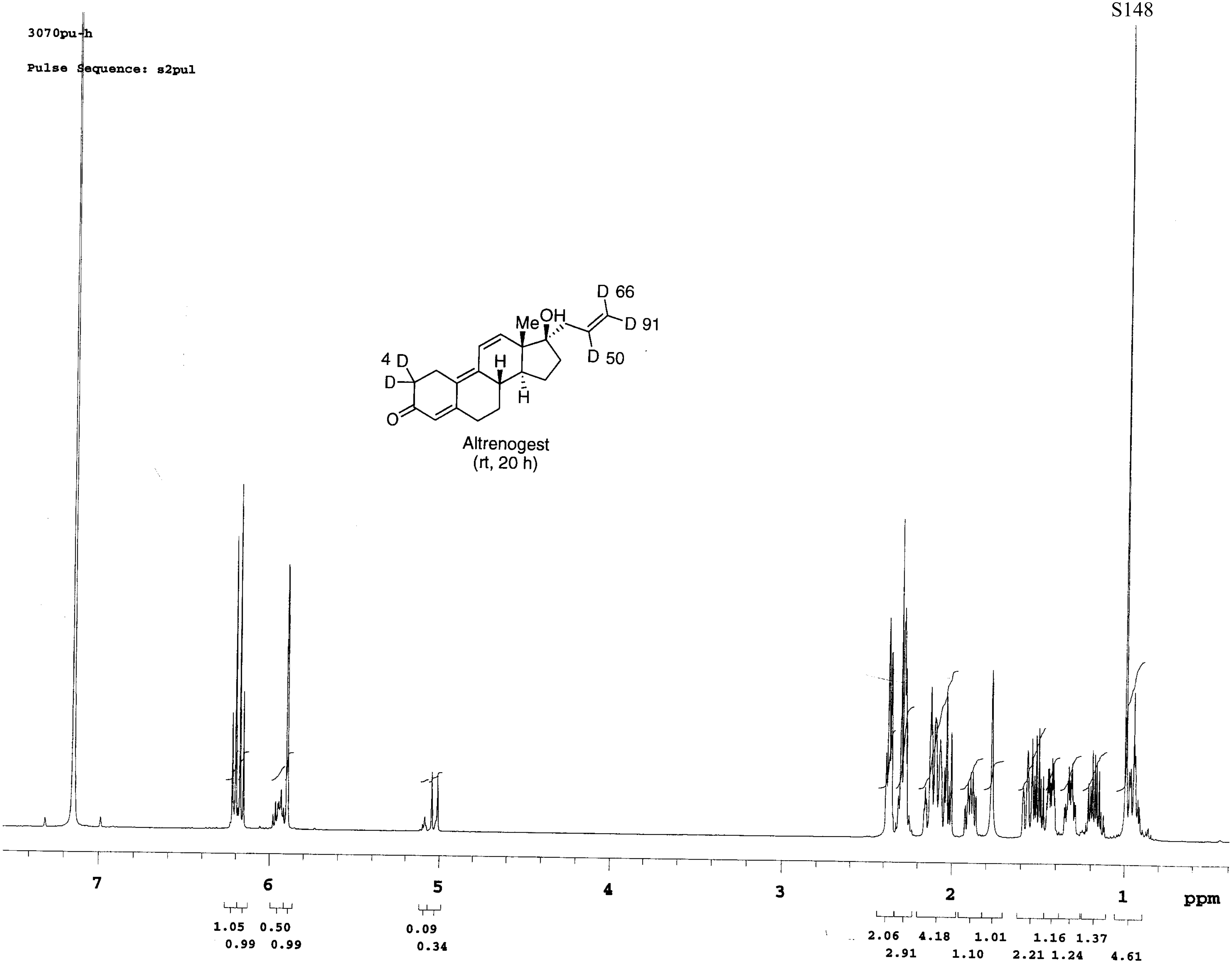


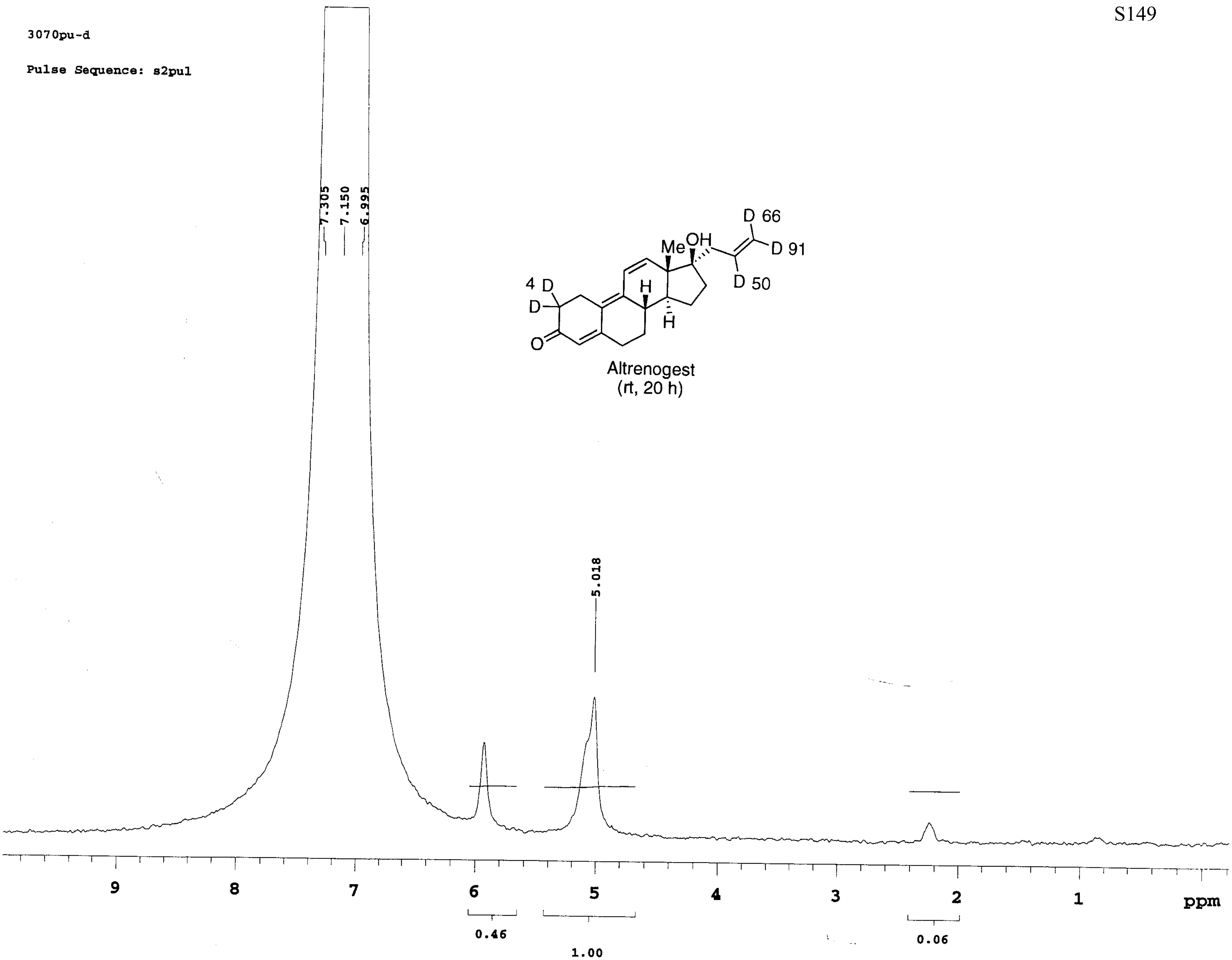
Tiamulin
(rt, 10 min)

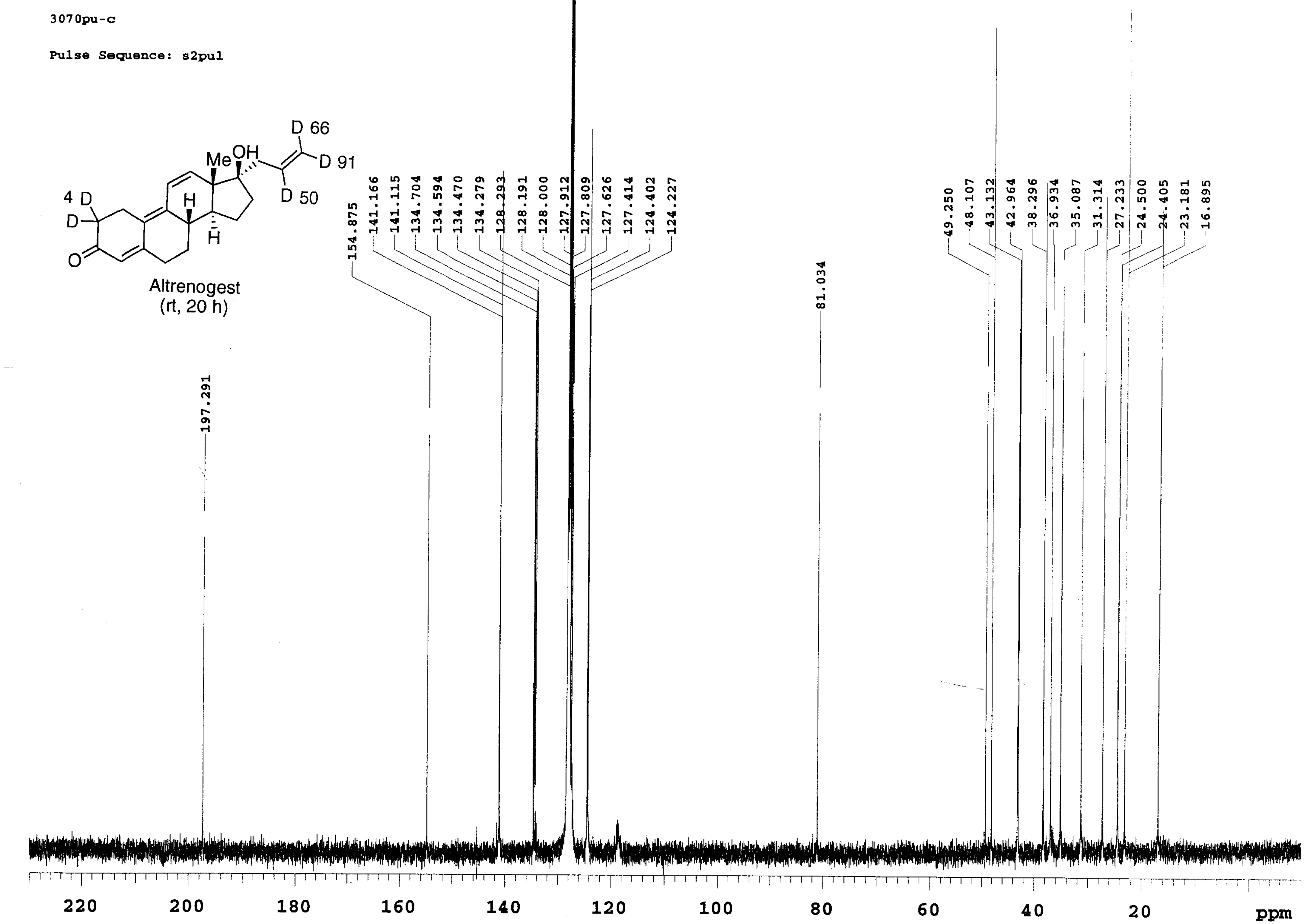


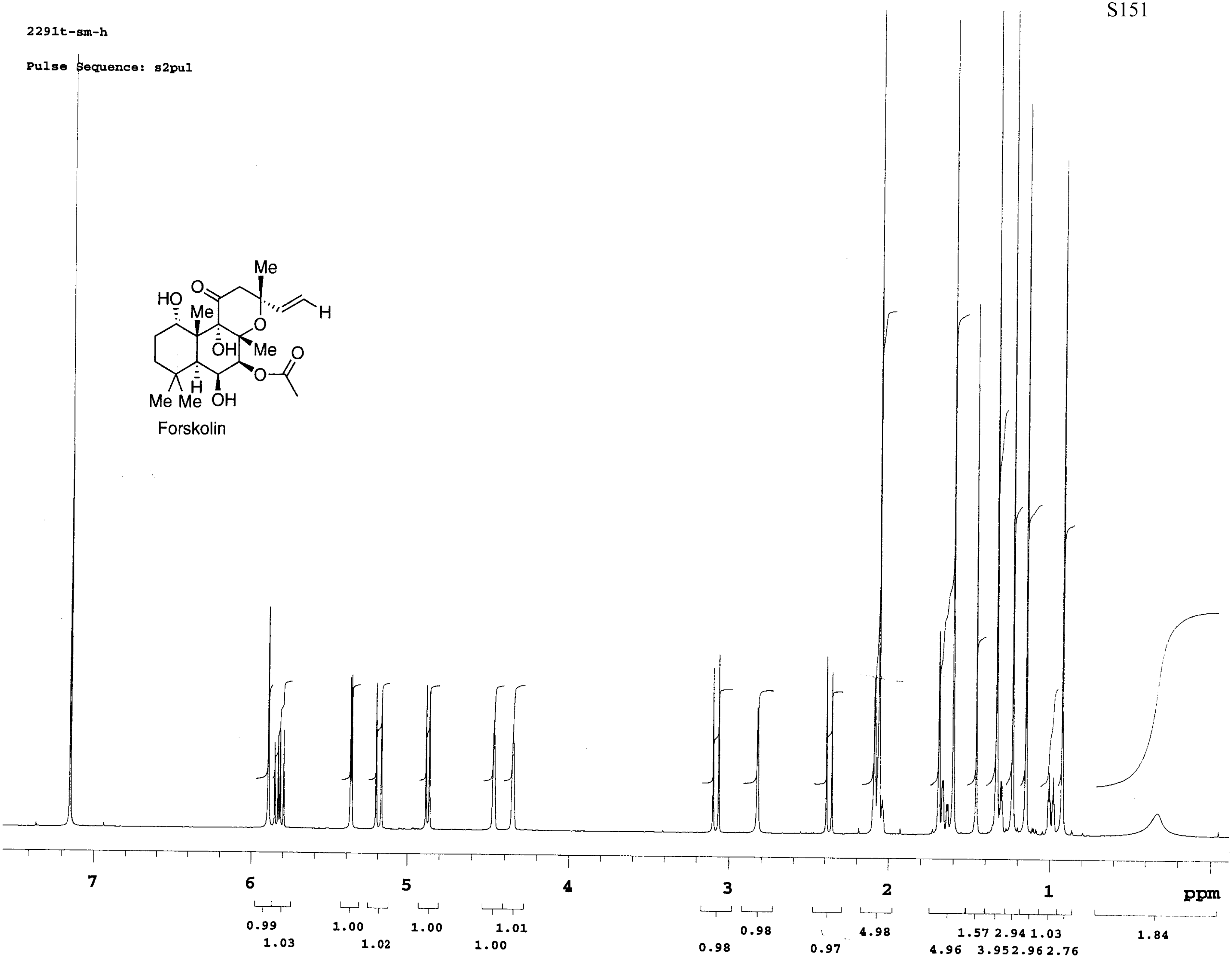

3070sm-h
Pulse Sequence: s2pul
Me
OH
H
H
H
H
H
H
H
O
Altrenogest
7
6
5
4
3
2
1
ppm
1.00
1.01
1.03
1.00
1.01
1.01
5.12
4.14
2.06
1.03
1.04
1.05
1.04
1.08
4.07

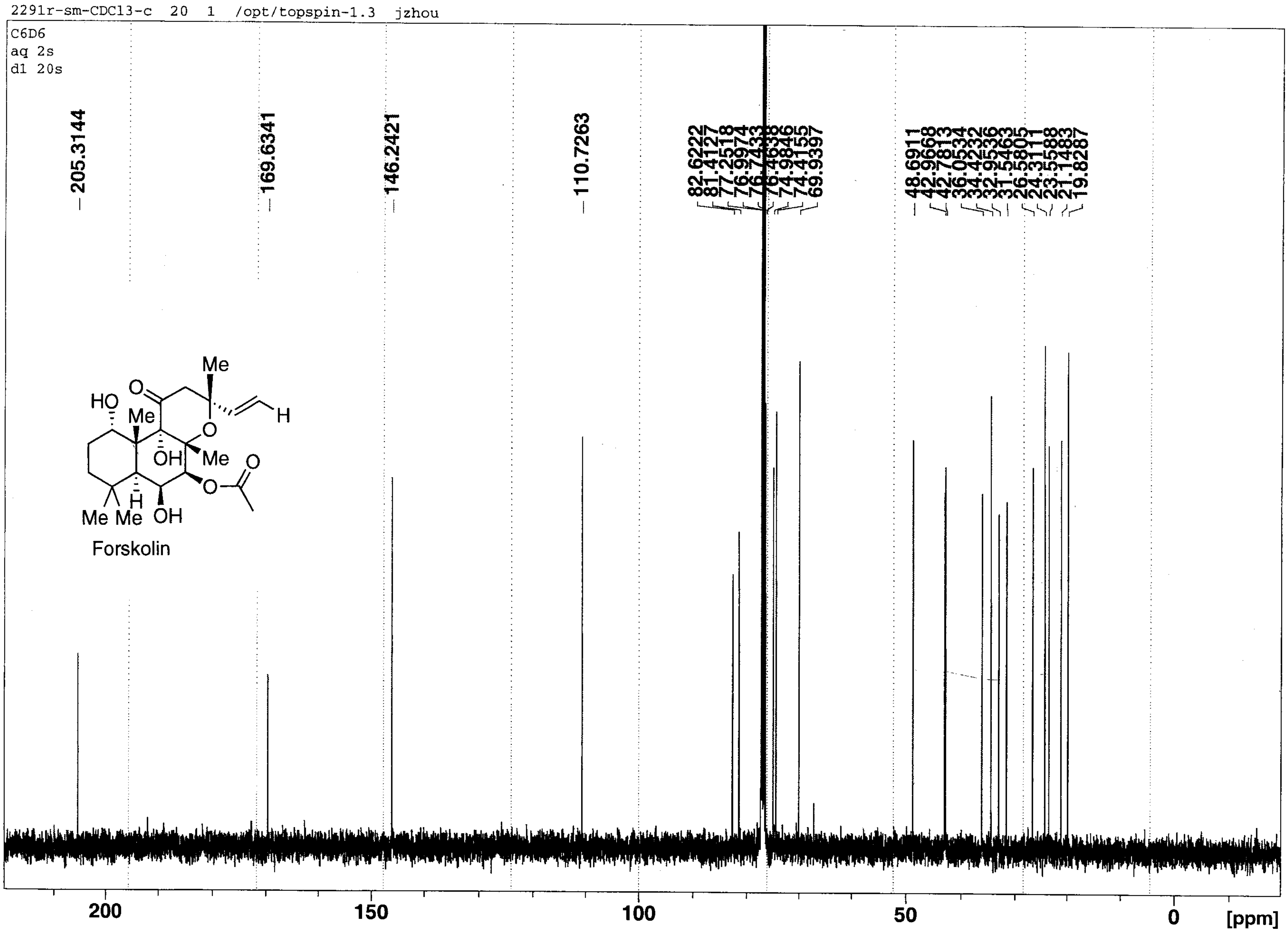

3070sm-c
Pulse Sequence: s2pul
Altrenogest
Me
OH
197.430
155.051
141.313
141.284
134.953
128.293
128.191
128.000
127.905
127.809
127.348
124.329
124.219
118.856
81.093
49.302
48.129
43.220
38.311
36.934
35.014
31.329
27.225
24.478
23.196
16.946
220
200
180
160
140
120
100
80
60
40
20
ppm


3070pu-h
Pulse Sequence: s2pul
D 66
Me OH
D 91
D 50
4 D
D
H
H
O
Altrenogest
(rt, 20 h)
7
6
5
4
3
2
1
ppm
1.05 0.50
0.99 0.99
0.09
0.34
2.06 4.18 1.01 1.16 1.37
2.91 1.10 2.21 1.24 4.61


3070pu-d
Pulse Sequence: s2pul
7.305
7.150
6.995
5.018
D 66
D 91
D 50
4 D
D
Me
OH
H
H
O
Altrenogest
(rt, 20 h)
9
8
7
6
5
4
3
2
1
ppm
0.46
1.00
0.06

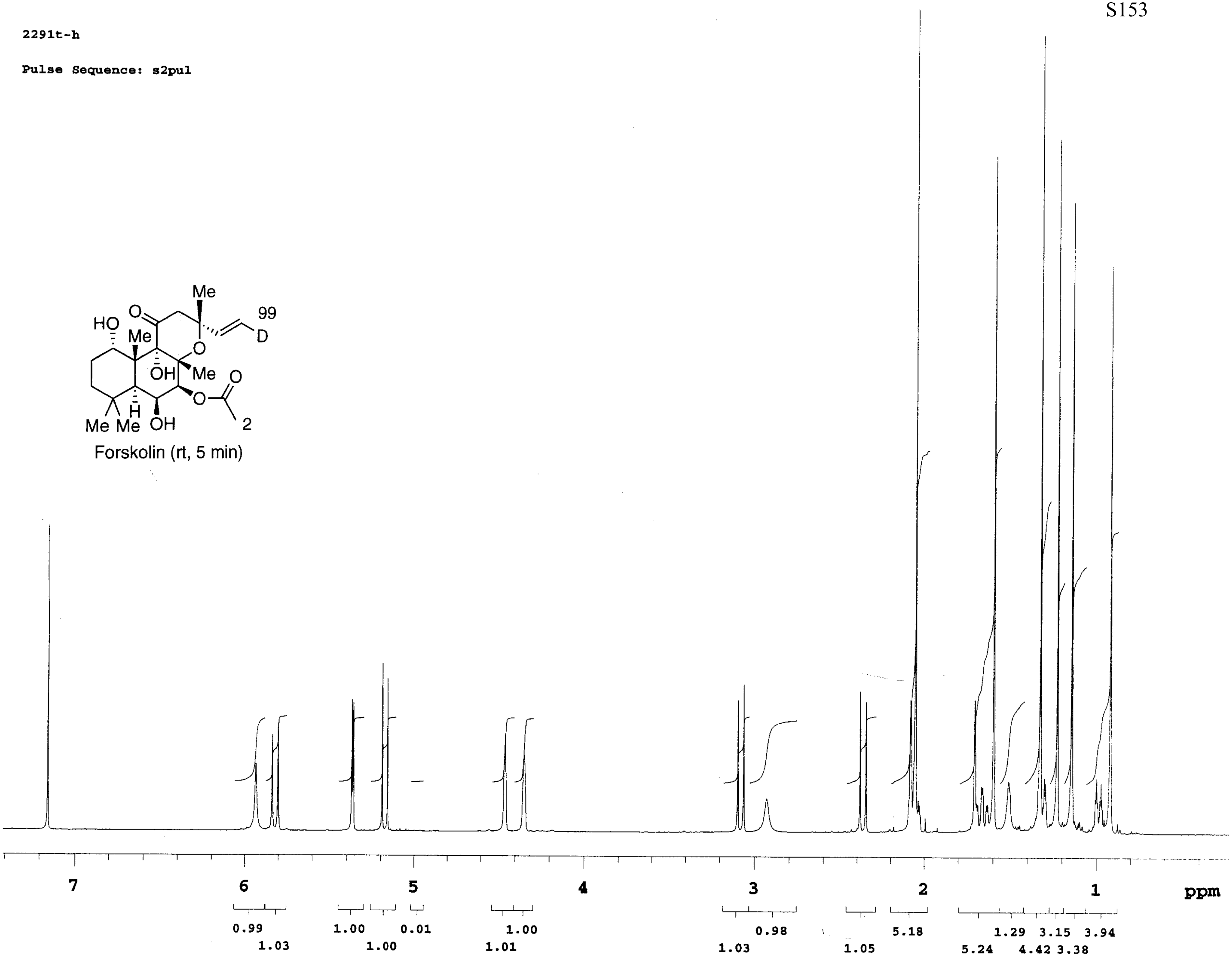

3070pu-c
Pulse Sequence: s2pul
D 66
D 91
D 50
4 D
D
Me
OH
H
H
O
Altrenogest
(rt, 20 h)
197.291
154.875
141.166
141.115
134.704
134.594
134.470
134.279
128.293
128.191
128.000
127.912
127.809
127.626
127.414
124.402
124.227
81.034
49.250
48.107
43.132
42.964
38.296
36.934
35.087
31.314
27.233
24.500
24.405
23.181
16.895
220
200
180
160
140
120
100
80
60
40
20
ppm


2291t-sm-h
Pulse Sequence: s2pul
HO
O
Me
Me
H
O
OH
Me
O
H
OH
Me Me
Forskolin
7
6
5
4
3
2
1
ppm
0.99
1.03
1.00
1.02
1.00
1.00
1.01
0.98
0.98
0.97
4.98
1.57 2.94 1.03
4.96 3.95 2.96 2.76
1.84


2291r-sm-CDCl3-c 20 1 /opt/topspin-1.3 jzhou
C6D6
aq 2s
d1 20s
205.3144
169.6341
146.2421
110.7263
82.6222
81.4127
77.2518
76.9974
76.7433
76.4638
74.9846
74.4155
69.9397
48.6911
42.9668
42.7813
36.0534
34.4232
32.9536
31.5463
26.5805
24.3111
23.5588
21.1483
19.8287
Me
O
HO
Me
H
O
OH
Me
O
O
H
Me Me OH
Forskolin
200
150
100
50
0
[ppm]

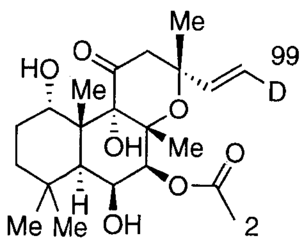
2291t-h

Pulse Sequence: s2pul

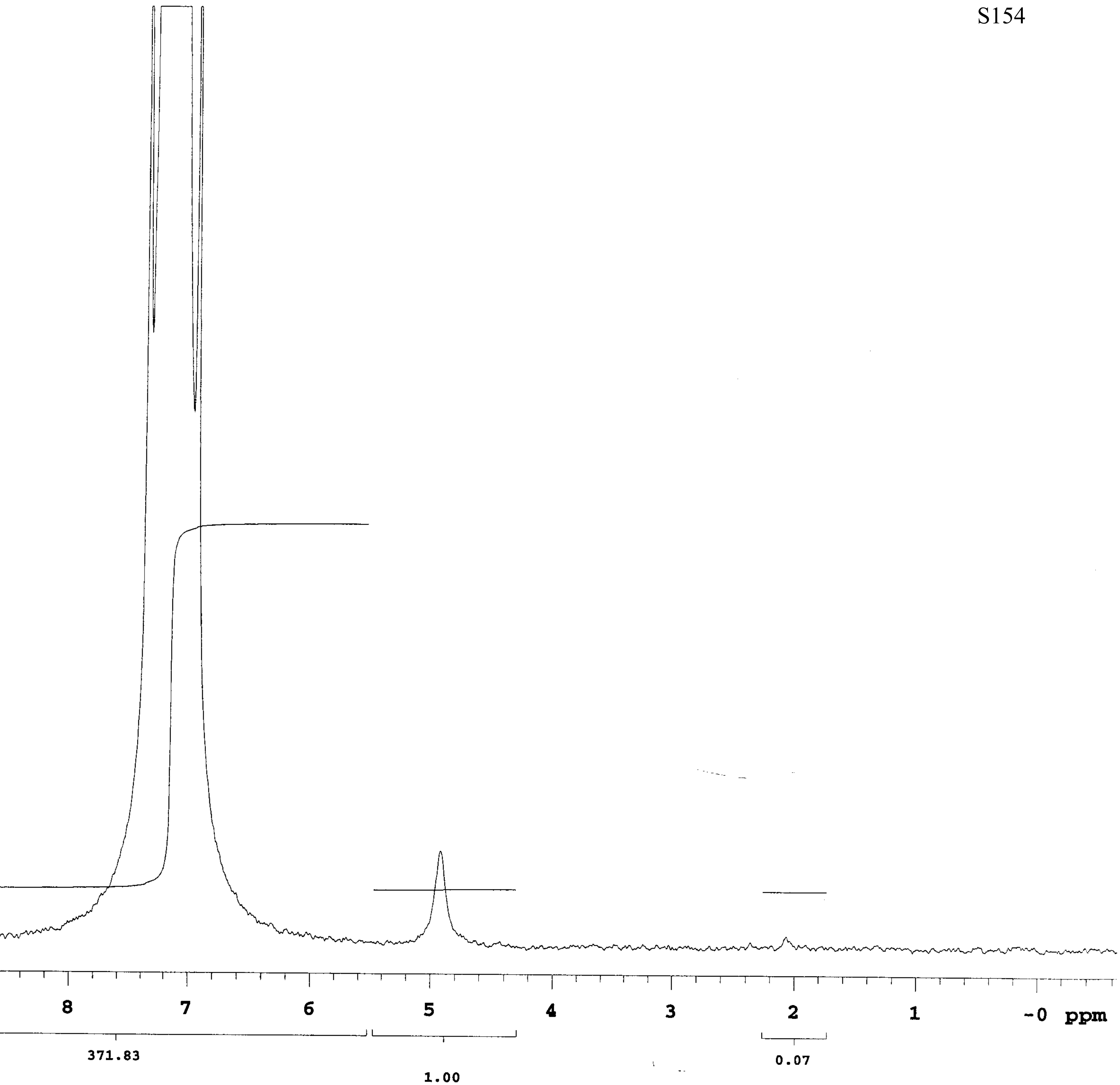


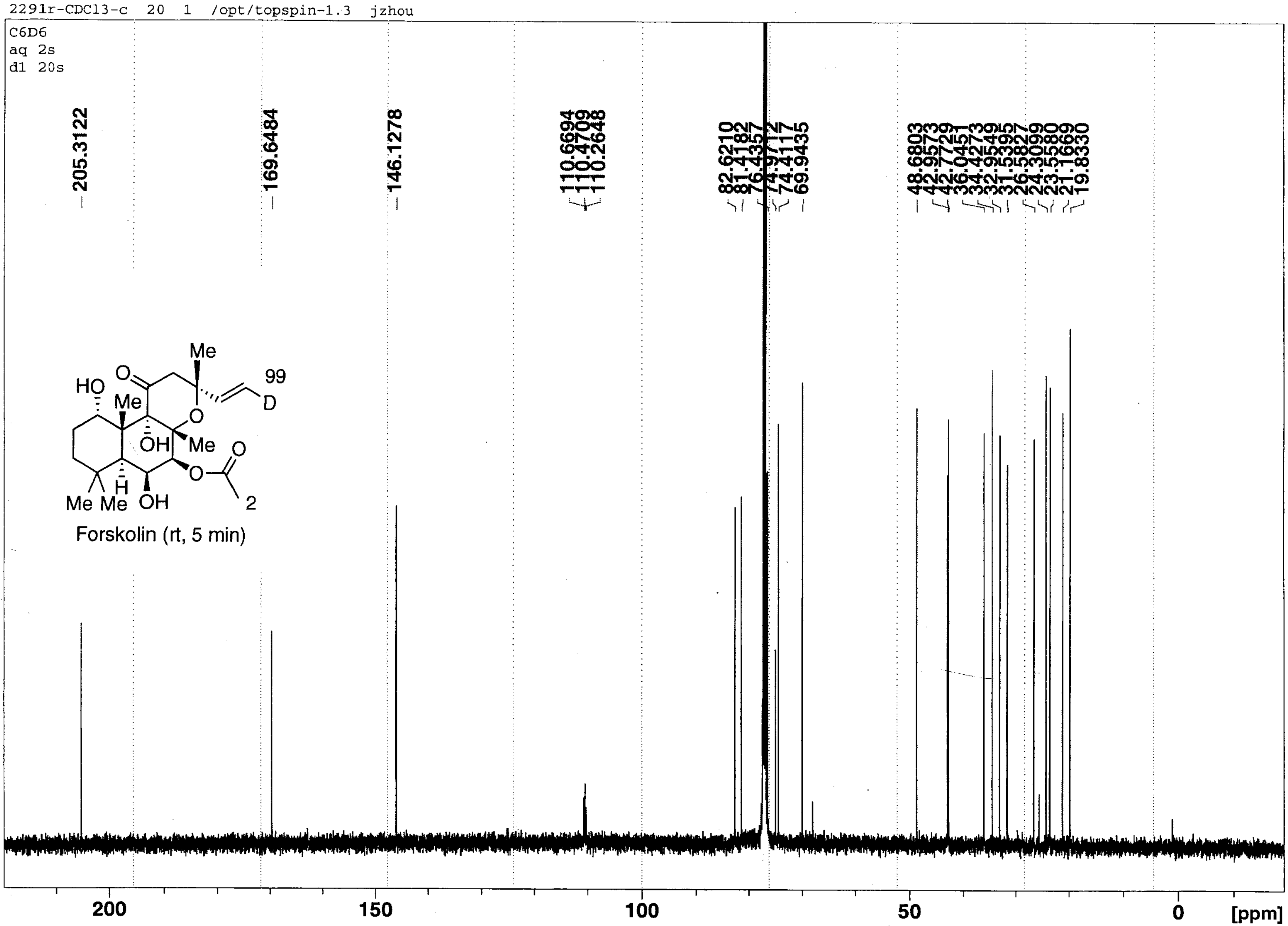
2291t-d

Pulse Sequence: s2pul



Forskolin (rt, 5 min)

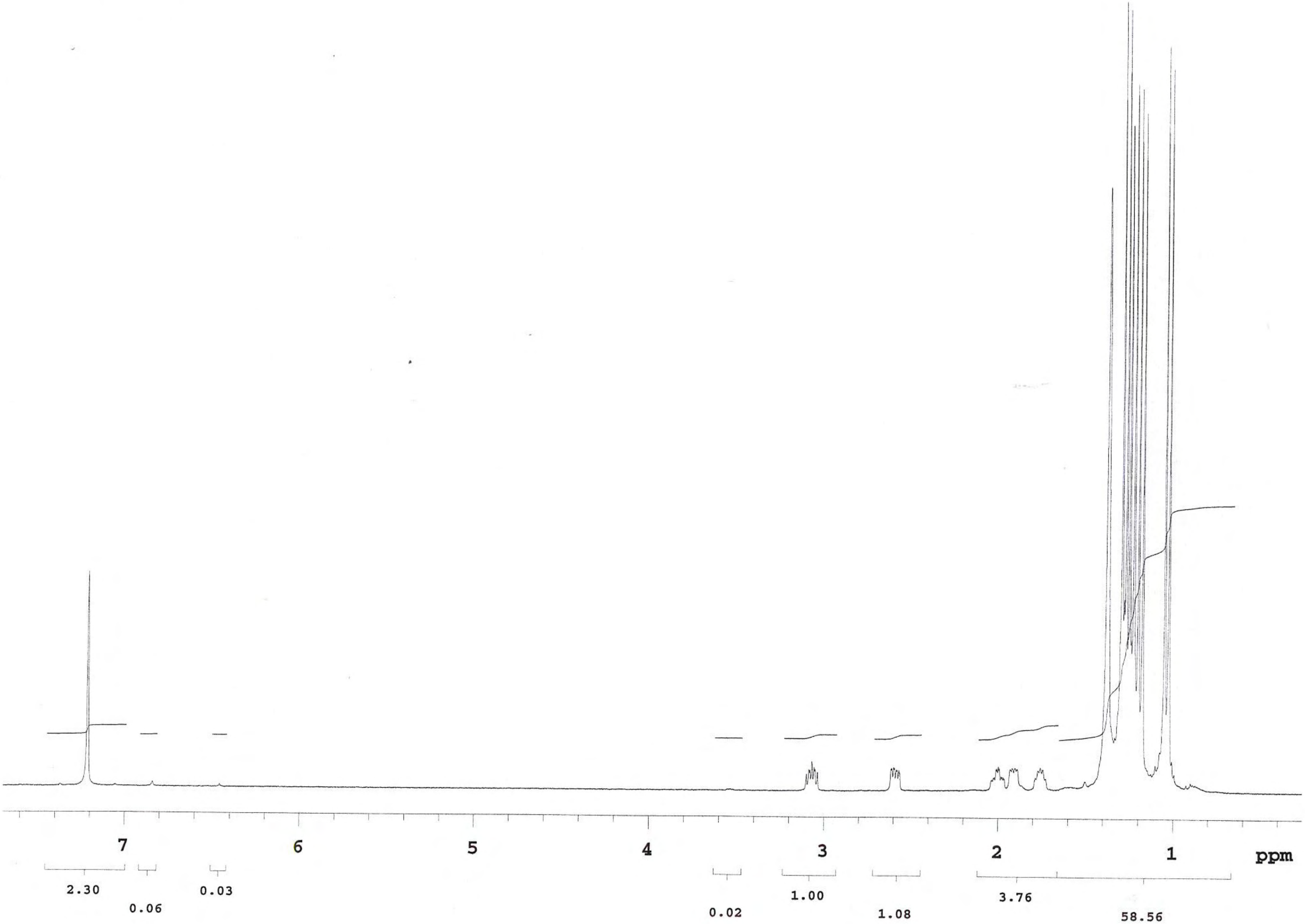


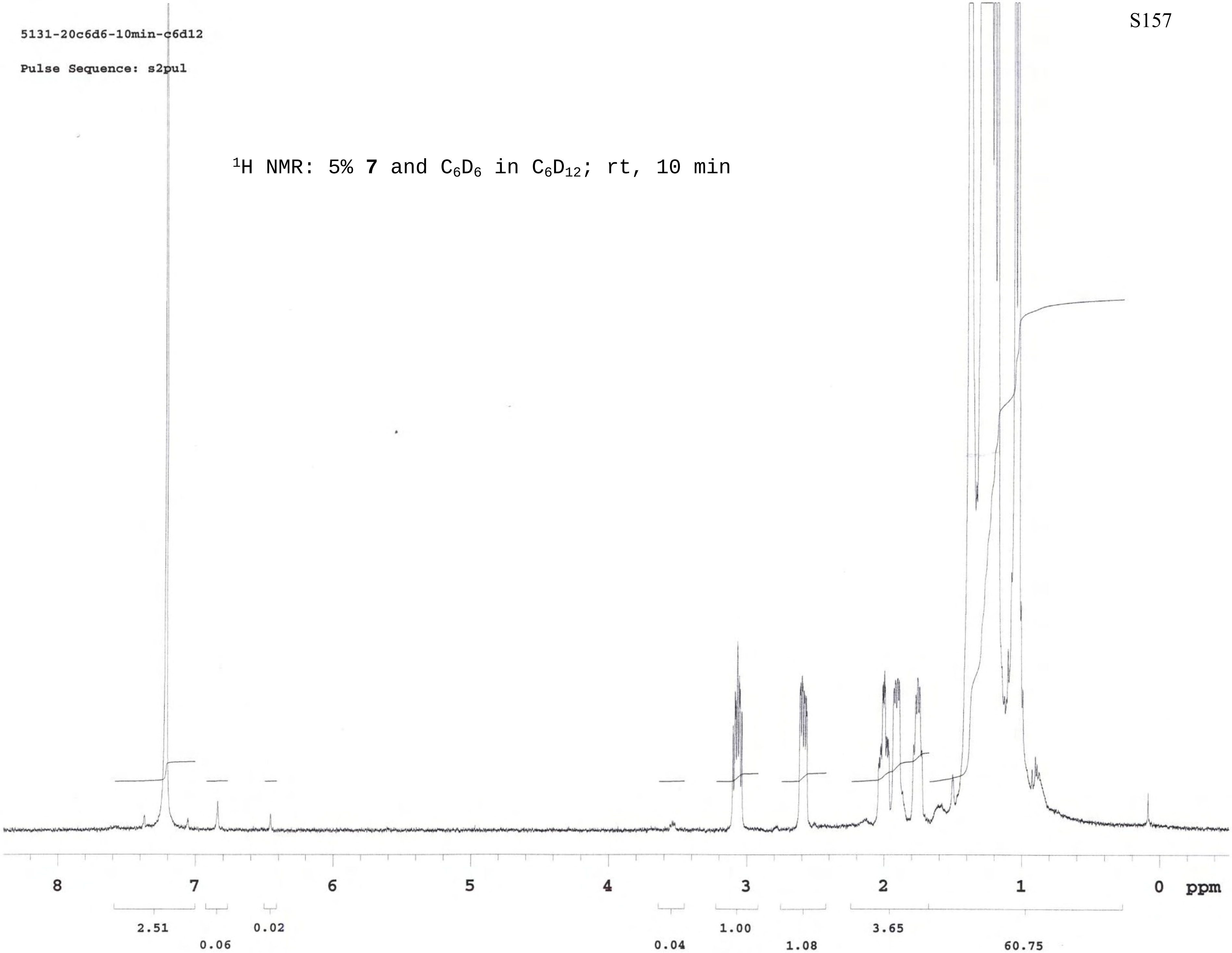

2291r-CDCl3-c 20 1 /opt/topspin-1.3 jzhou
C6D6
aq 2s
d1 20s
205.3122
169.6484
146.1278
110.6694
110.4709
110.2648
82.6210
81.4182
76.4357
74.9712
74.4117
69.9435
48.6803
42.9573
42.7729
36.0451
34.4273
32.9549
31.5395
26.5827
24.3099
23.5580
21.1669
19.8330
Me
O
HO
Me
99
D
O
OH
Me
O
O
H
Me Me
OH
2
Forskolin (rt, 5 min)
200
150
100
50
0
[ppm]

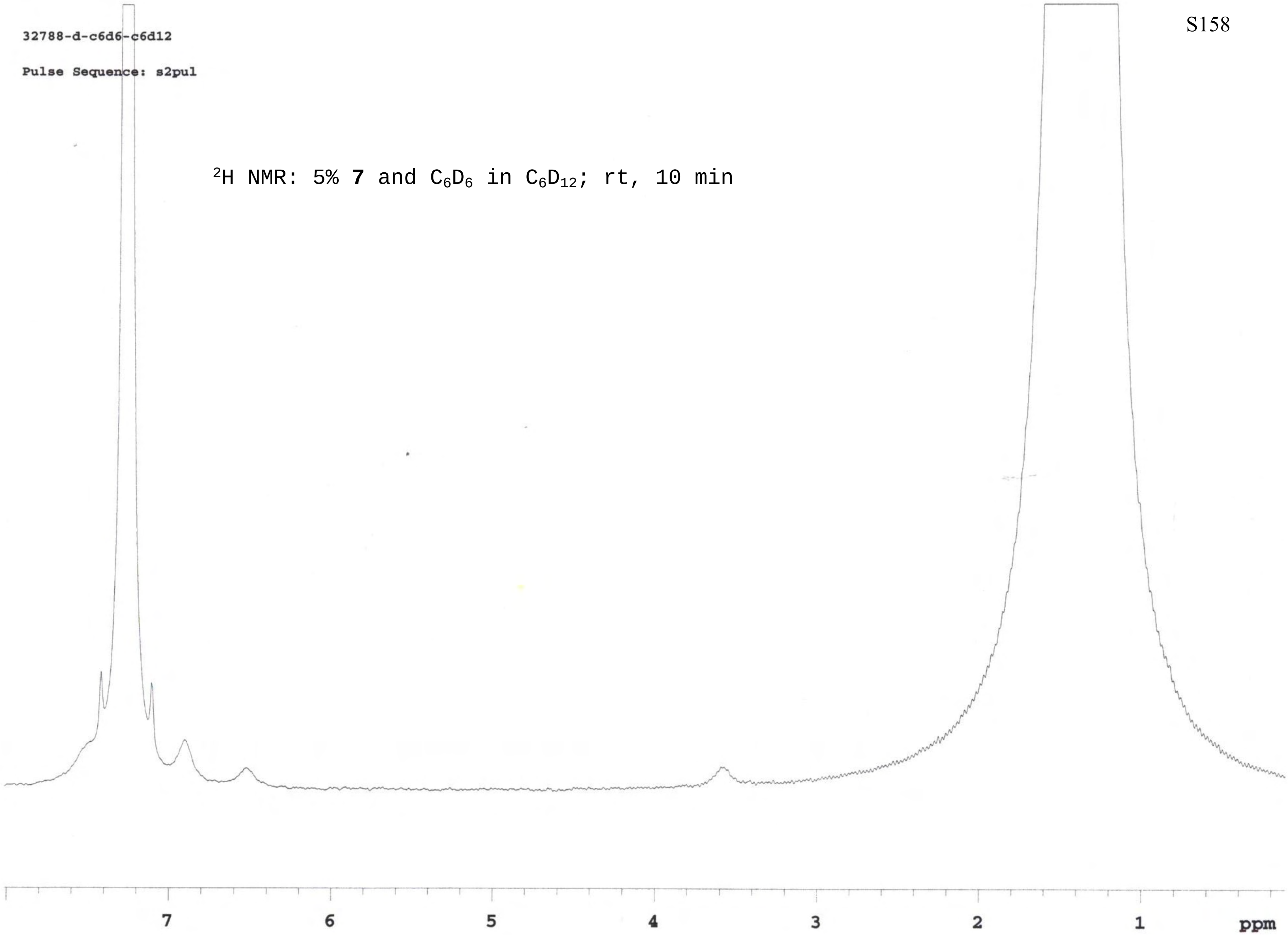
5131-5min-c6d6-c6d12

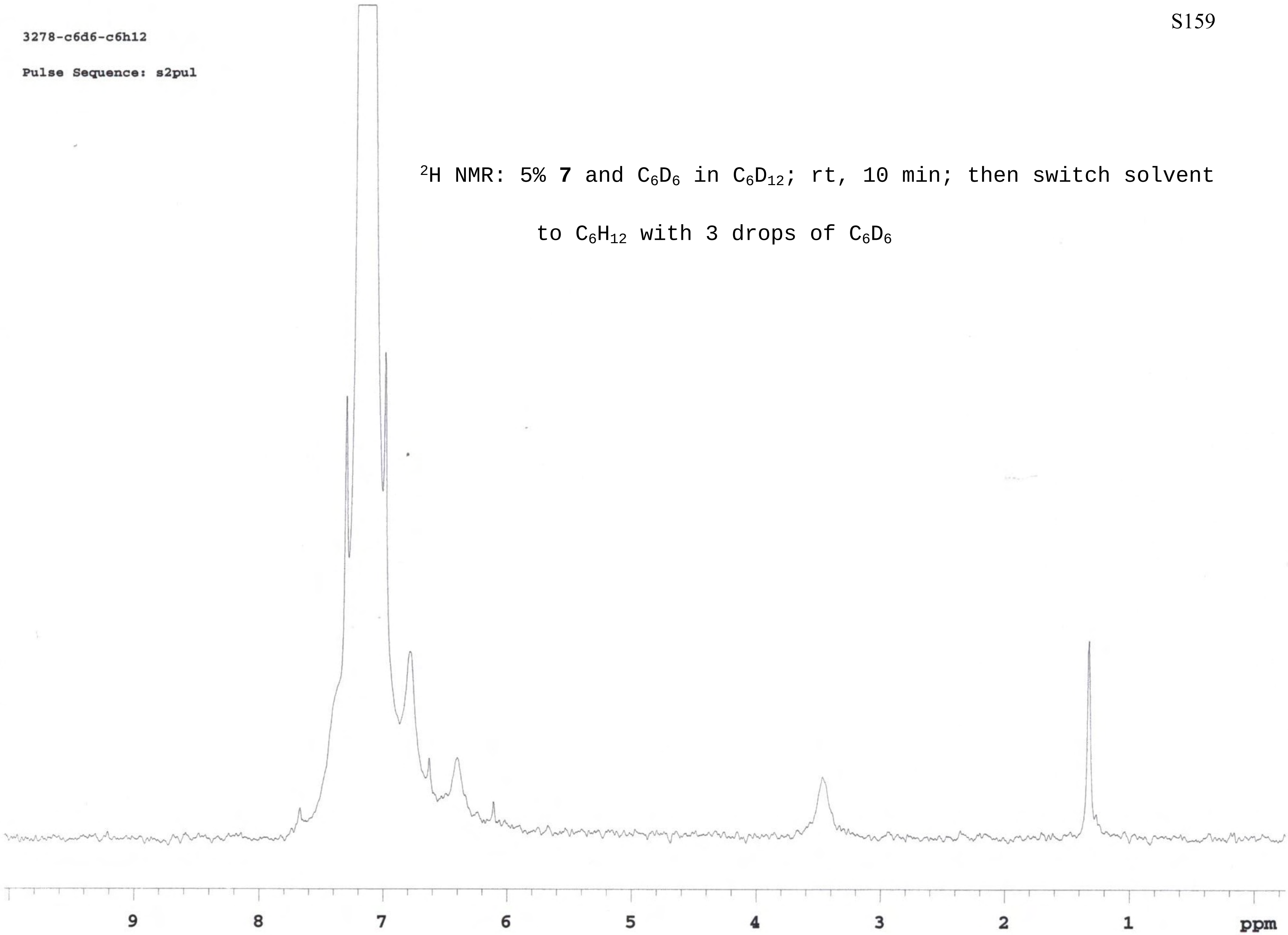
Pulse Sequence: s2pul

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




5131-20c6d6-10min-c6d12
Pulse Sequence: s2pul
^1H NMR: 5% **7** and C_6D_6 in C_6D_{12}; rt, 10 min
8
7
6
5
4
3
2
1
0
ppm
2.51
0.06
0.02
0.04
1.00
1.08
3.65
60.75


32788-d-c6d6-c6d12
Pulse Sequence: s2pul
^{2}H NMR: 5% **7** and C_6D_6 in C_6D_{12}; rt, 10 min
7
6
5
4
3
2
1
ppm

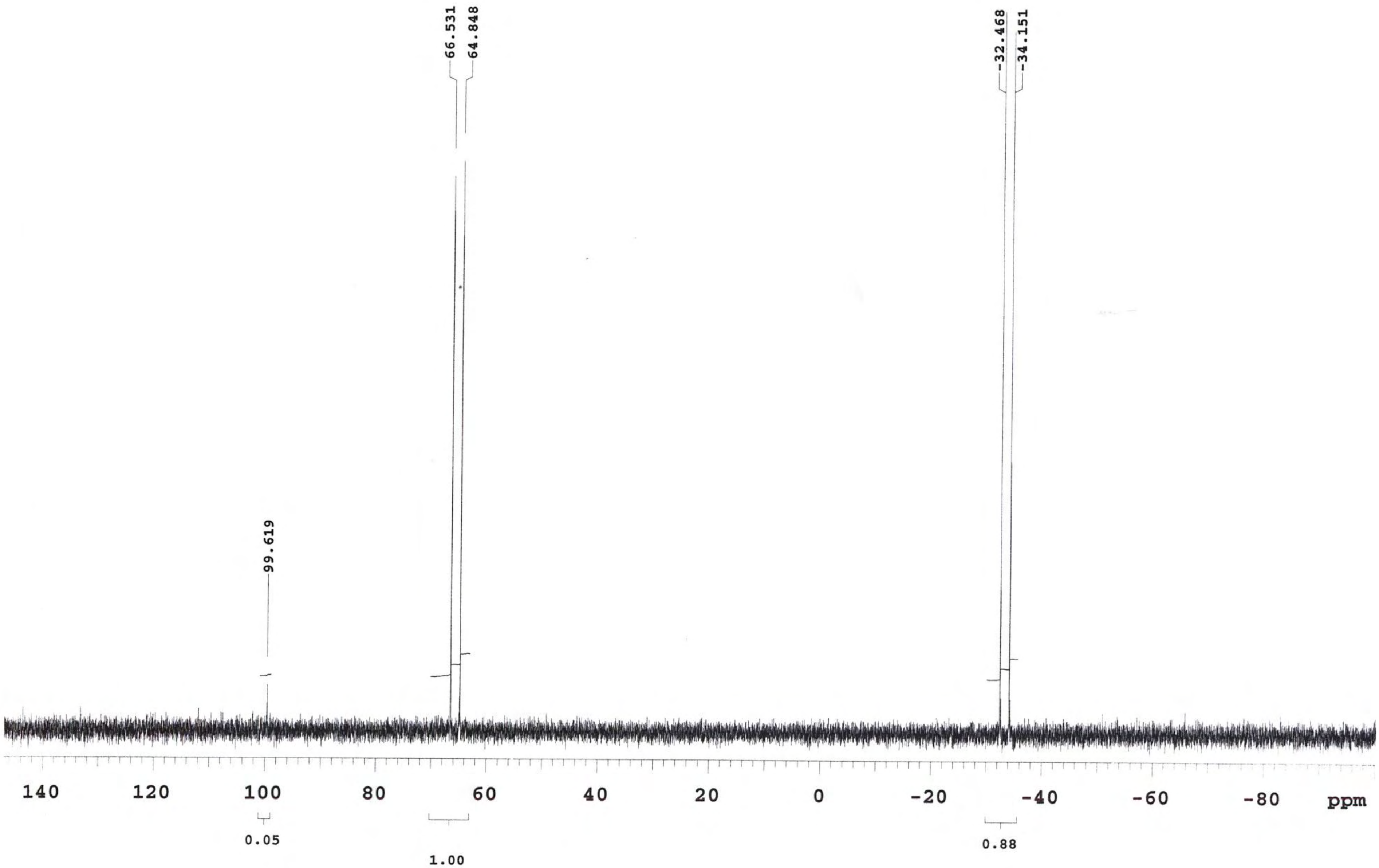


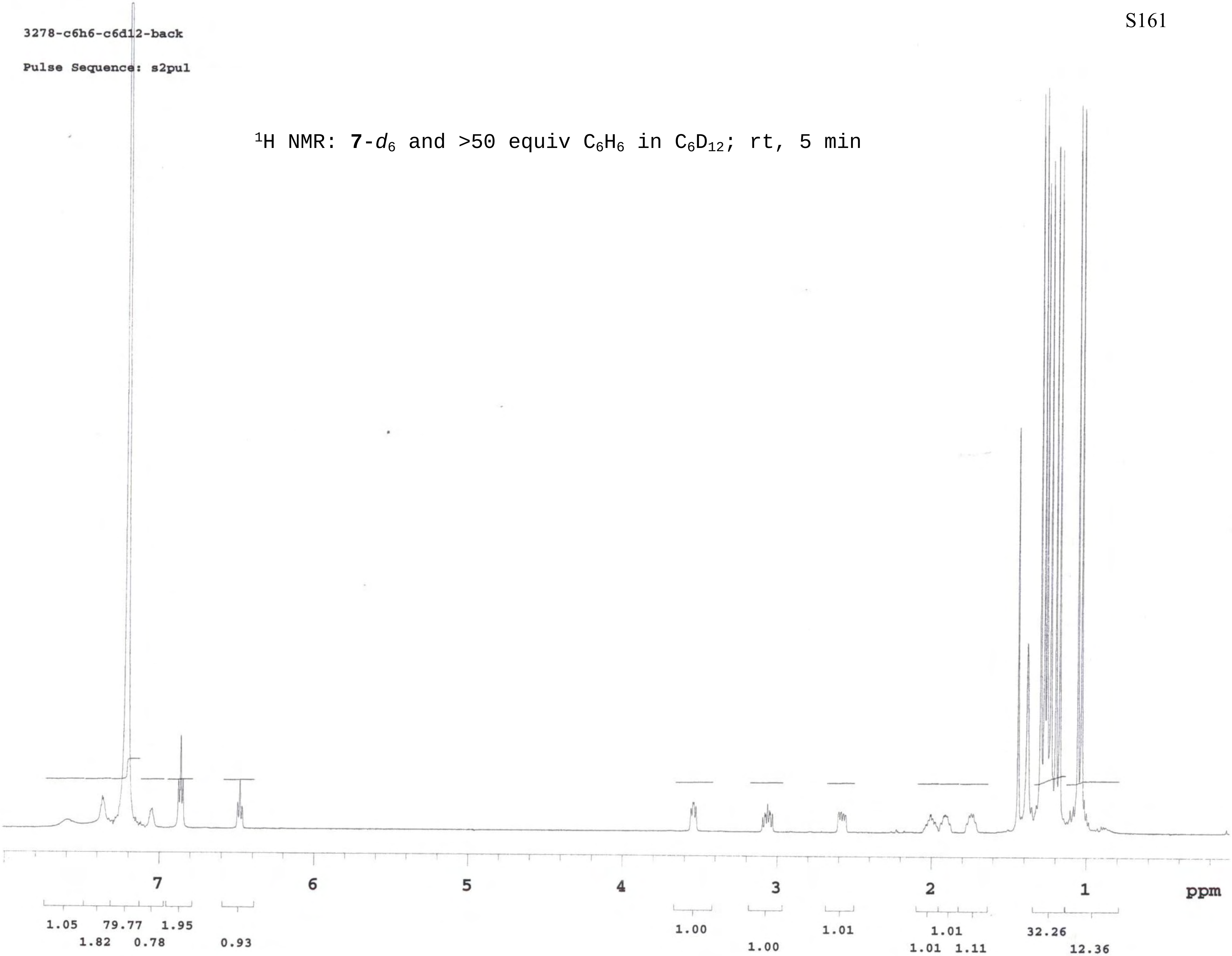
^2H NMR: 5% **7** and C_6D_6 in C_6D_{12}; rt, 10 min; then switch solvent to C_6H_{12} with 3 drops of C_6D_6

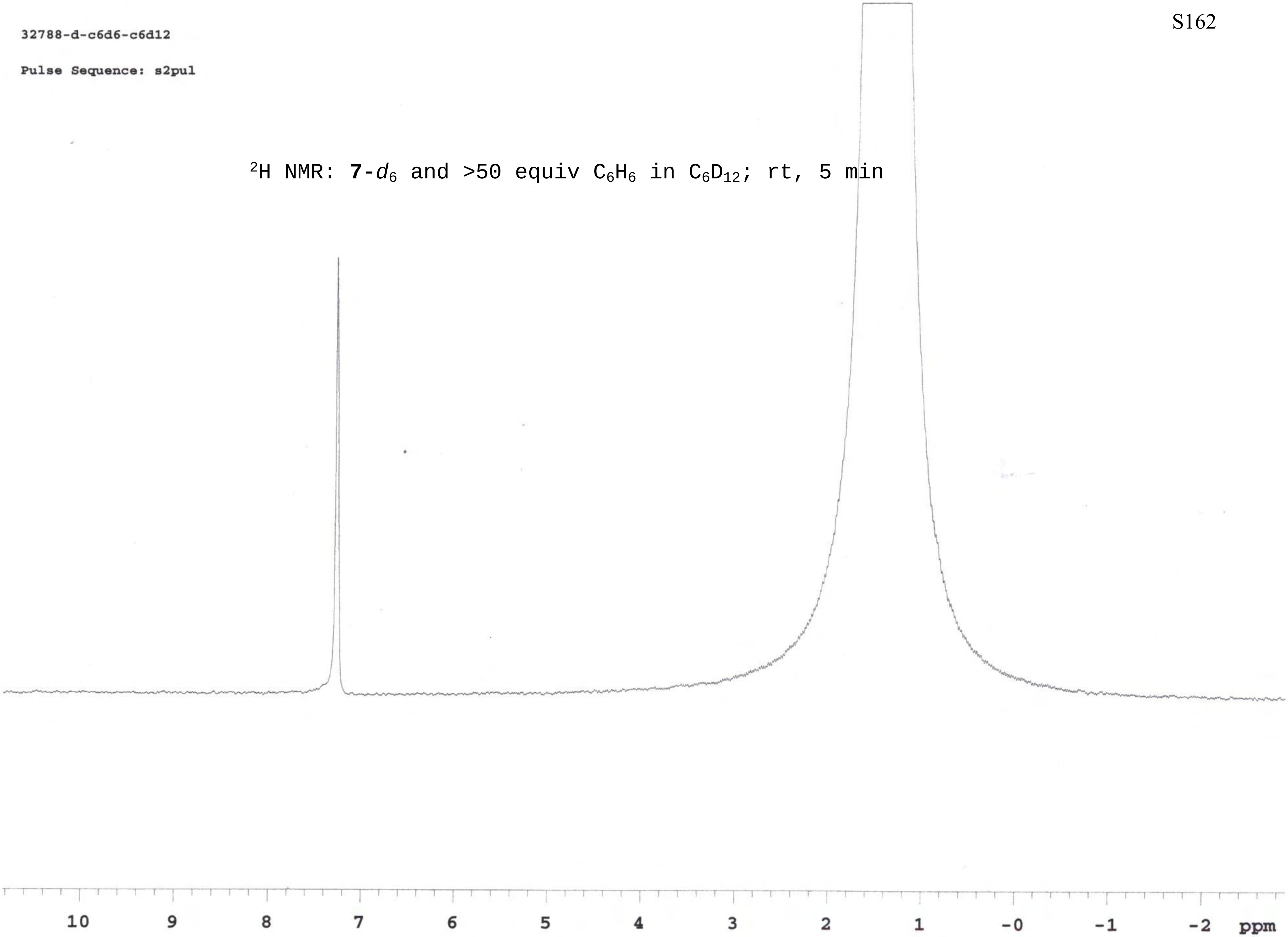
3278-c6d6-30min-c6d12

Pulse Sequence: s2pul

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



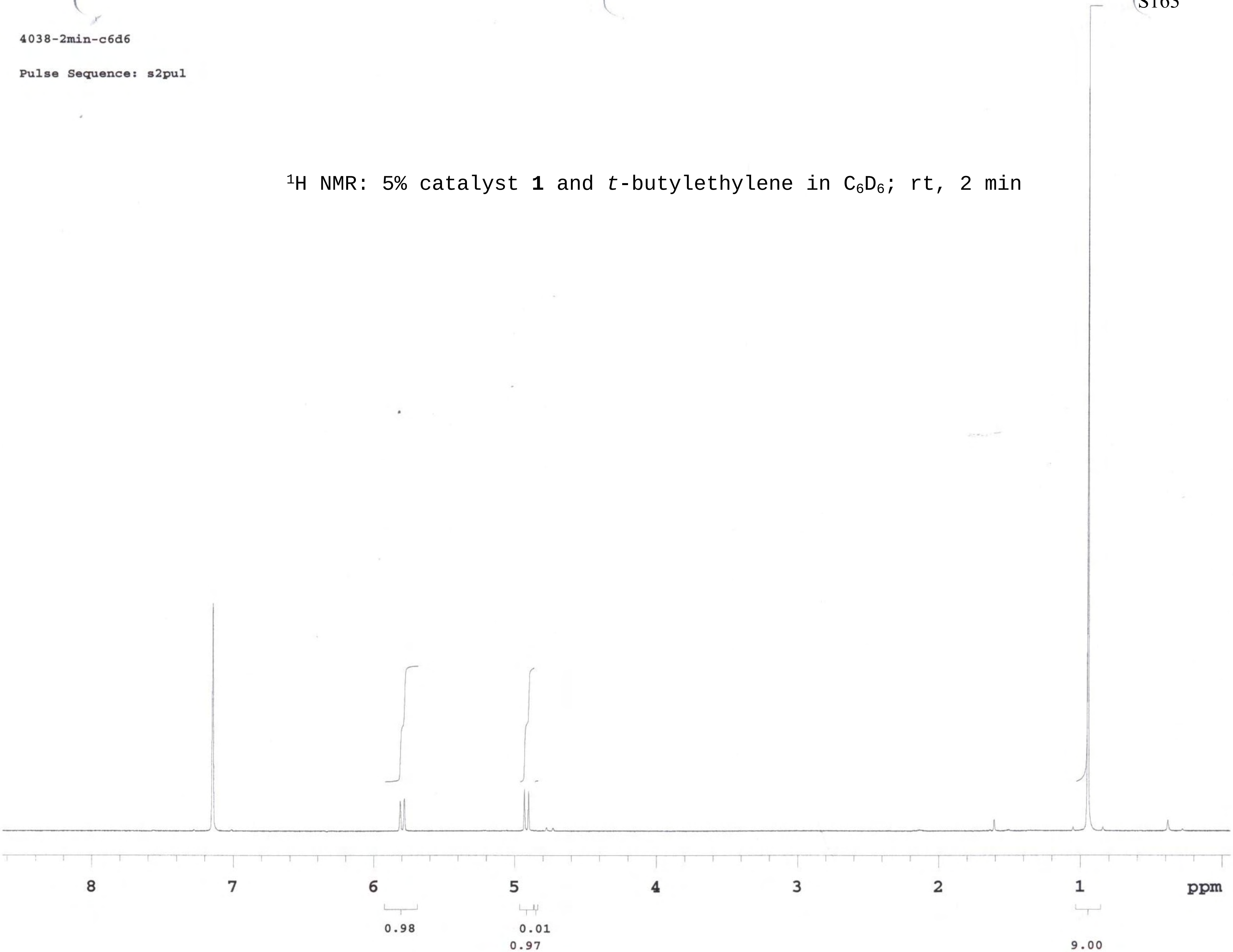

3278-c6h6-c6d12-back
Pulse Sequence: s2pul
^{1}H NMR: **7**-d_6 and >50 equiv C_6H_6 in C_6D_{12}; rt, 5 min
7
6
5
4
3
2
1
ppm
1.05
1.82
79.77
0.78
1.95
0.93
1.00
1.00
1.01
1.01
1.01
1.11
32.26
12.36

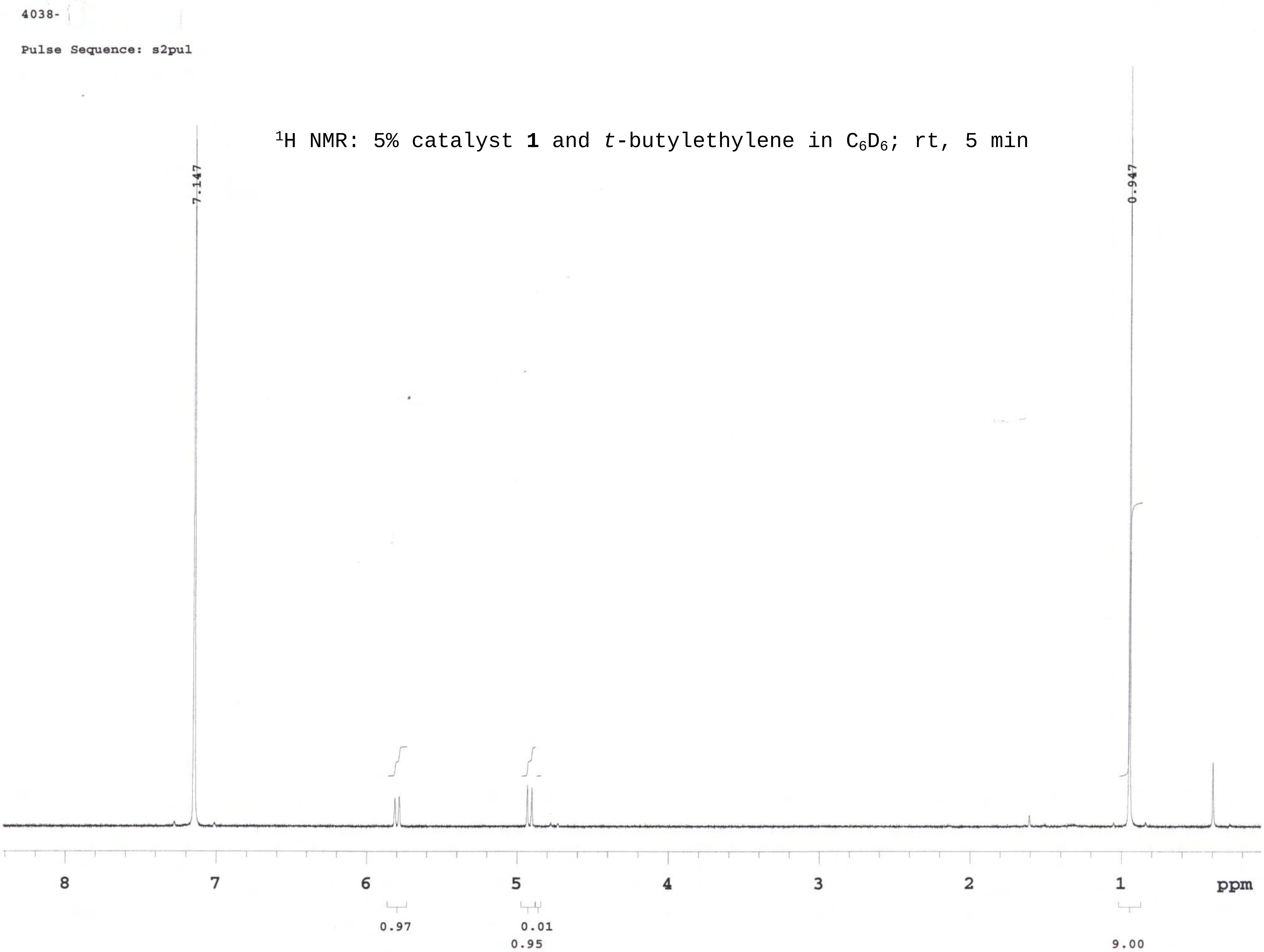

32788-d-c6d6-c6d12
Pulse Sequence: s2pul
^{2}H NMR: **7**-d_6 and >50 equiv C_6H_6 in C_6D_{12}; rt, 5 min
10
9
8
7
6
5
4
3
2
1
-0
-1
-2
ppm

4038-2min-c6d6

Pulse Sequence: s2pul

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

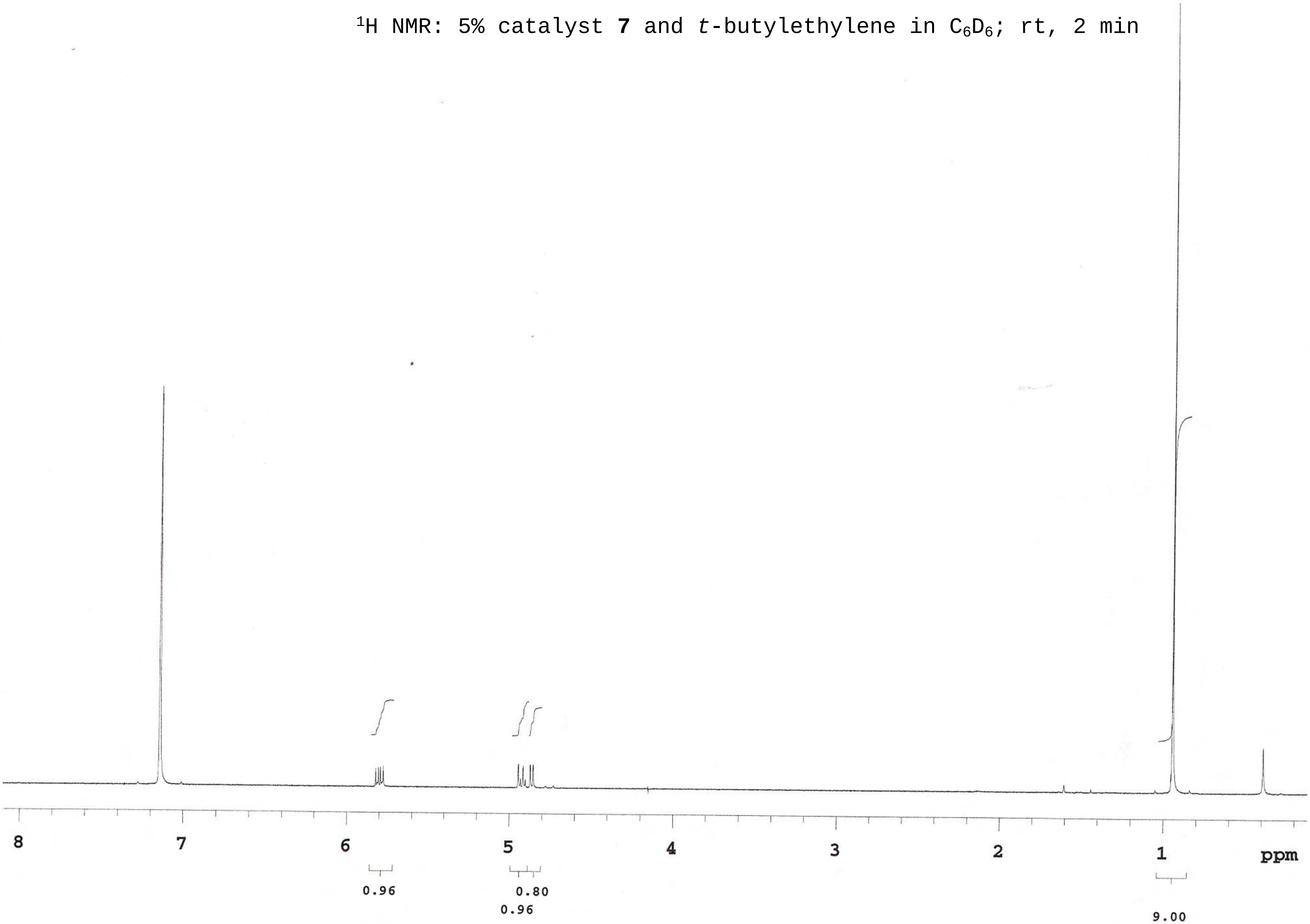



4038-
Pulse Sequence: s2pul
^{1}H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6; rt, 5 min
7.147
0.947
8
7
6
5
4
3
2
1
ppm
0.97
0.01
0.95
9.00

4039-2min

Pulse Sequence: s2pul

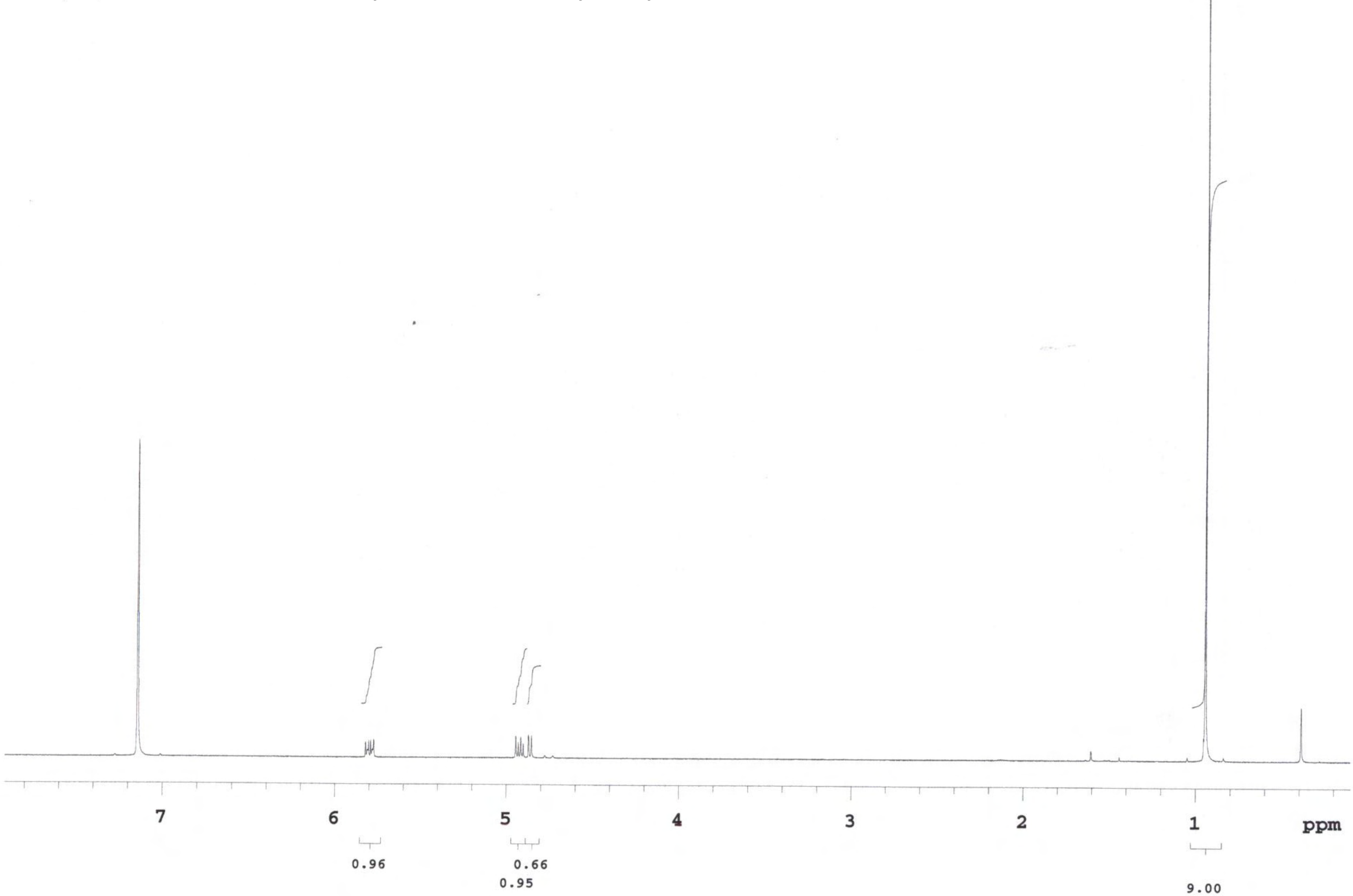
^{1}H NMR: 5% catalyst **7** and *t*-butylethylene in C_6D_6; rt, 2 min



4029-5min

Pulse Sequence: s2pul

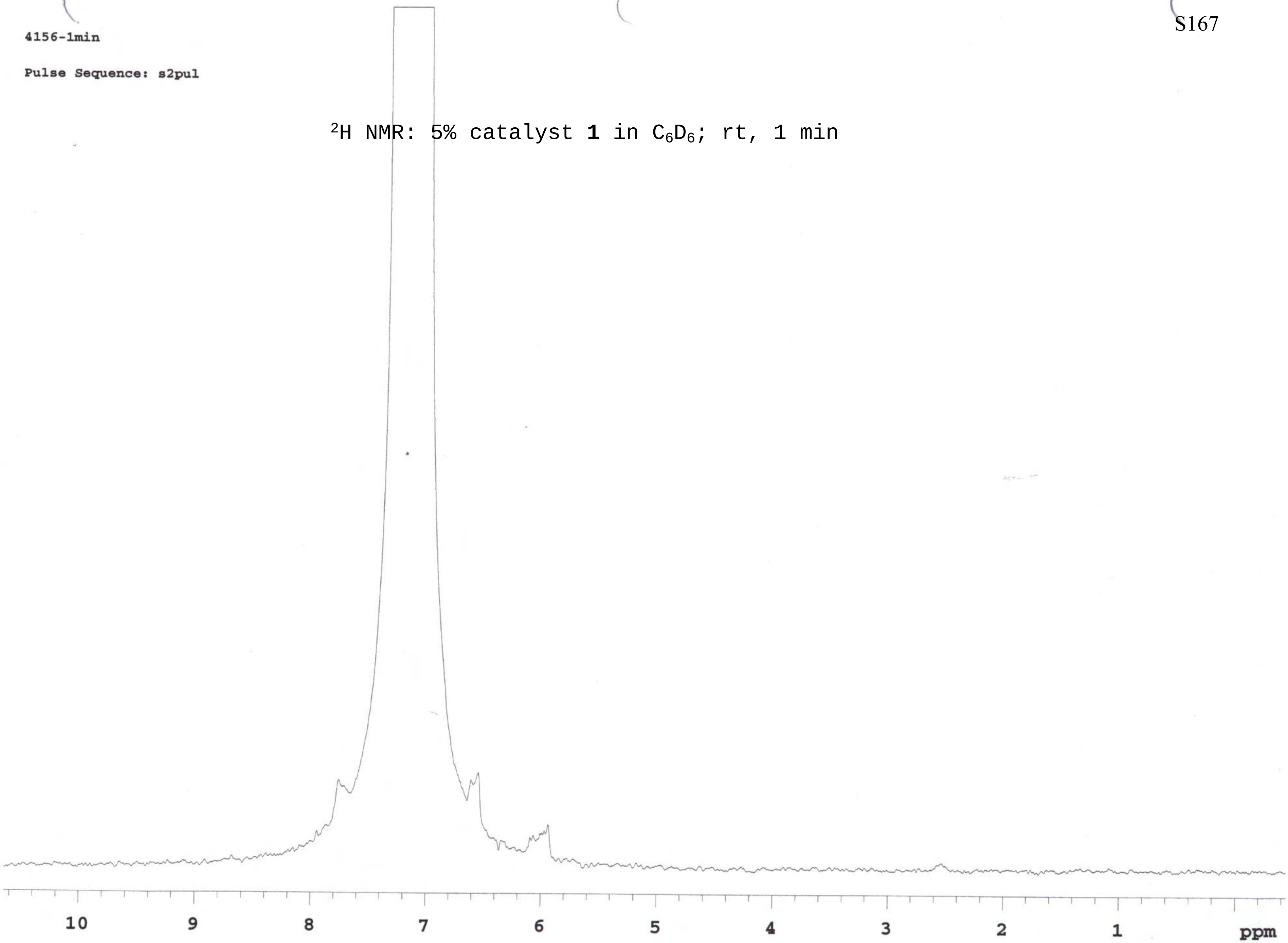
^{1}H NMR: 5% catalyst **7** and *t*-butylethylene in C_6D_6; rt, 5



4156-1min

Pulse Sequence: s2pul

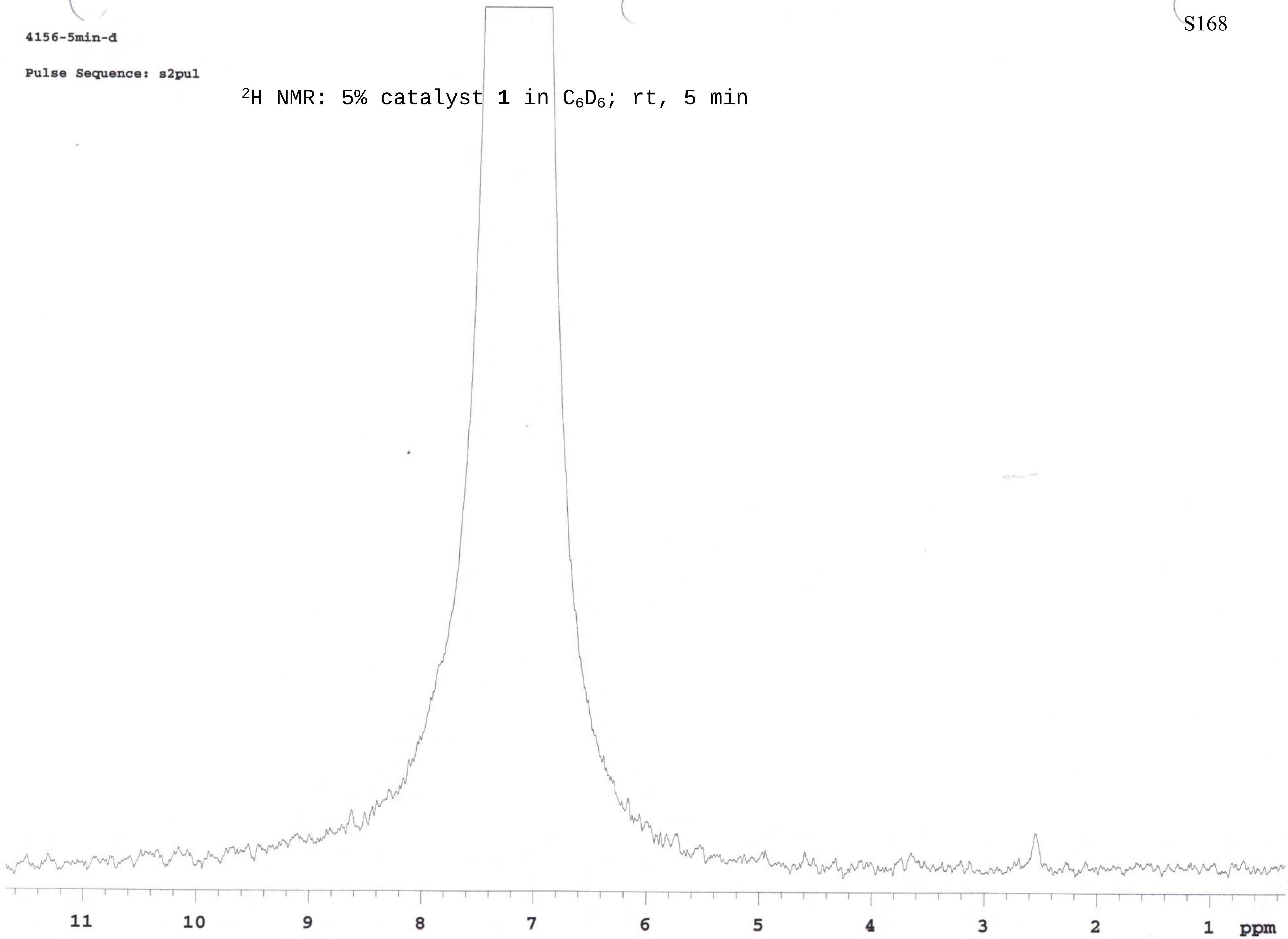
^{2}H NMR: 5% catalyst **1** in C_6D_6; rt, 1 min



4156-5min-d

Pulse Sequence: s2pul

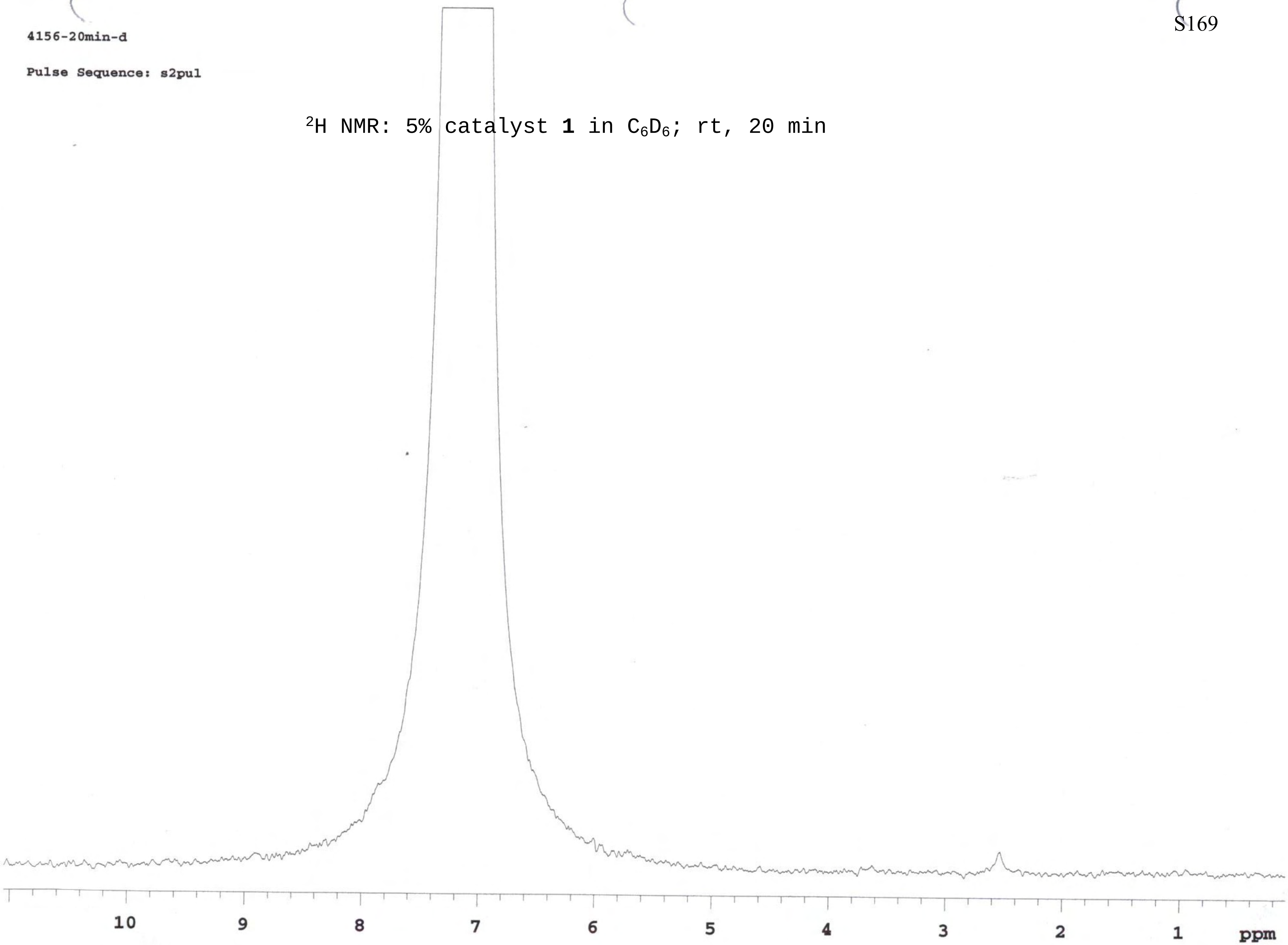
^{2}H NMR: 5% catalyst **1** in C_6D_6; rt, 5 min

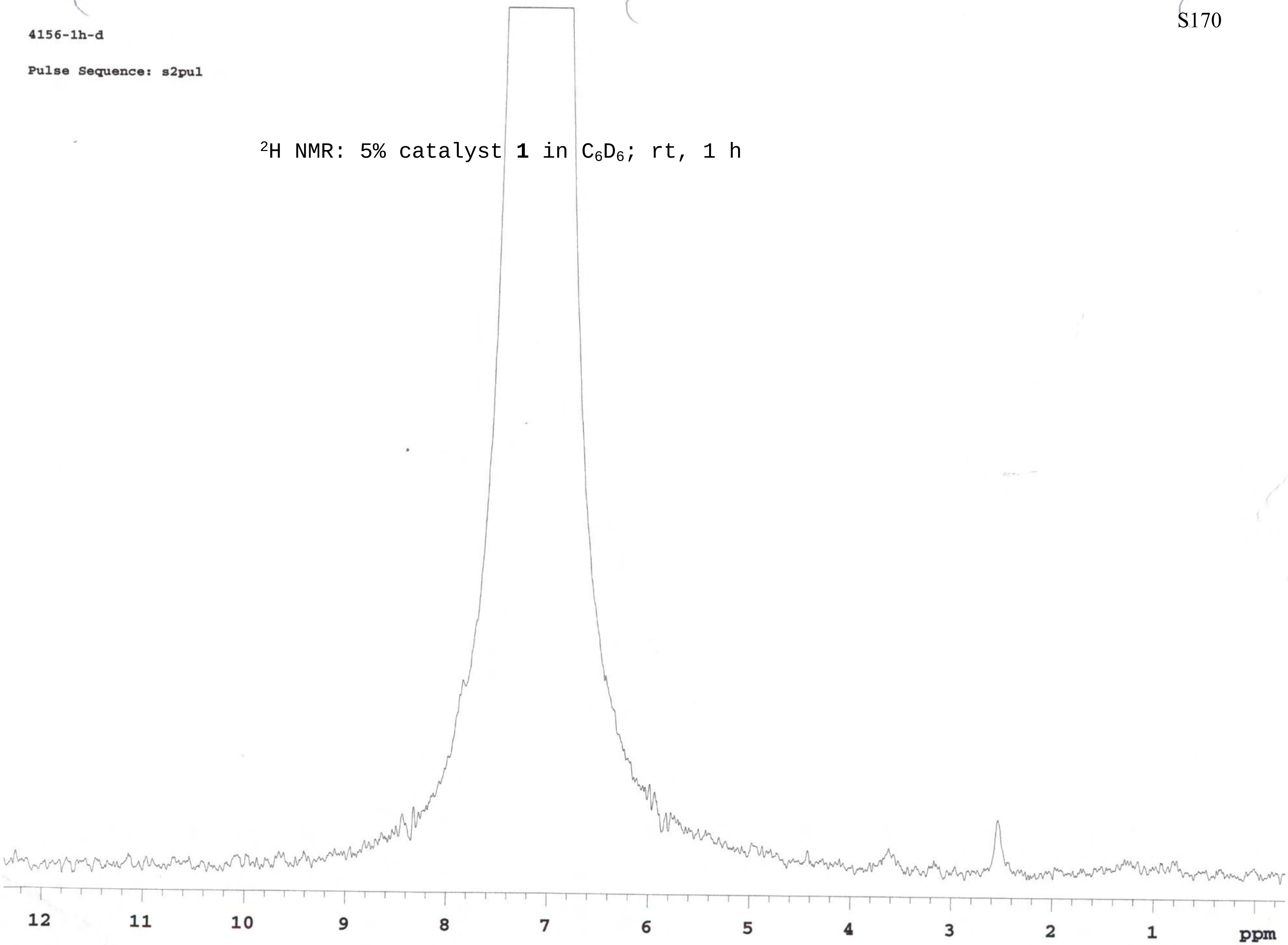


4156-20min-d

Pulse Sequence: s2pul

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

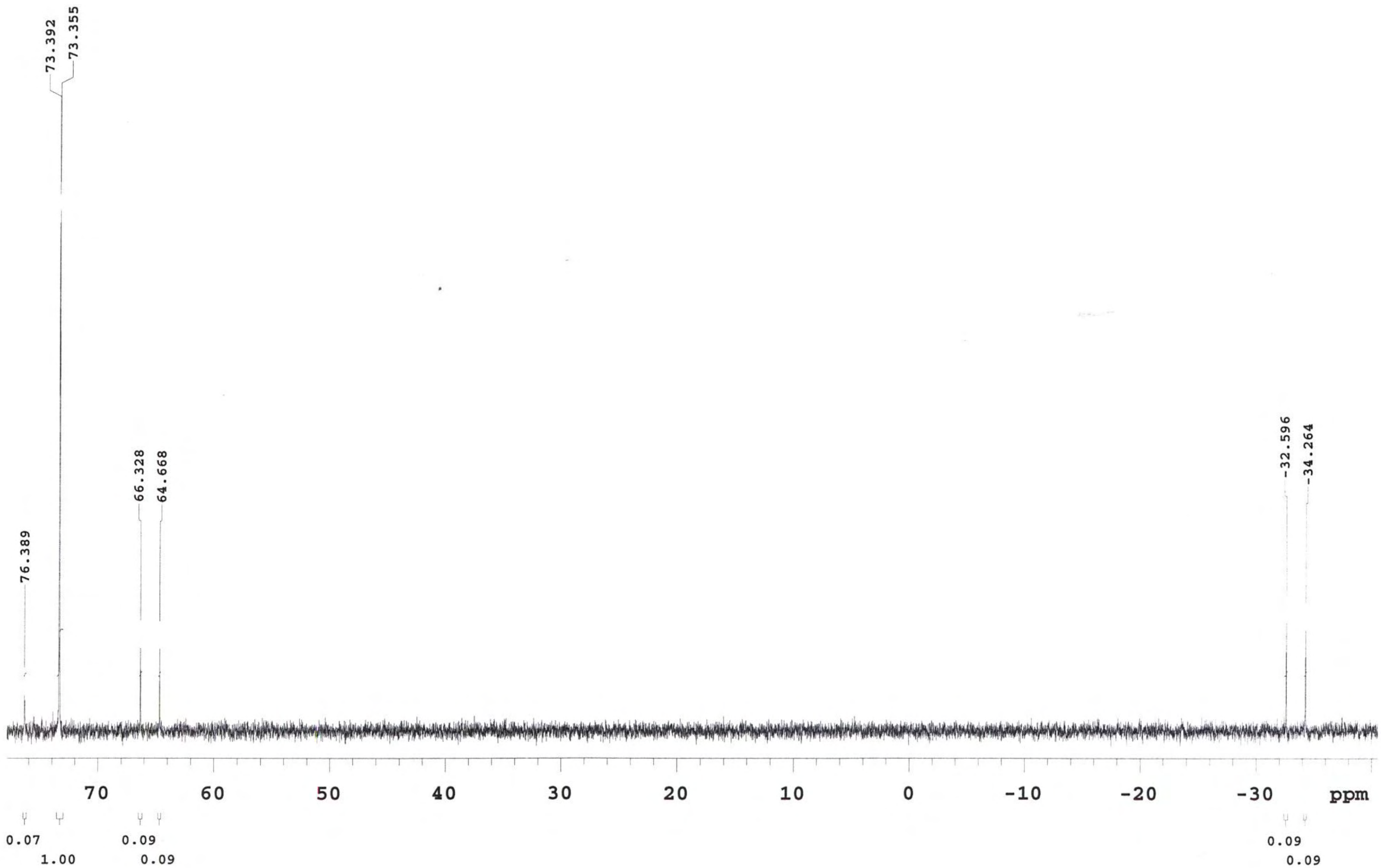



4156-1h-d
Pulse Sequence: s2pul
^{2}H NMR: 5% catalyst **1** in C_6D_6; rt, 1 h
12
11
10
9
8
7
6
5
4
3
2
1
ppm

4156-5min

Pulse Sequence: s2pul

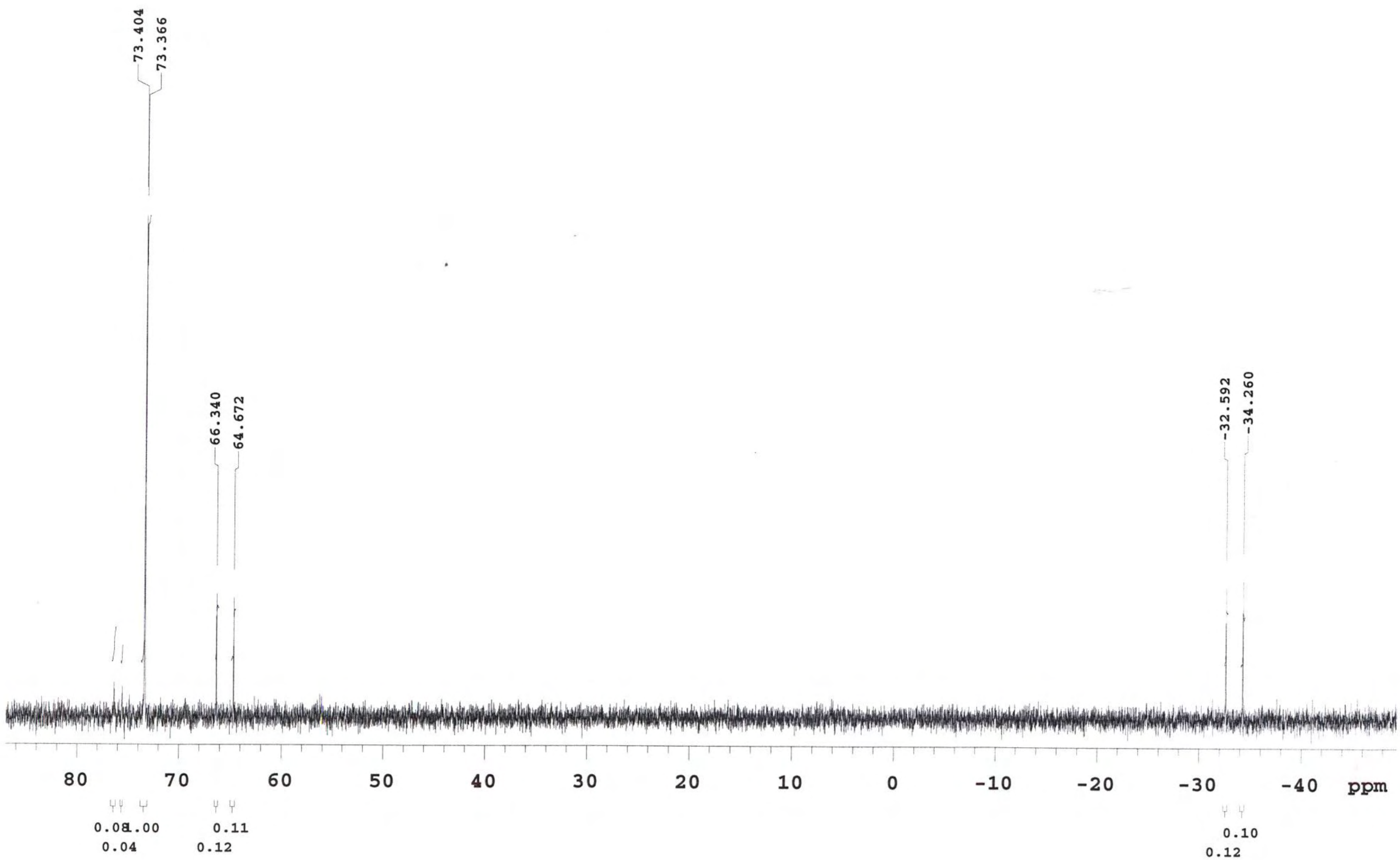
^{31}P NMR: 5% catalyst **1** in C_6D_6; rt, 5 min



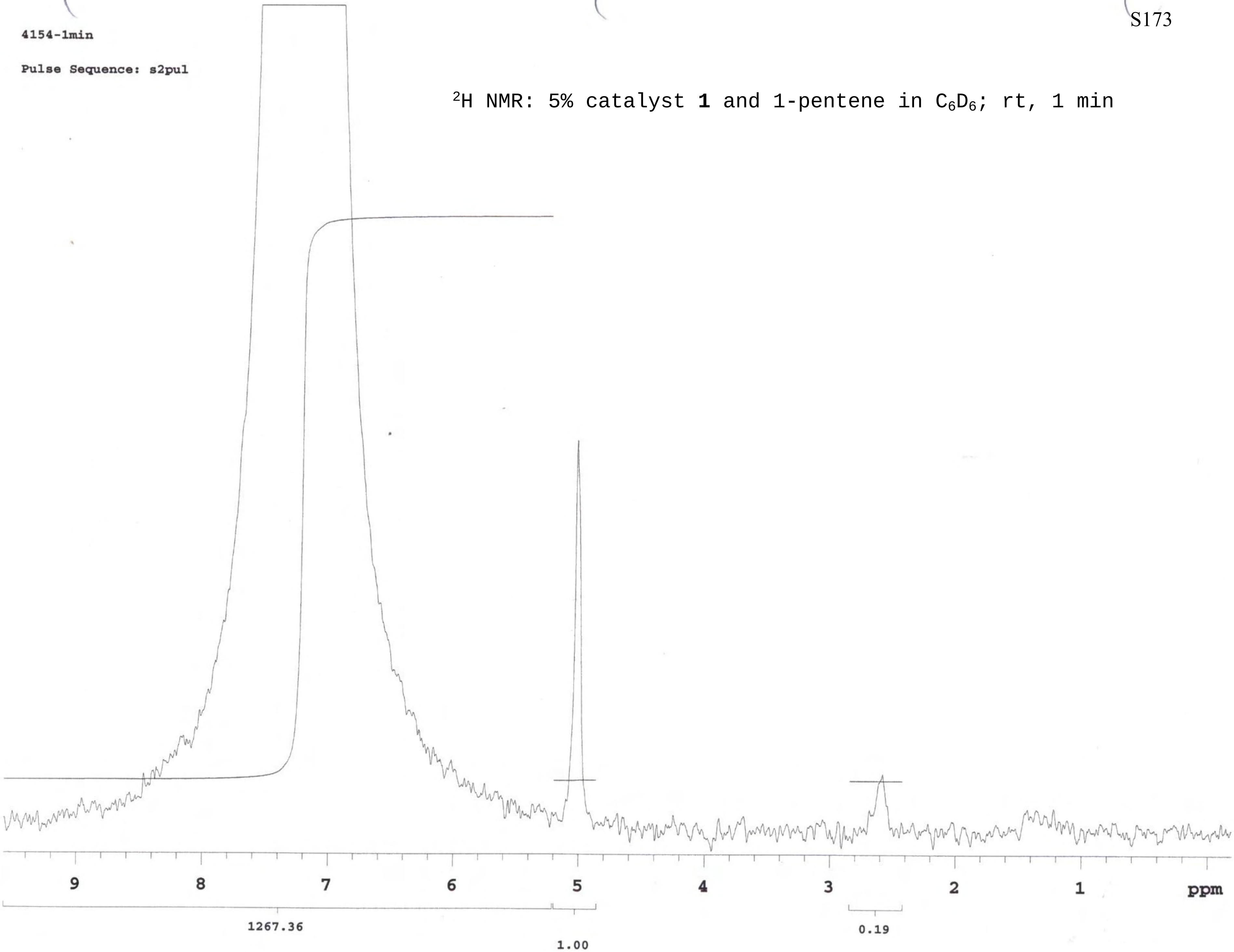
4156-1h

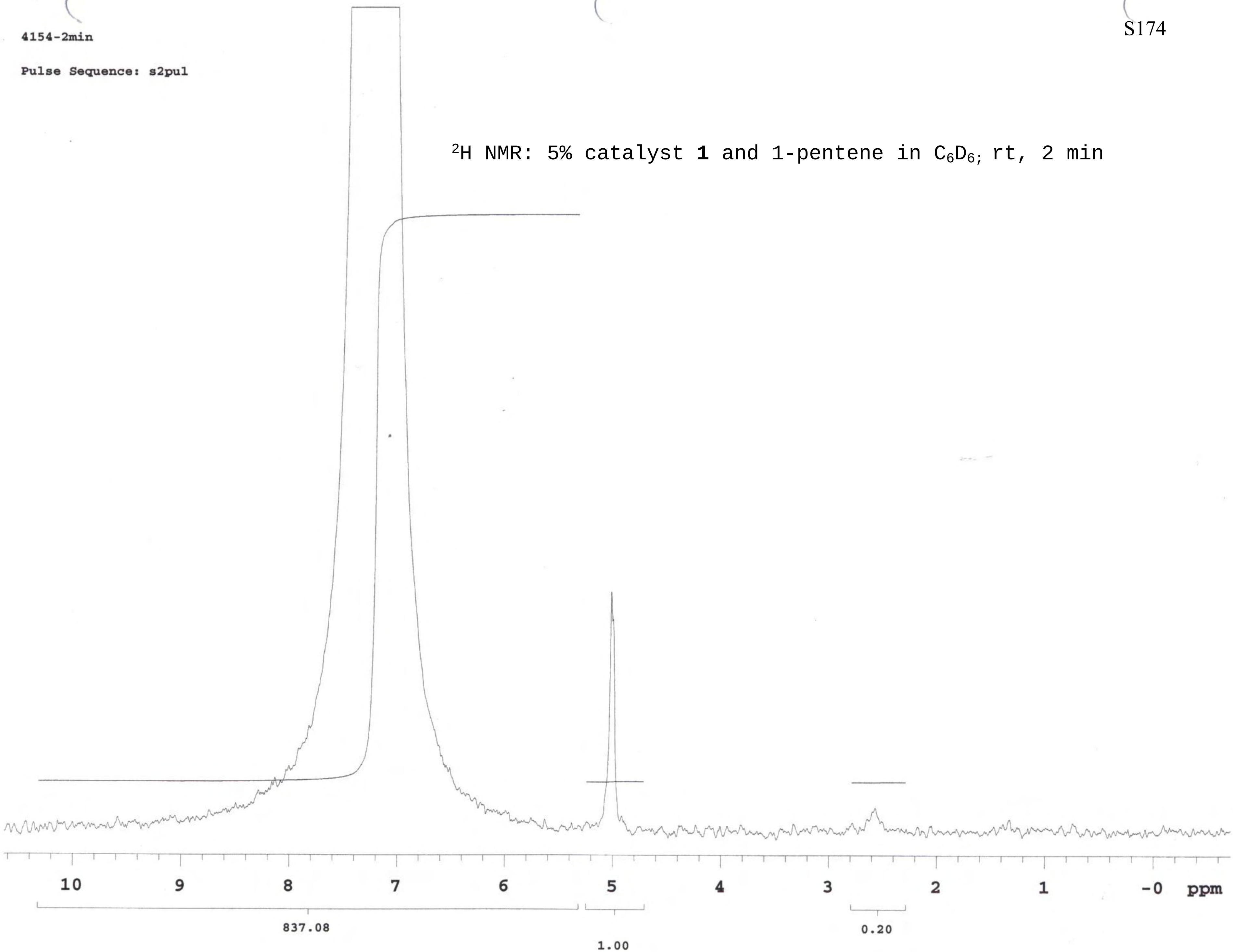
Pulse Sequence: s2pul

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



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

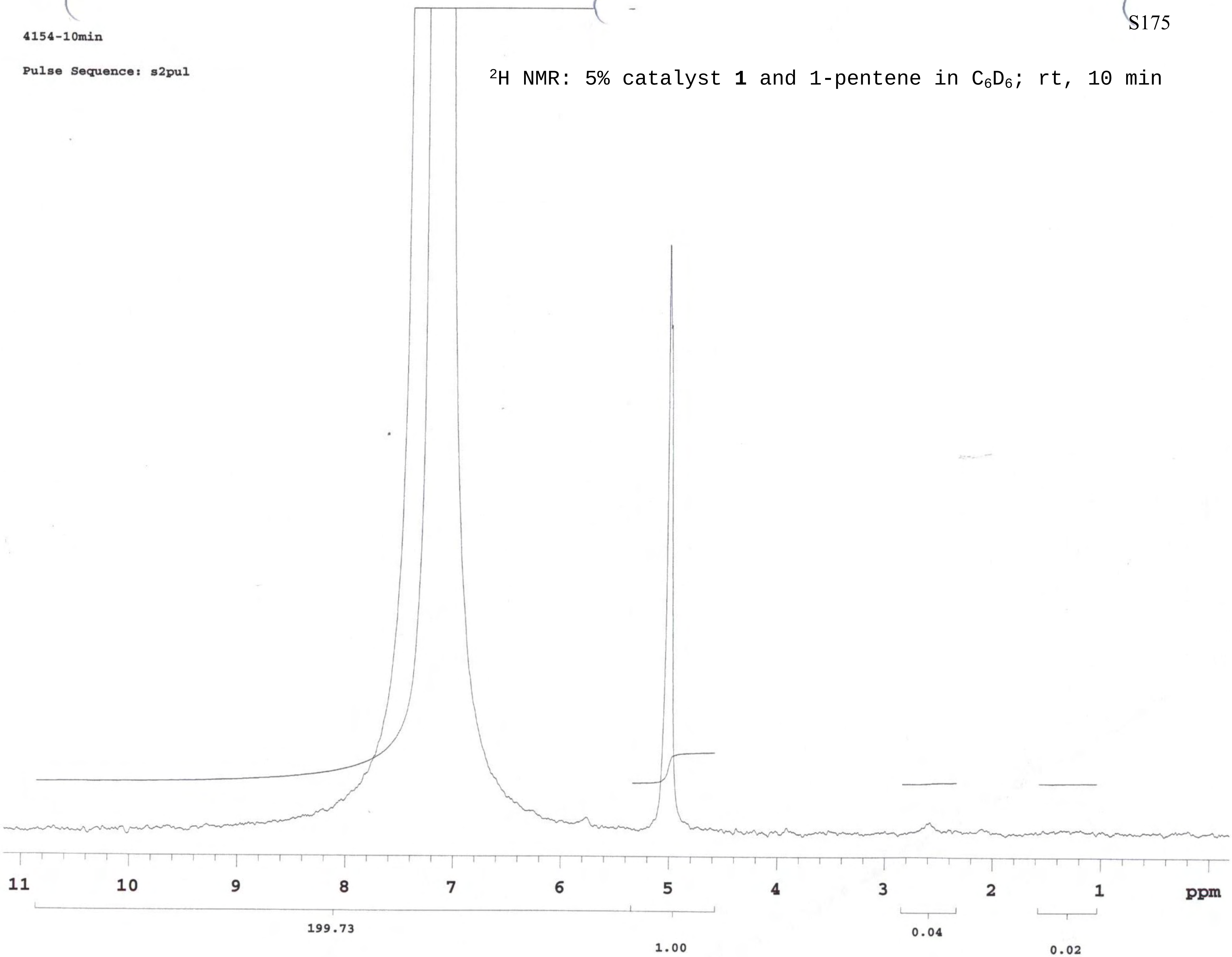



4154-2min
Pulse Sequence: s2pul
^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6; rt, 2 min
10
9
8
7
6
5
4
3
2
1
-0
ppm
837.08
1.00
0.20

4154-10min

Pulse Sequence: s2pul

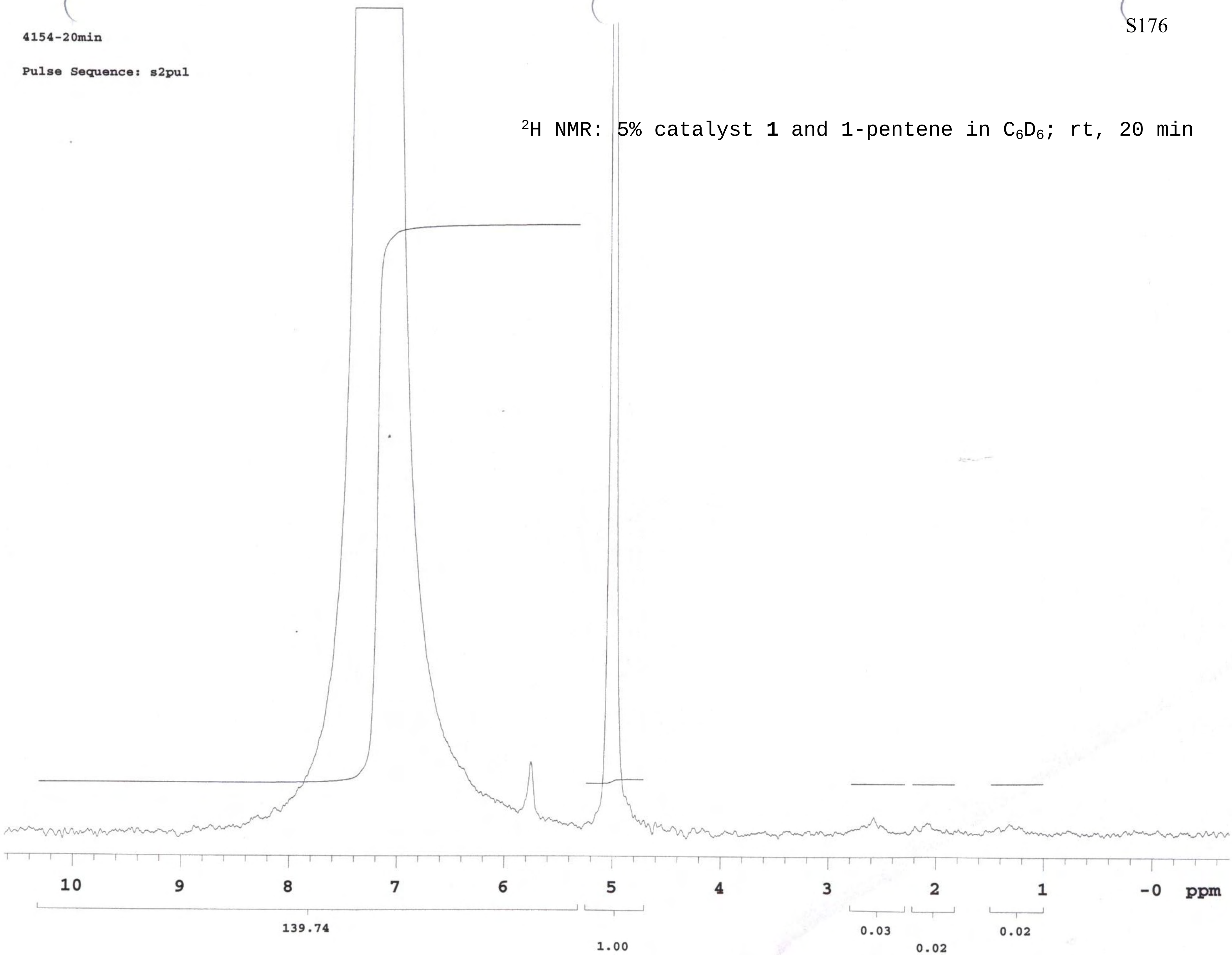
^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6; rt, 10 min



4154-20min

Pulse Sequence: s2pul

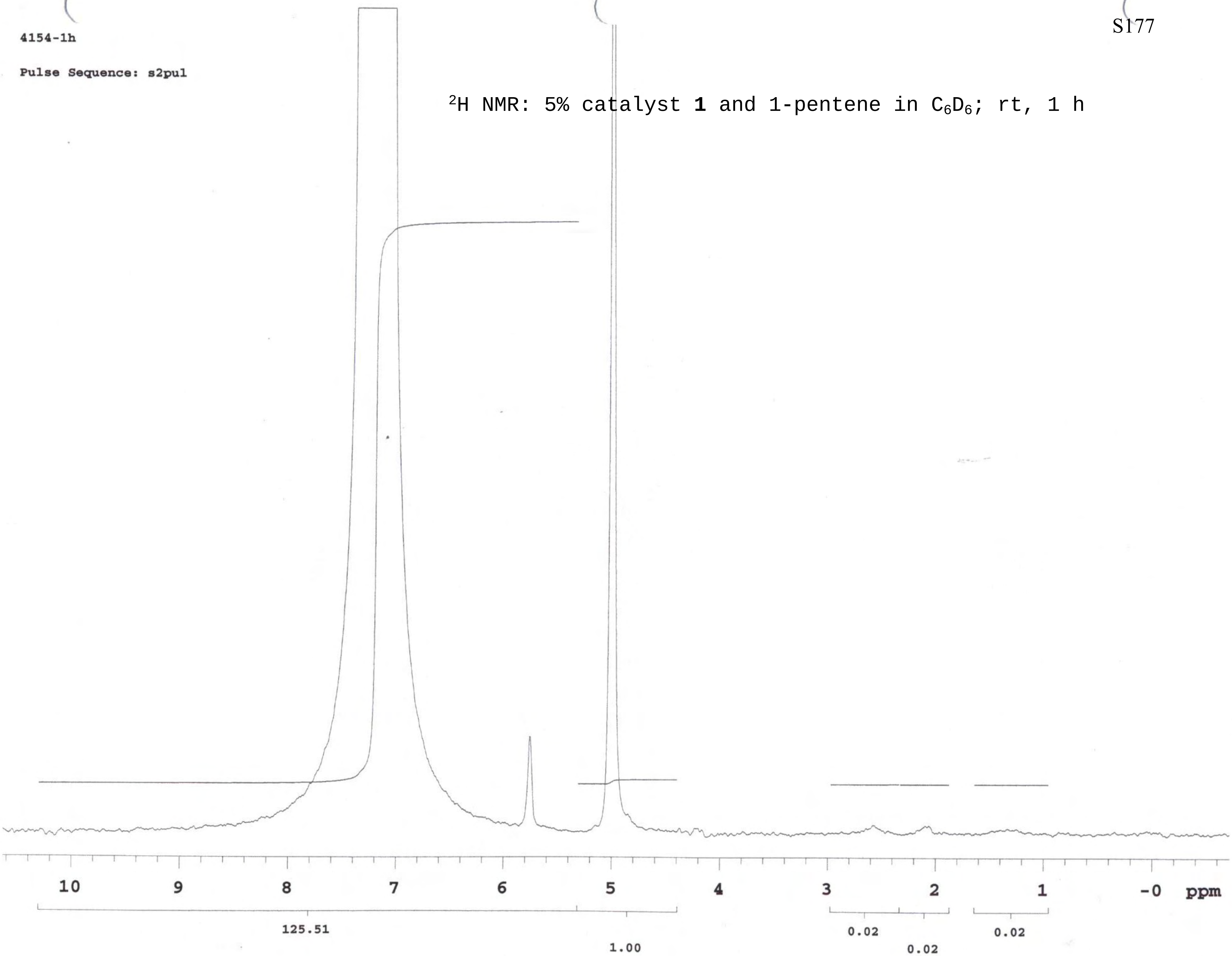
^{2}H NMR: 5% catalyst **1** and 1-pentene in C_6D_6; rt, 20 min



4154-1h

Pulse Sequence: s2pul

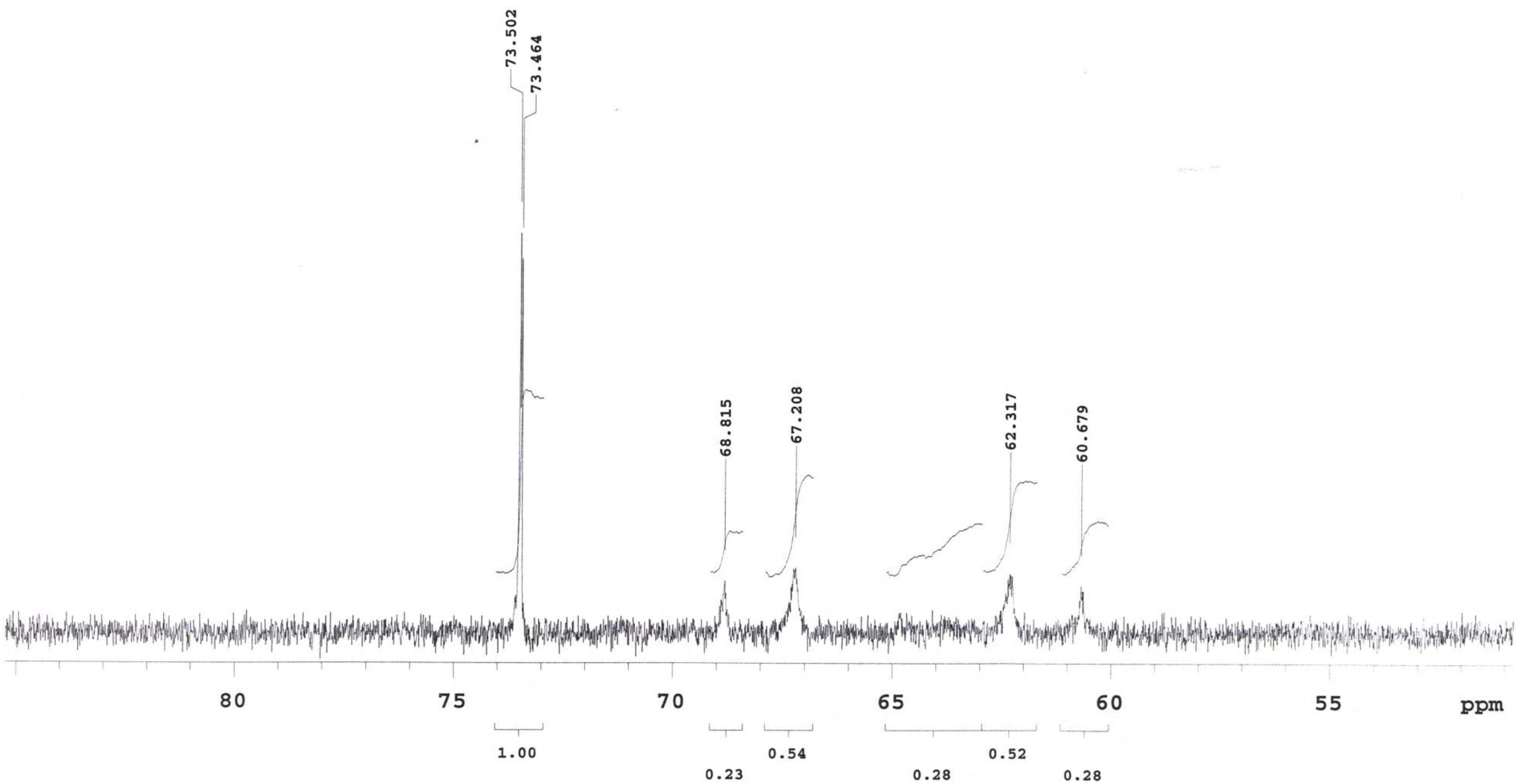
^2H NMR: 5% catalyst **1** and 1-pentene in C_6D_6; rt, 1 h



4154-20min-p

Pulse Sequence: s2pul

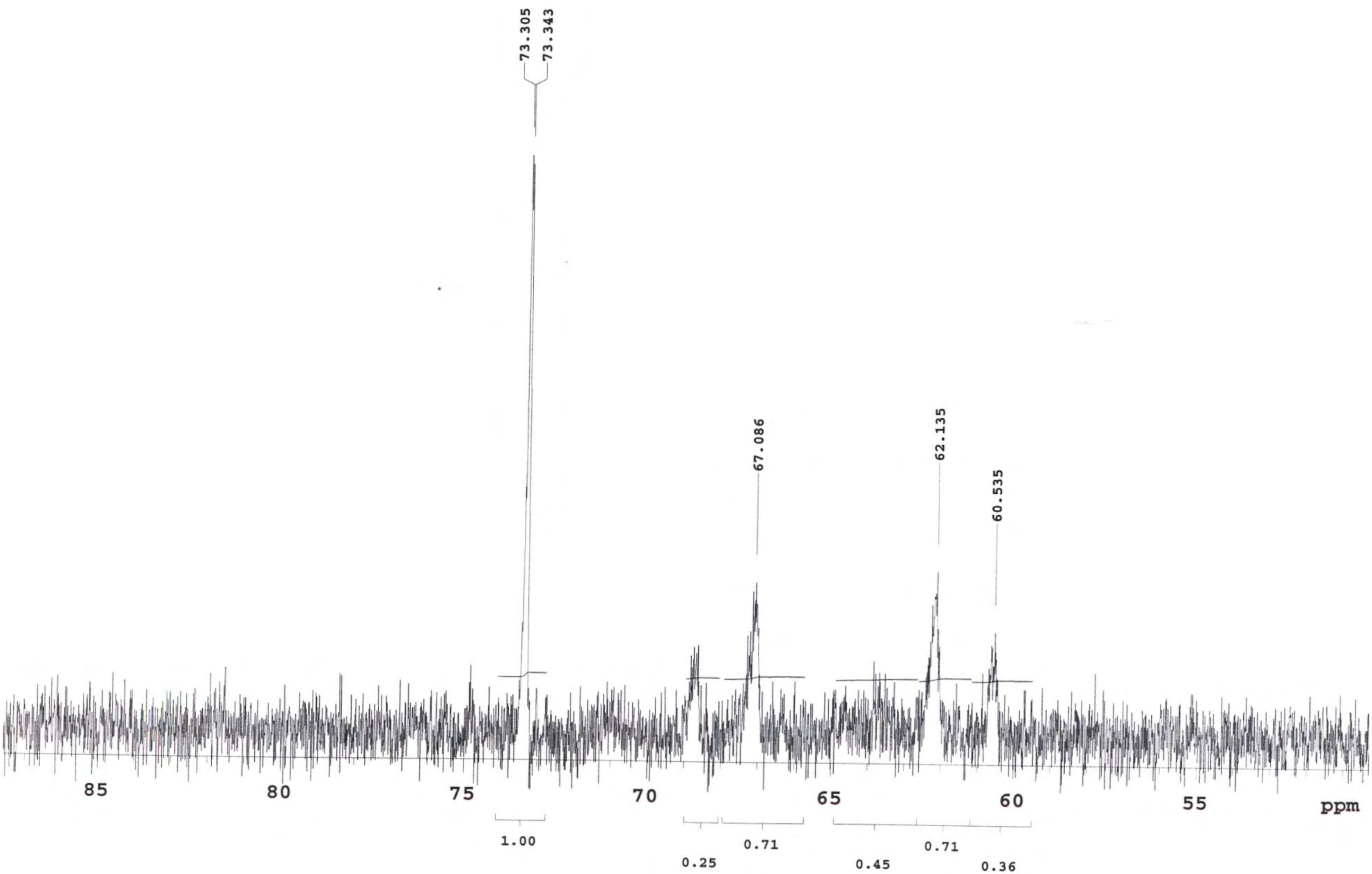
^{31}P NMR: 5% catalyst **1** and 1-pentene in C_6D_6; rt, 20 min



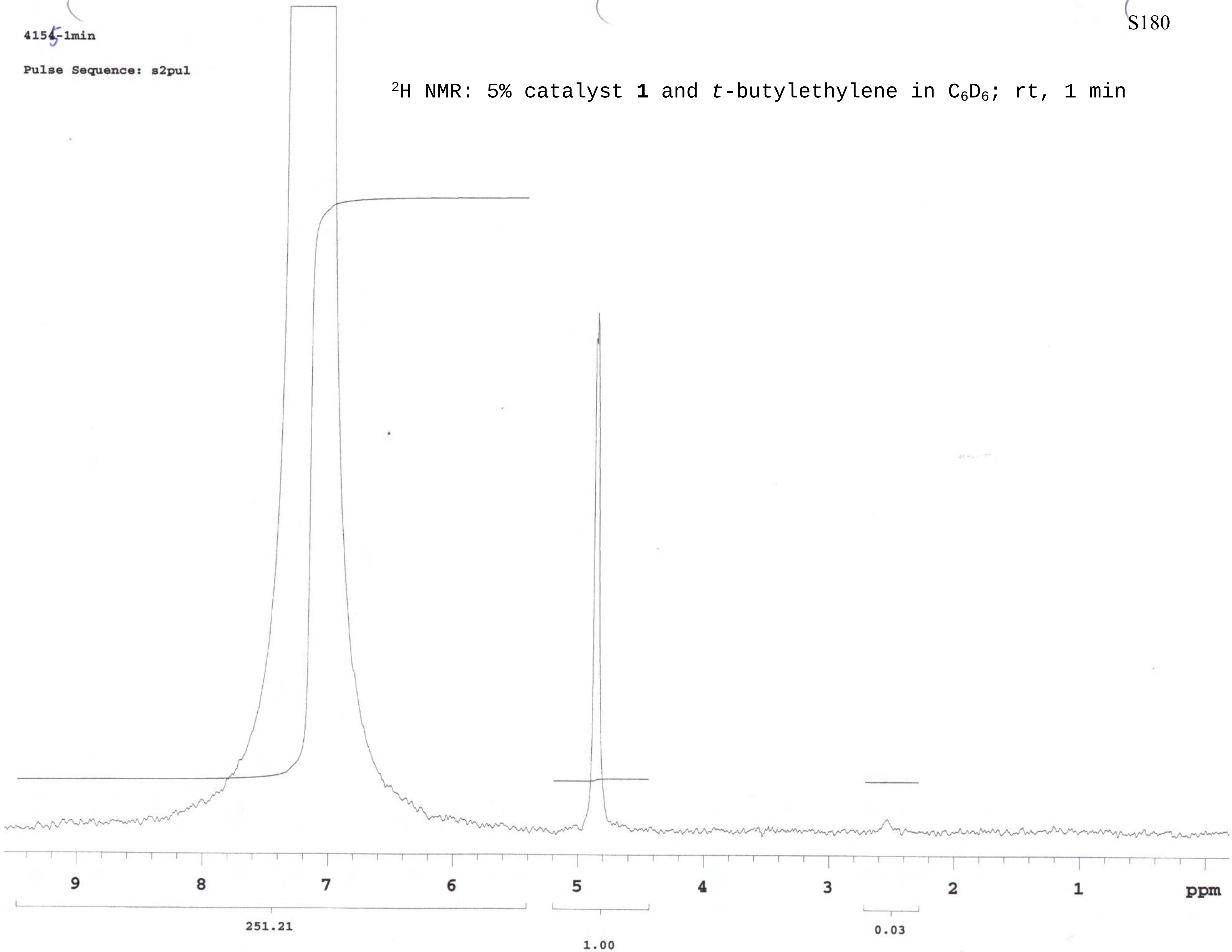
4154-1h

Pulse Sequence: s2pul

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



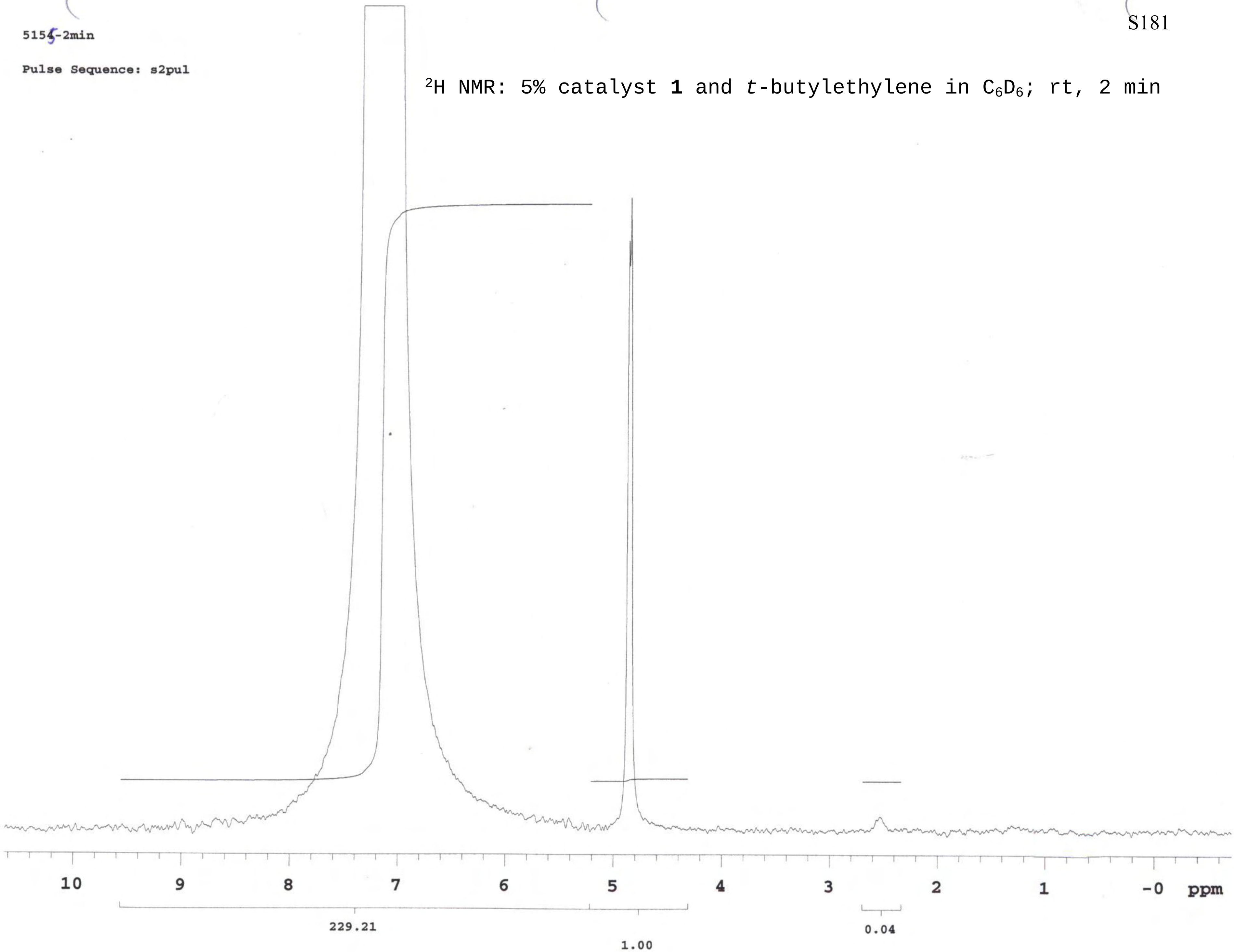
^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6; rt, 1 min



5155-2min

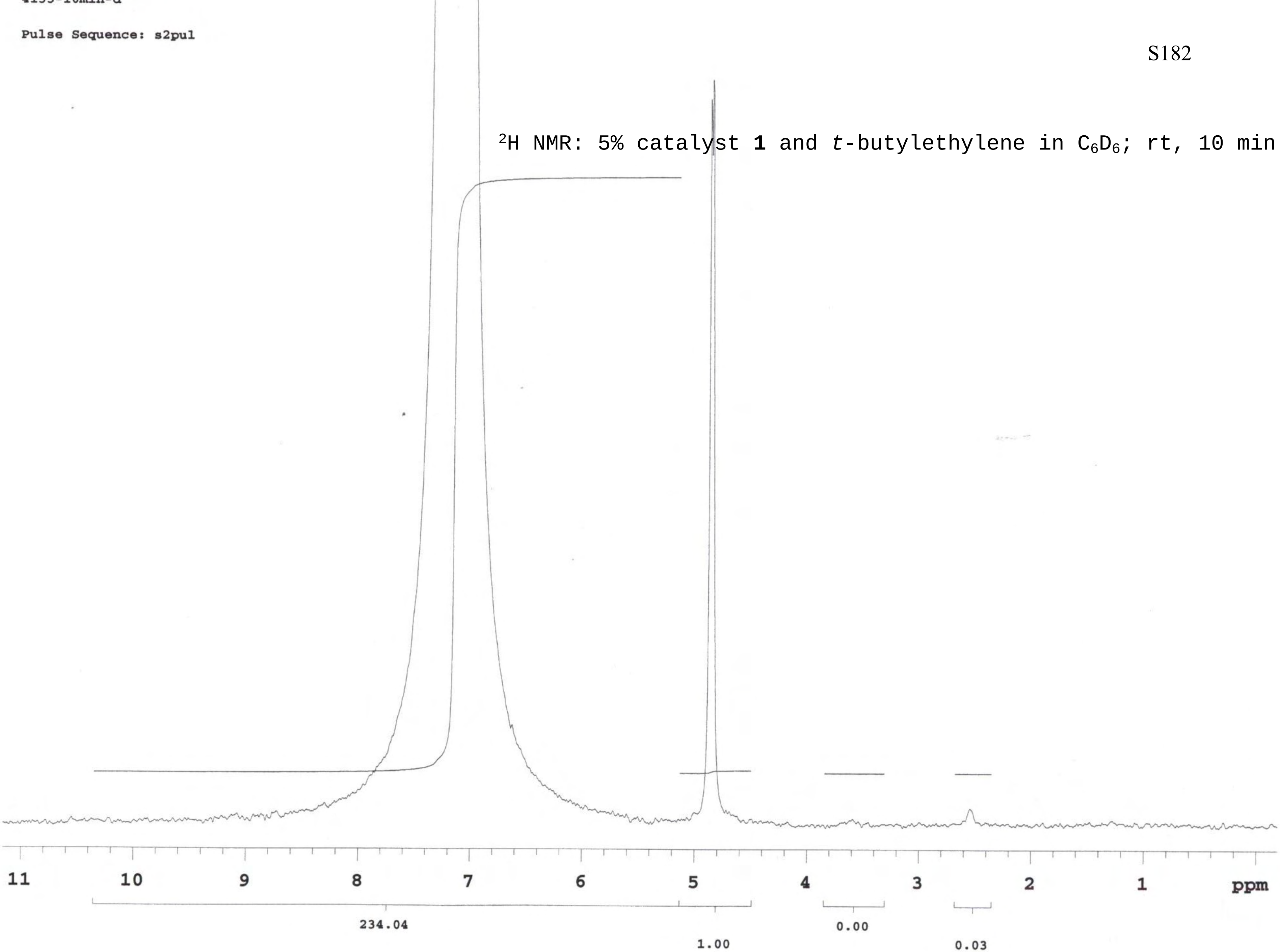
Pulse Sequence: s2pul

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

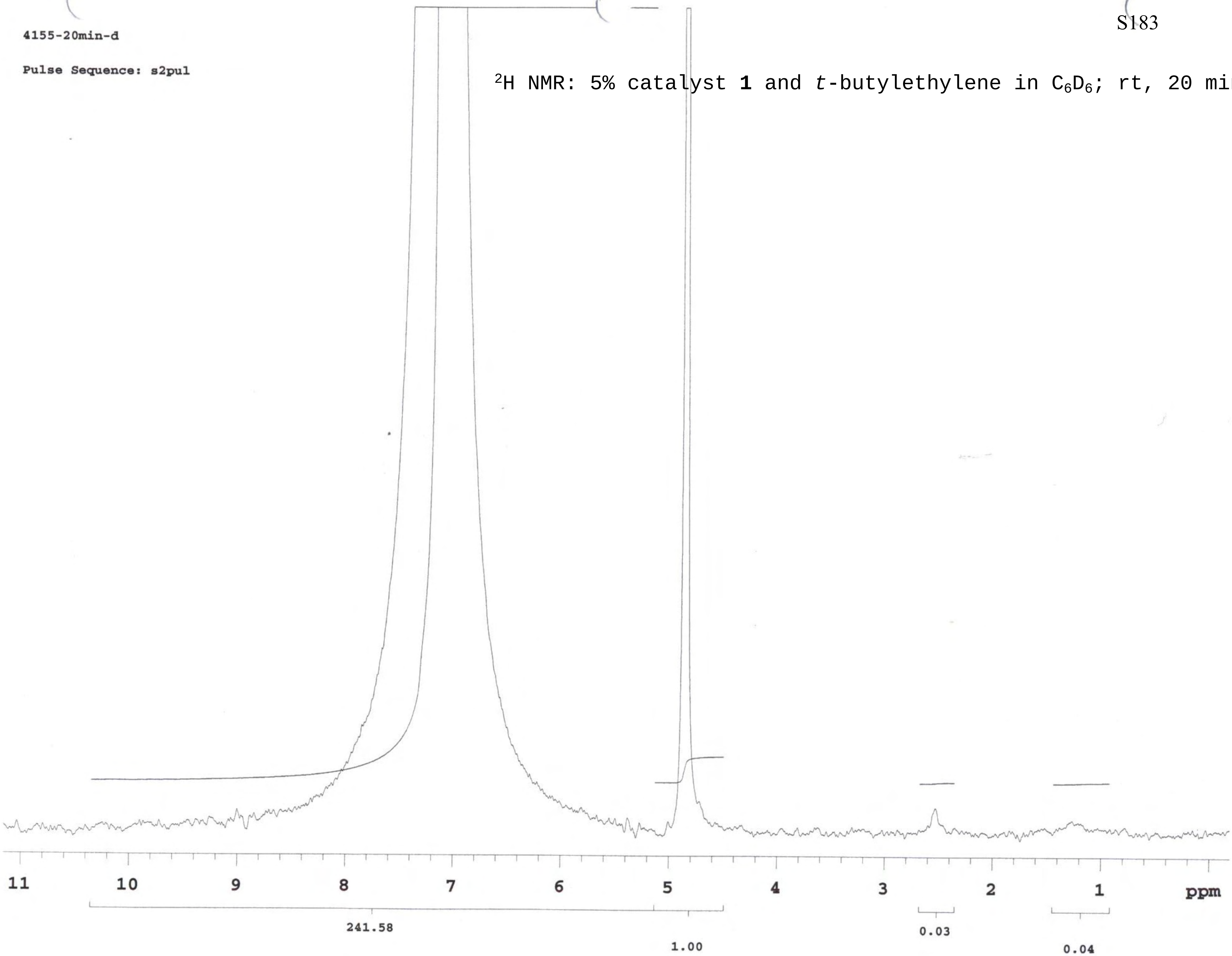


Pulse Sequence: s2pul

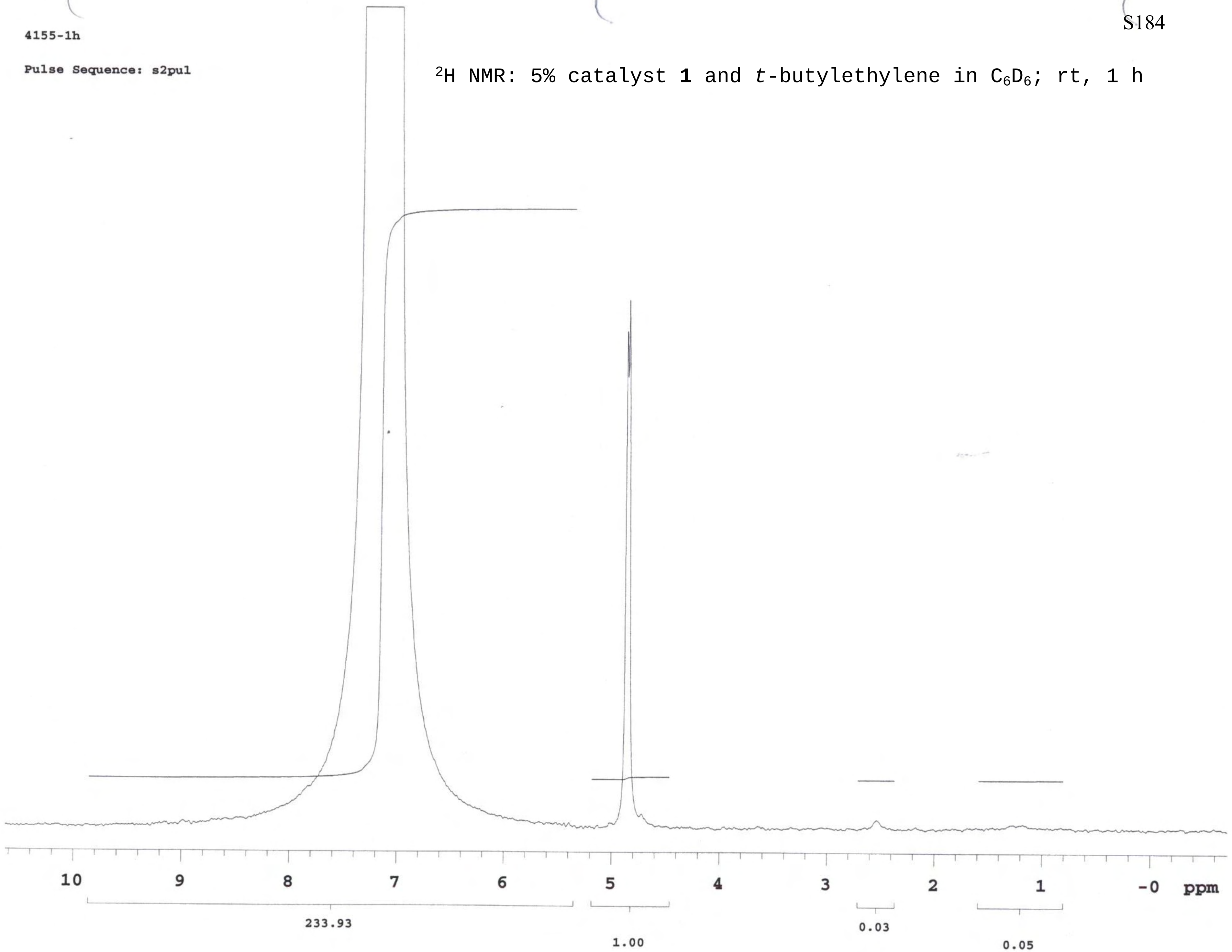
^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6; rt, 10 min



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



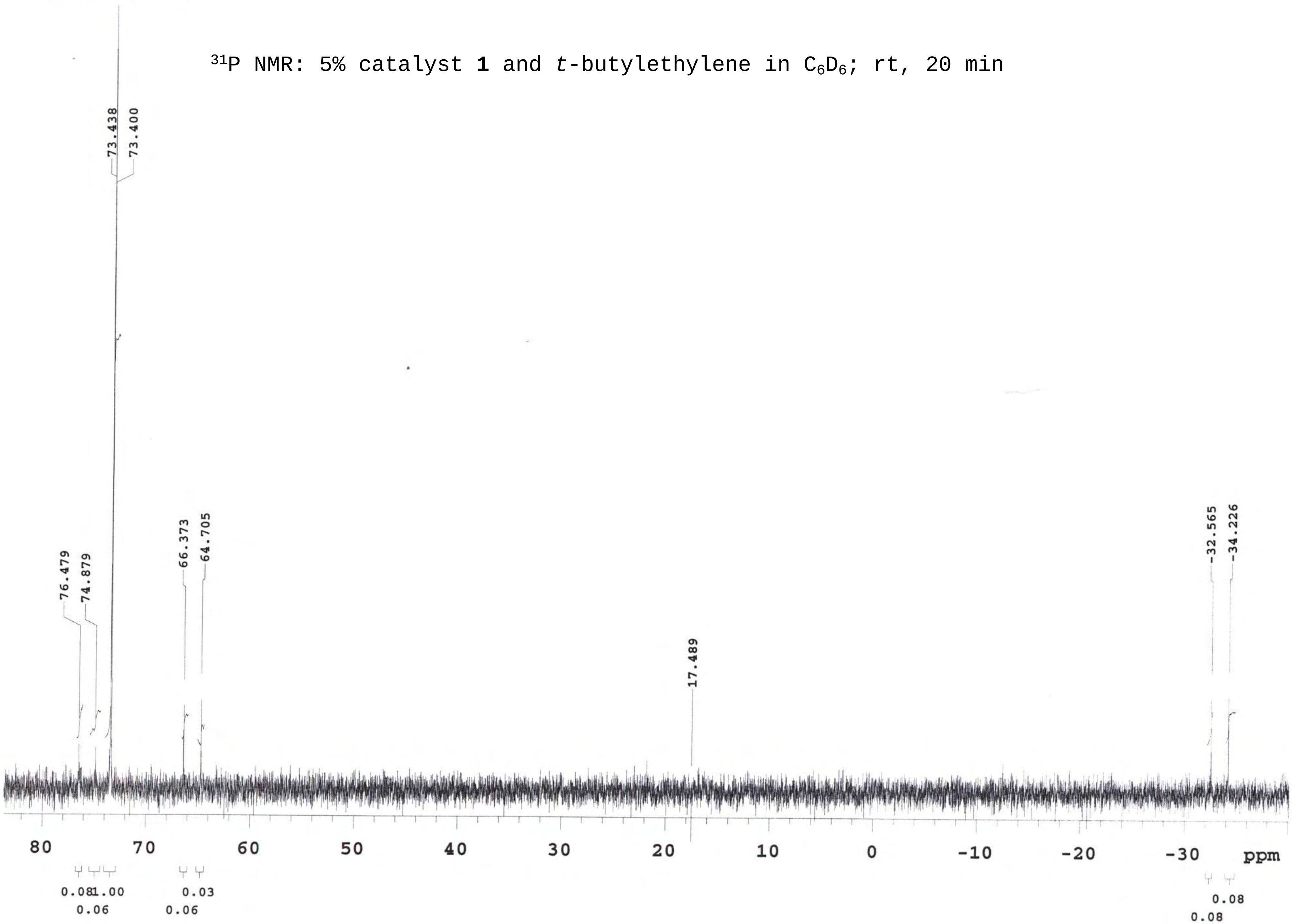
^2H NMR: 5% catalyst **1** and *t*-butylethylene in C_6D_6; rt, 1 h



4155-20min-p

Pulse Sequence: s2pul

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



4155-1h

Pulse Sequence: s2pul

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