Intramolecular thermal allenyne [2 + 2] cycloadditions; facile construction of the 5-6-4 ring core of sterpurene

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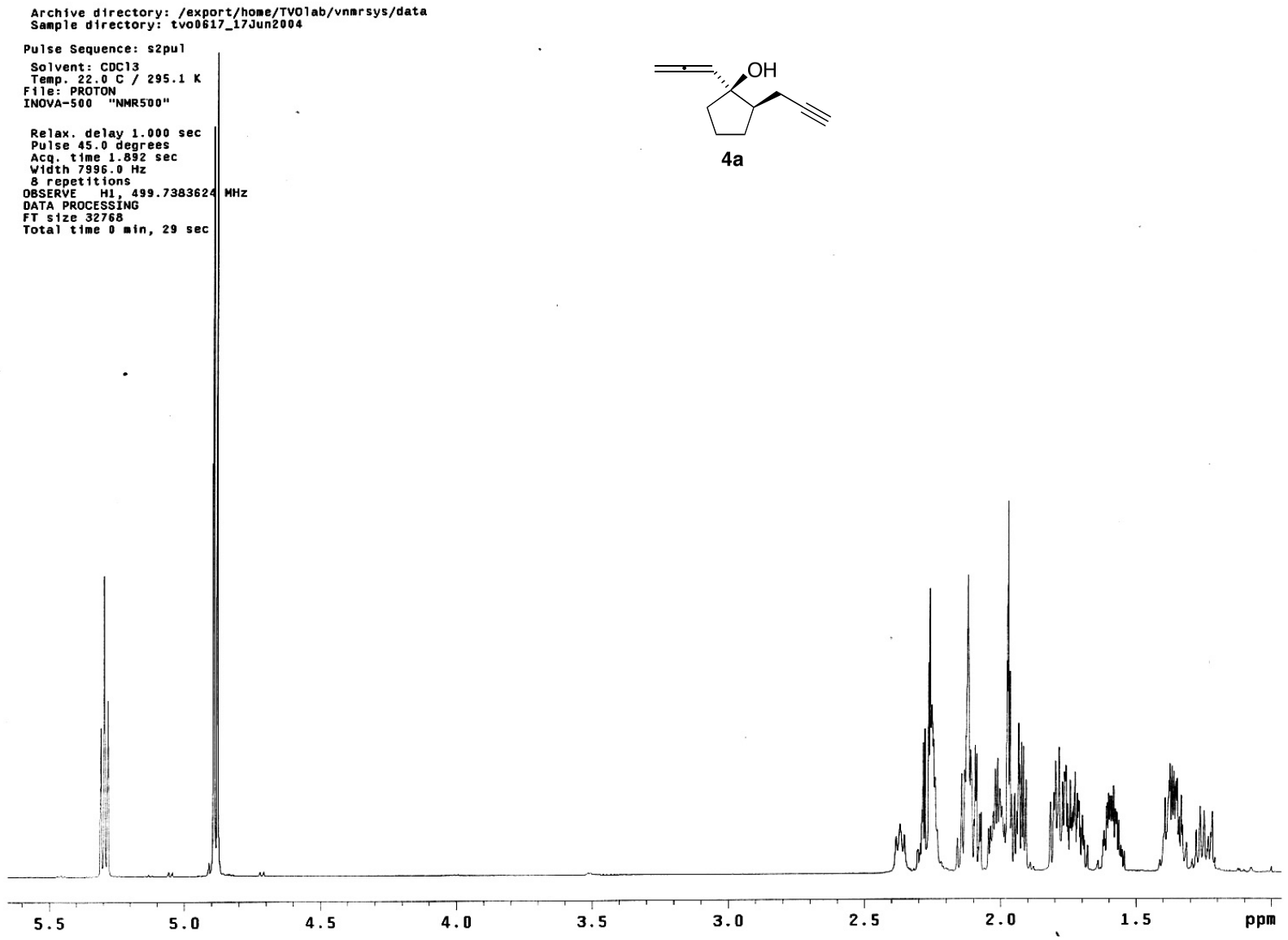
Supporting Information

Contents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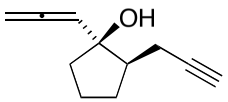
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: PROTON
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7383624 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec
OH
4a
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

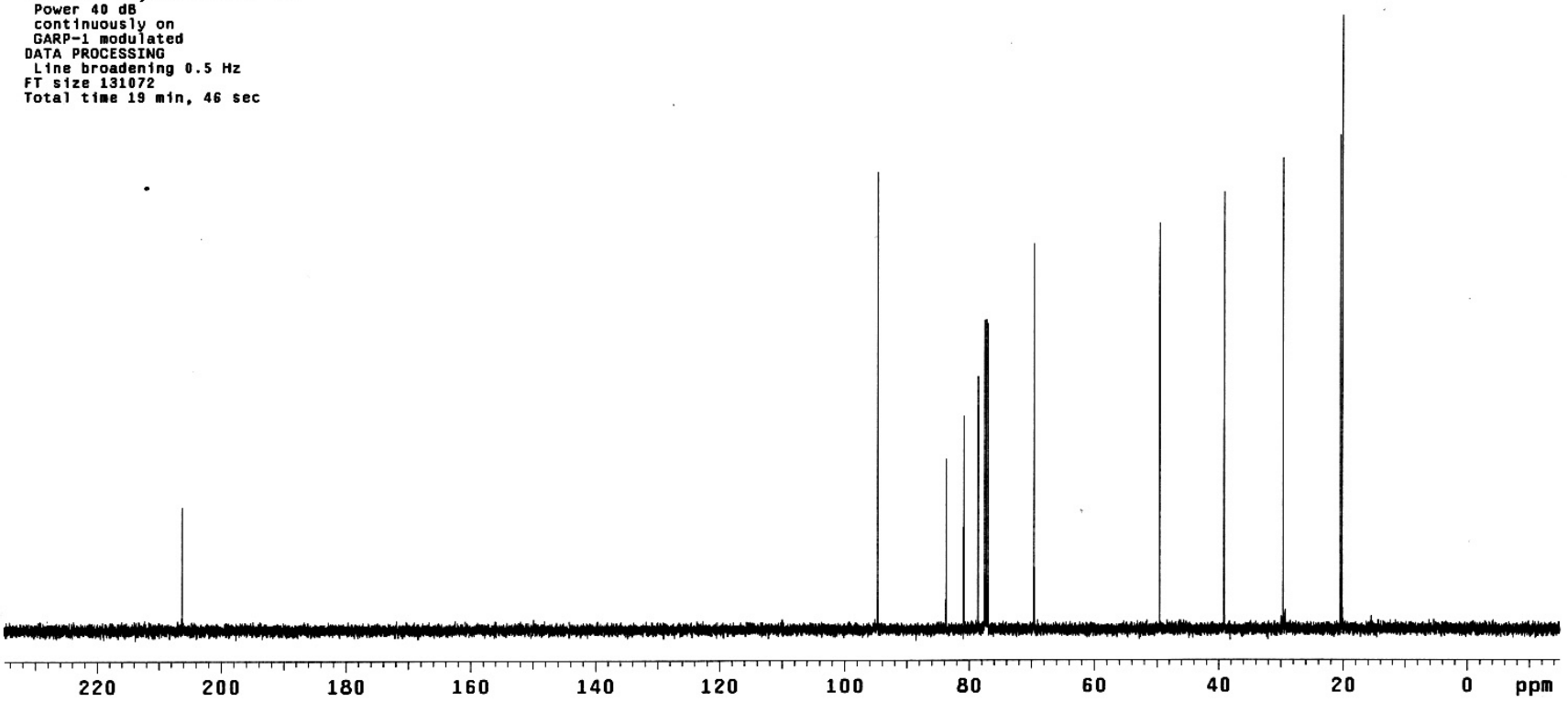


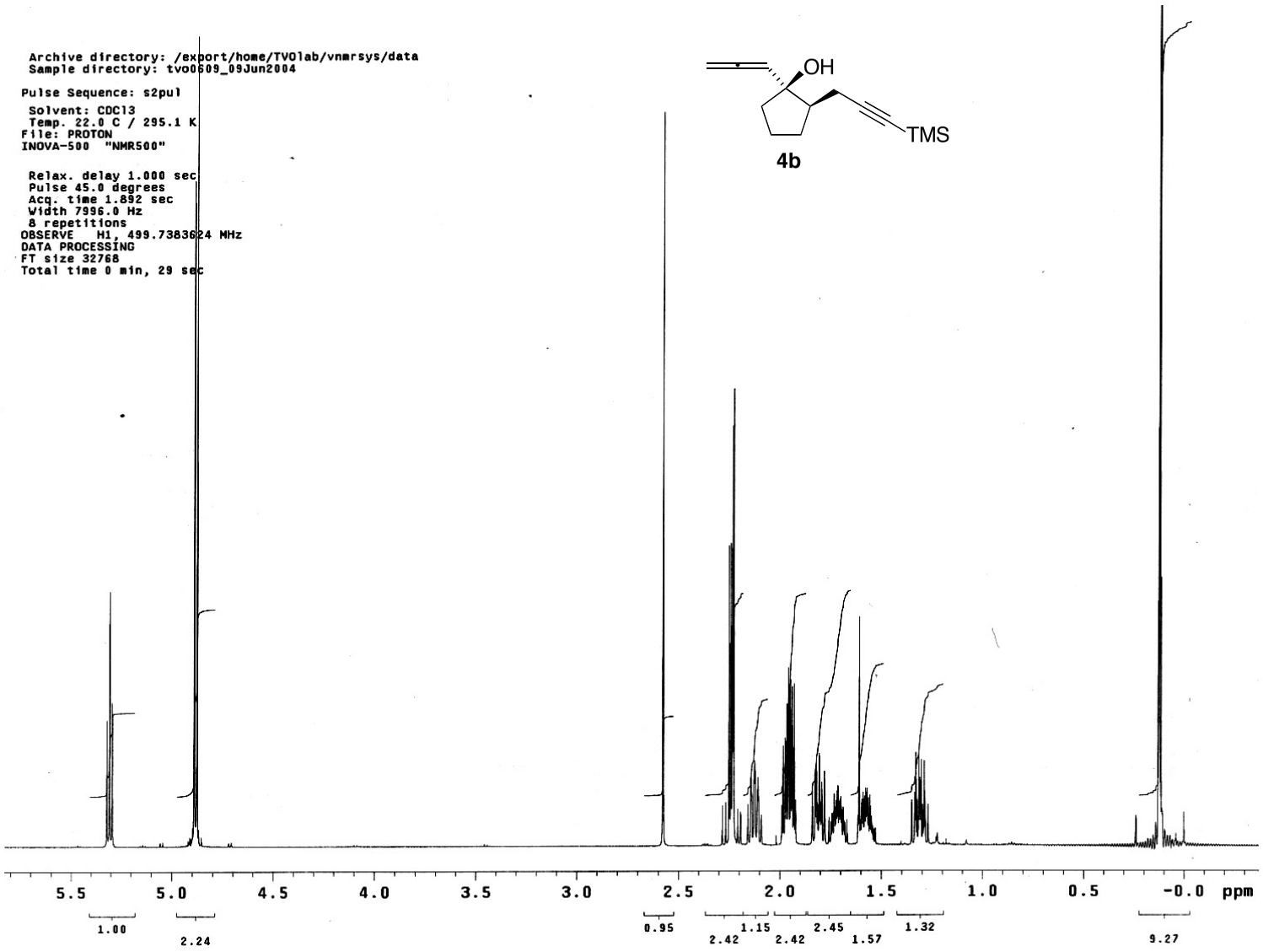
4a

```
 Archive directory: /export/home/TVOlab/vnmrsys/data
 Sample directory: tvo0617_17Jun2004
 File: CARBON

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 22.0 C / 295.1 K
User:  1-14-87
INOVA-500  "NMR500"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 31409.5 Hz
 128 repetitions
OBSERVE  C13, 125.6592773 MHz
DECOUPLE  H1, 499.7408456 MHz
 Power 40 dB
 continuously on
 GARP-1 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 46 sec
```

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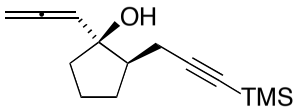
Sample directory: tvo0609_09Jun2004
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: PROTON
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7383624 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec
OH
TMS
4b
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
ppm
1.00
2.24
0.95
2.42
1.15
2.42
2.45
1.57
1.32
9.27



4b

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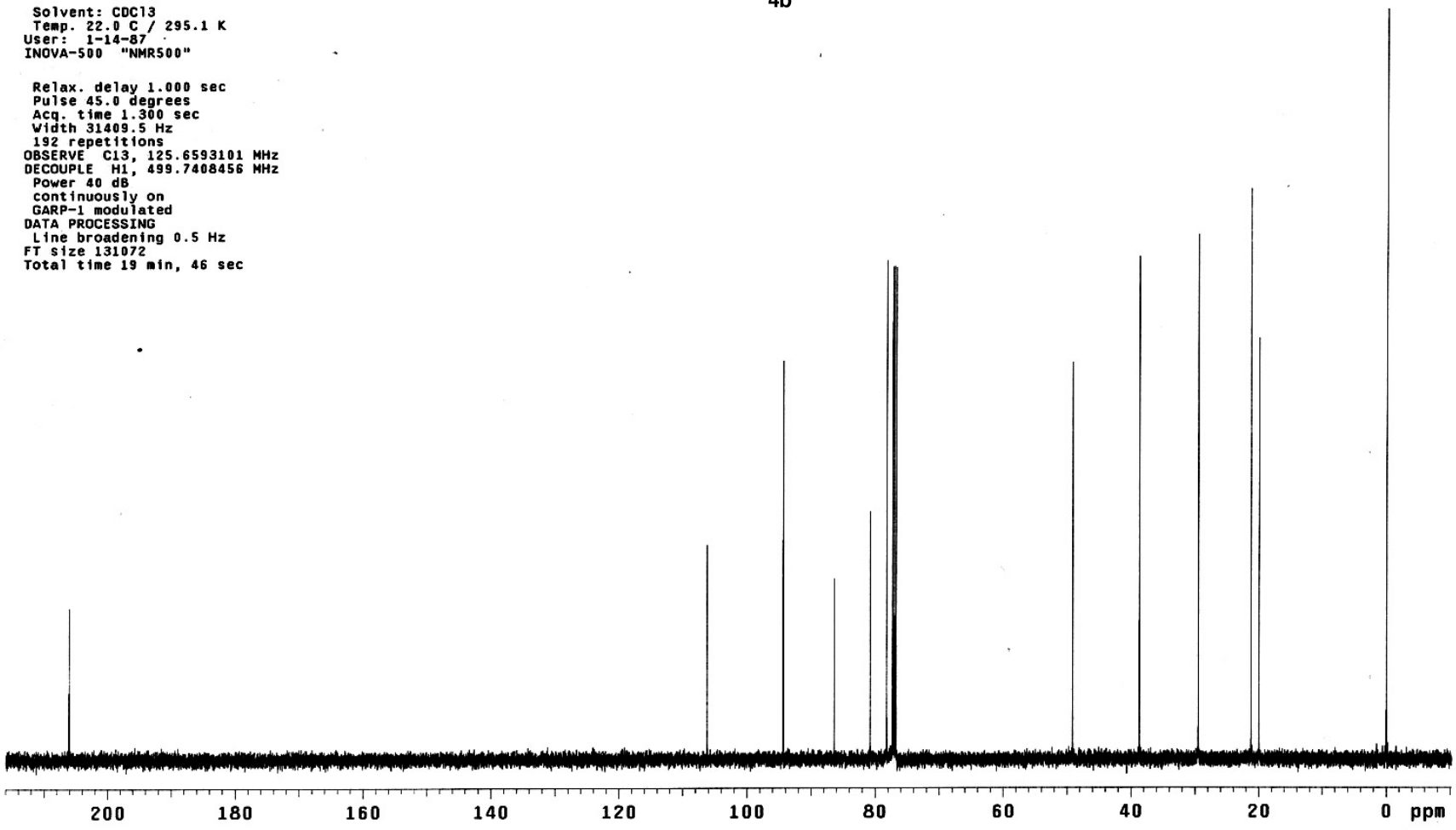
Sample directory: tvo0609_09Jun2004
File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
User:  1-14-87
INOVA-500  "NMR500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
192 repetitions
OBSERVE  C13, 125.6593101 MHz
DECOUPLE  H1, 499.7408456 MHz
Power 40 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 46 sec
```



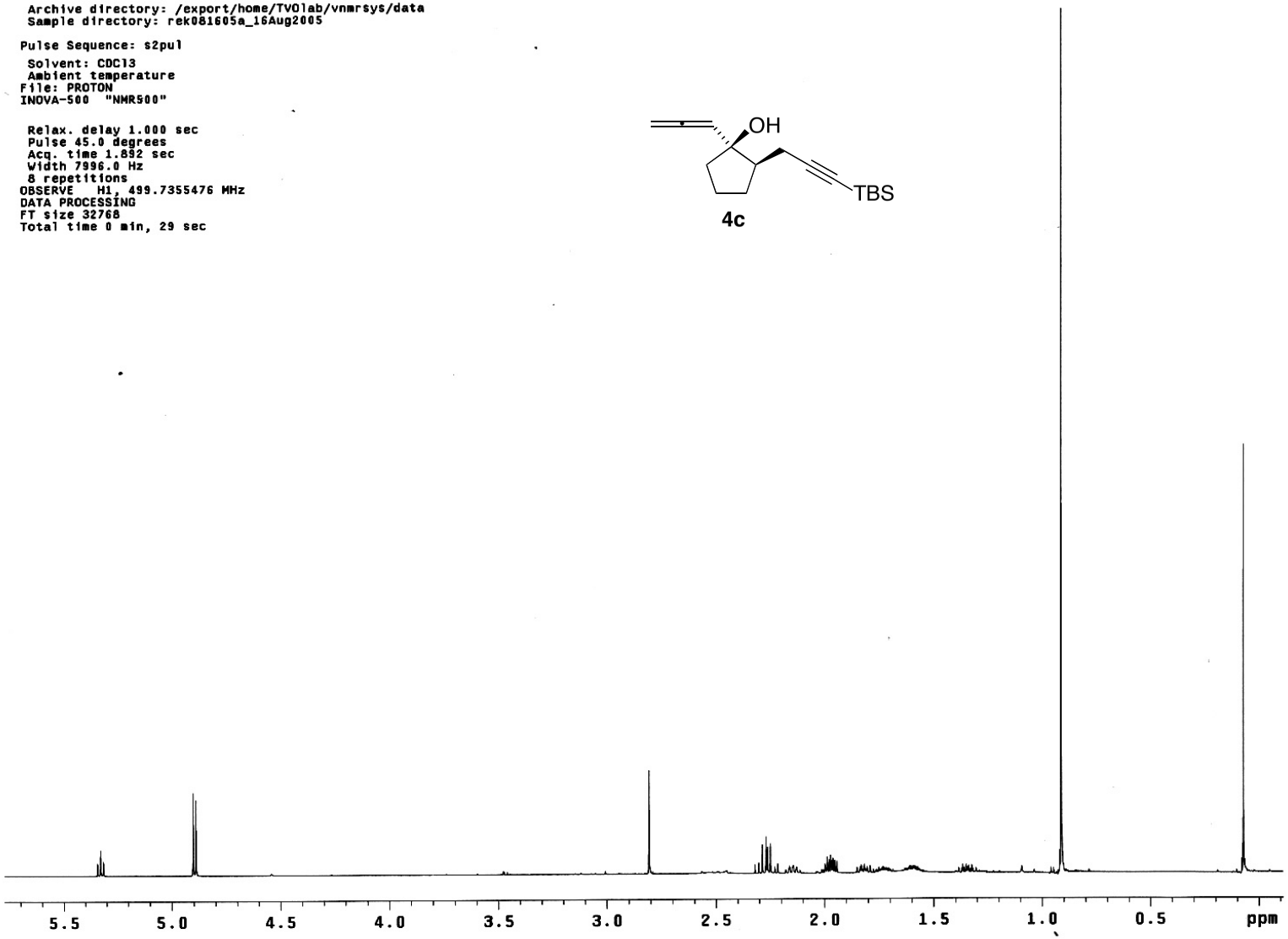
Archive directory: /export/home/TVOlab/vnmrsys/data
Sample directory: rek081605a_16Aug2005

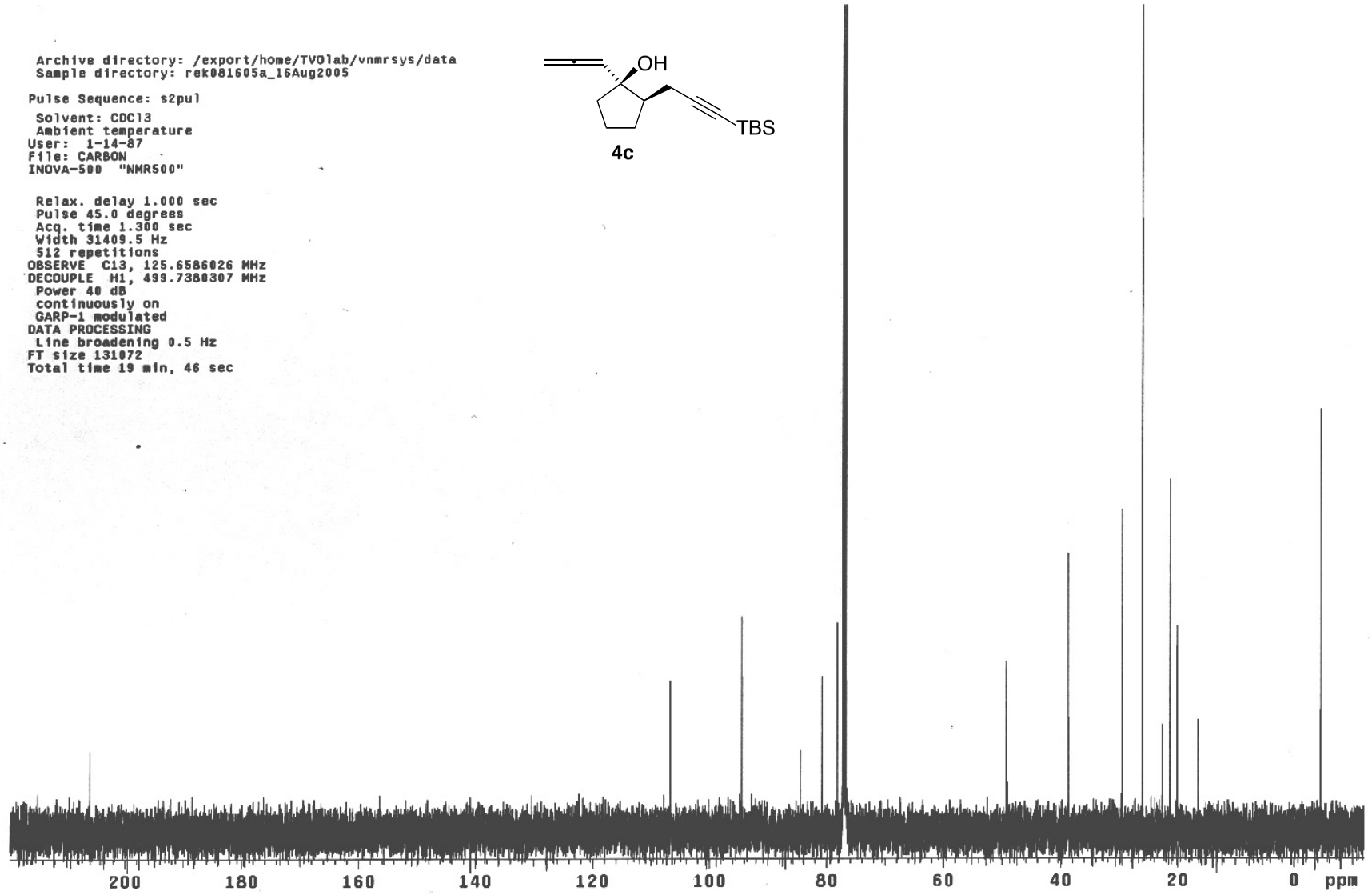
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: PROTON
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7355476 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec

4c

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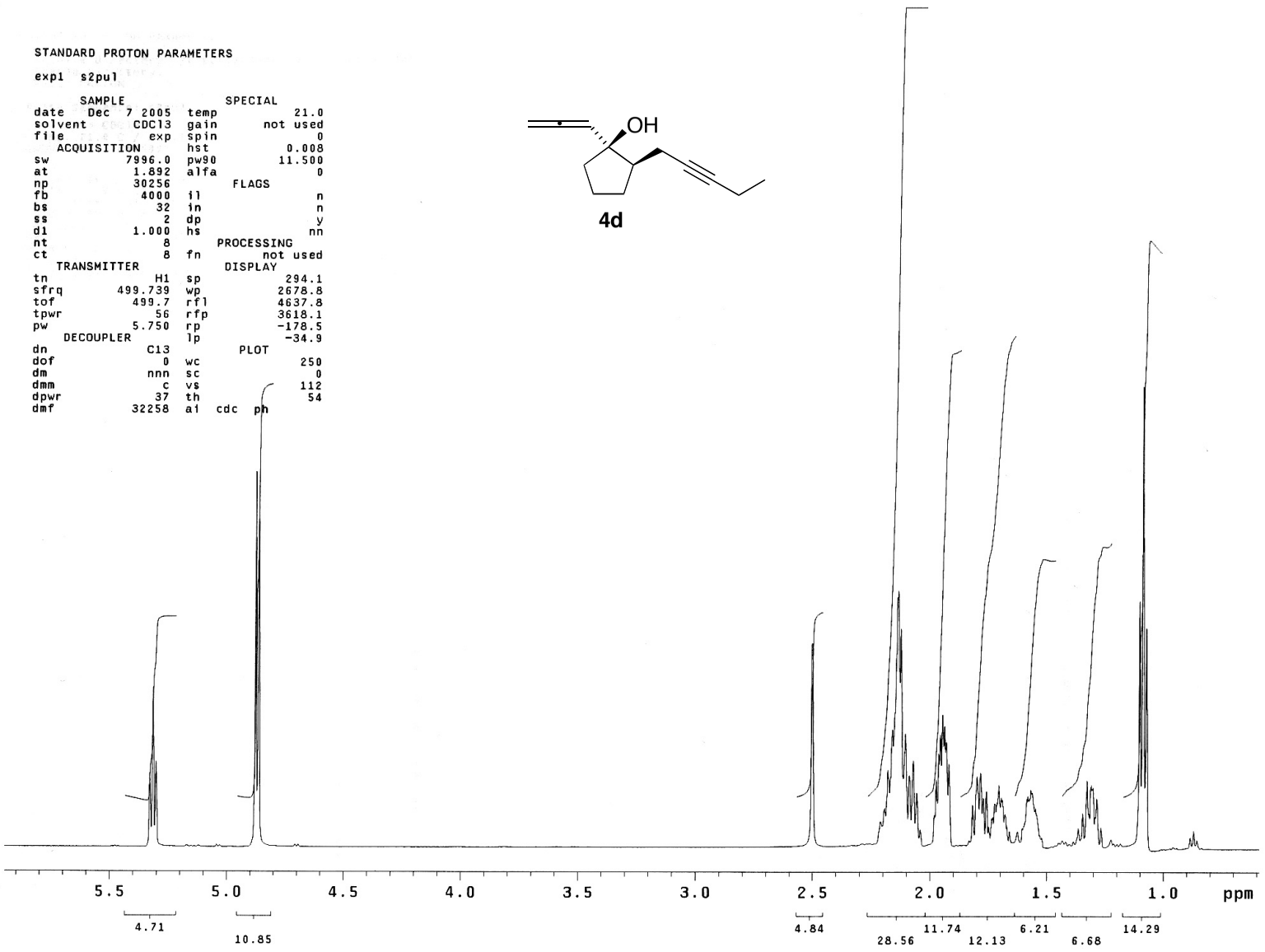
Sample directory: rek081605a_16Aug2005
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: CARBON
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
512 repetitions
OBSERVE C13, 125.6586026 MHz
DECOUPLE H1, 499.7380307 MHz
Power 40 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 46 sec
OH
TBS
4c
200
180
160
140
120
100
80
60
40
20
0
ppm

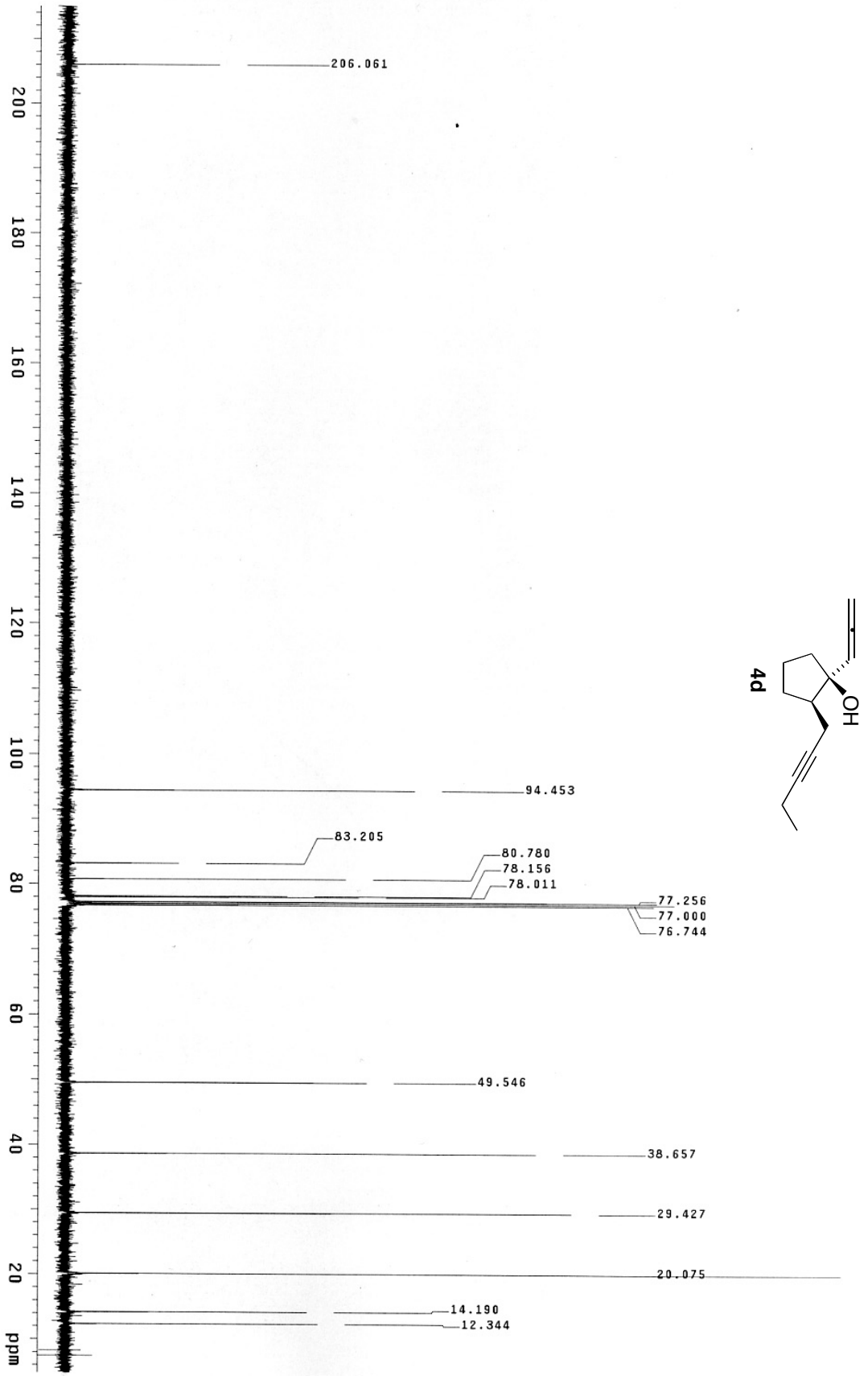
STANDARD PROTON PARAMETERS

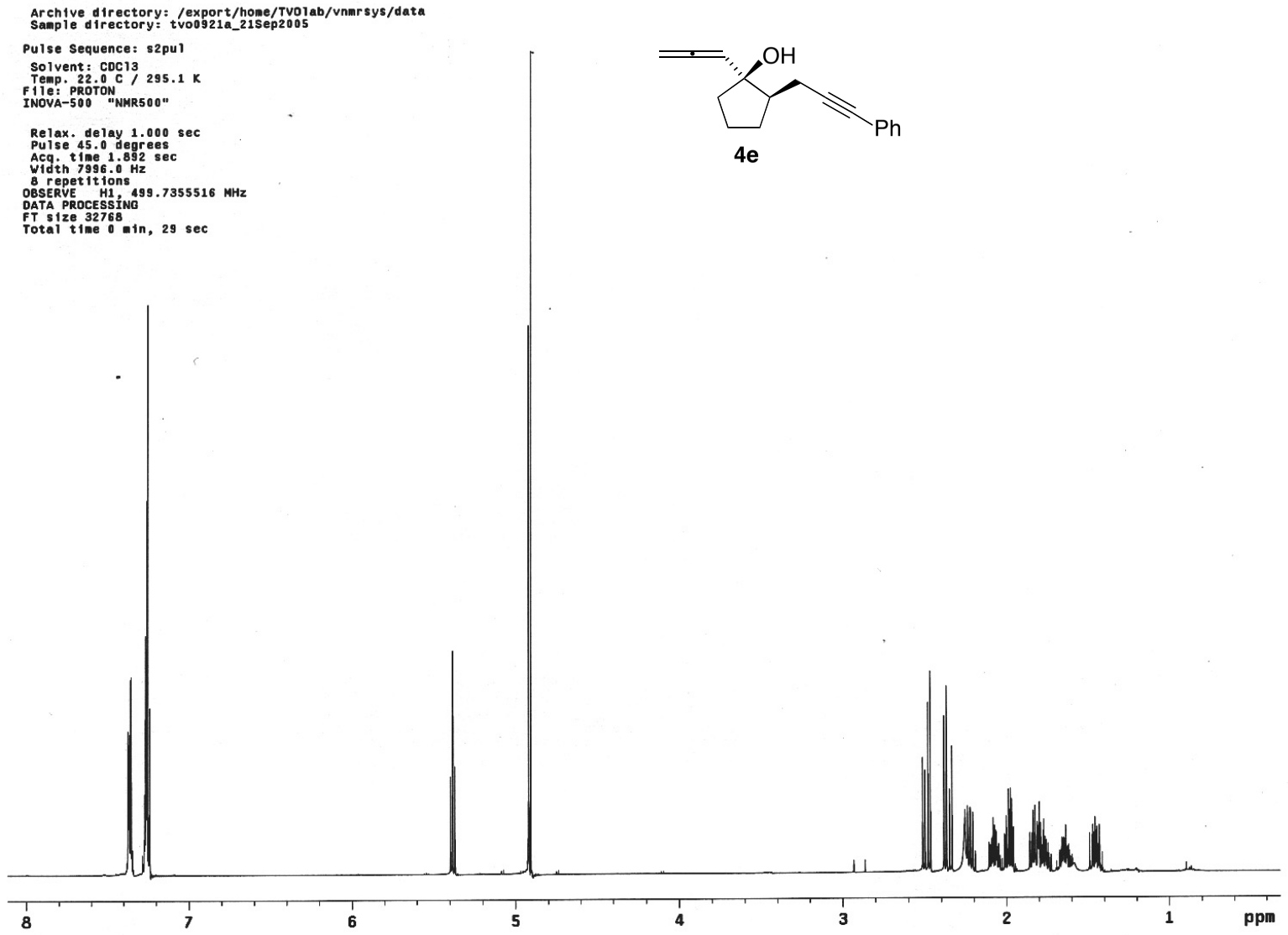
exp1 s2pul

SAMPLE		SPECIAL	
date	Dec 7 2005	temp	21.0
solvent	CDCl3	gain	not used
file	exp	spin	0
ACQUISITION		hst	0.008
sw	7996.0	pw90	11.500
at	1.892	alfa	0
np	30256	FLAGS	
fb	4000	il	n
bs	32	in	n
ss	2	dp	y
d1	1.000	hs	nn
nt	8	PROCESSING	
ct	8	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	294.1
sfrq	499.739	wp	2678.8
tof	499.7	rfl	4637.8
tpwr	56	rfp	3618.1
pw	5.750	rp	-178.5
DECOUPLER		lp	-34.9
dn	C13	PLOT	
dof	0	wc	250
dm	nnn	sc	0
dmm	c	vs	112
dpwr	37	th	54
dmf	32258	ai cdc ph	

4d




206.061
94.453
83.205
80.780
78.156
78.011
77.256
77.000
76.744
49.546
38.657
29.427
20.075
14.190
12.344
ppm
200
180
160
140
120
100
80
60
40
20
4d
OH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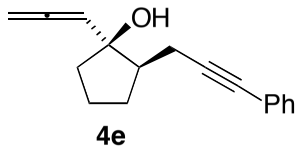
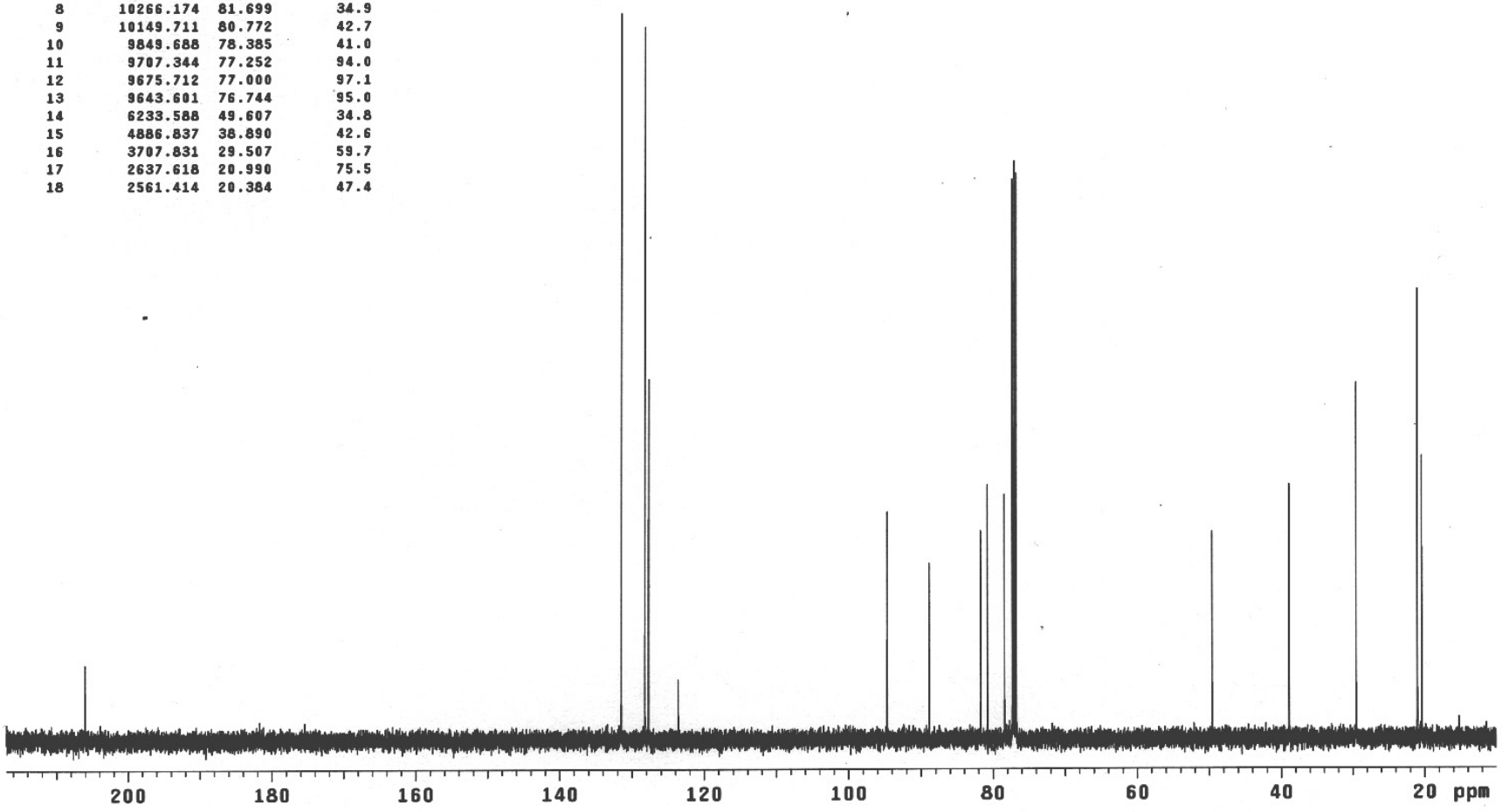
Sample directory: tvo0921a_21Sep2005
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: PROTON
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7355516 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec
OH
Ph
4e
8
7
6
5
4
3
2
1
ppm



4e

INDEX	FREQUENCY	PPM	HEIGHT
1	25889.928	206.034	12.6
2	16520.660	131.473	122.0
3	16111.842	128.219	119.8
4	16046.661	127.700	60.6
5	15533.362	123.616	10.0
6	11896.175	94.671	38.1
7	11167.683	88.873	29.4
8	10266.174	81.699	34.9
9	10149.711	80.772	42.7
10	9849.688	78.385	41.0
11	9707.344	77.252	94.0
12	9675.712	77.000	97.1
13	9643.601	76.744	95.0
14	6233.588	49.607	34.8
15	4886.837	38.890	42.6
16	3707.831	29.507	59.7
17	2637.618	20.990	75.5
18	2561.414	20.384	47.4



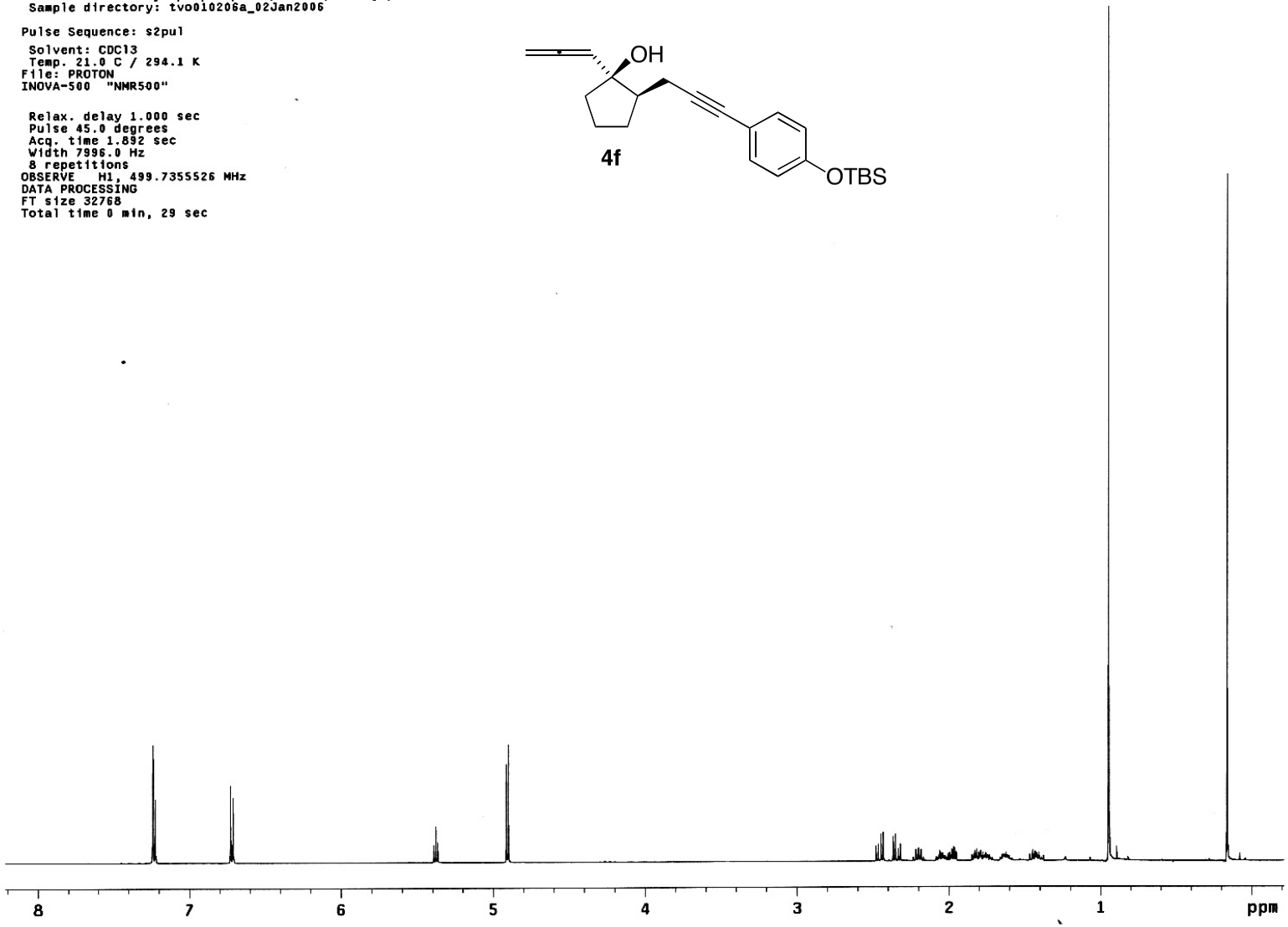
Archive directory: /export/home/TVOlab/vnmrsys/data
Sample directory: tvo010206a_02Jan2006

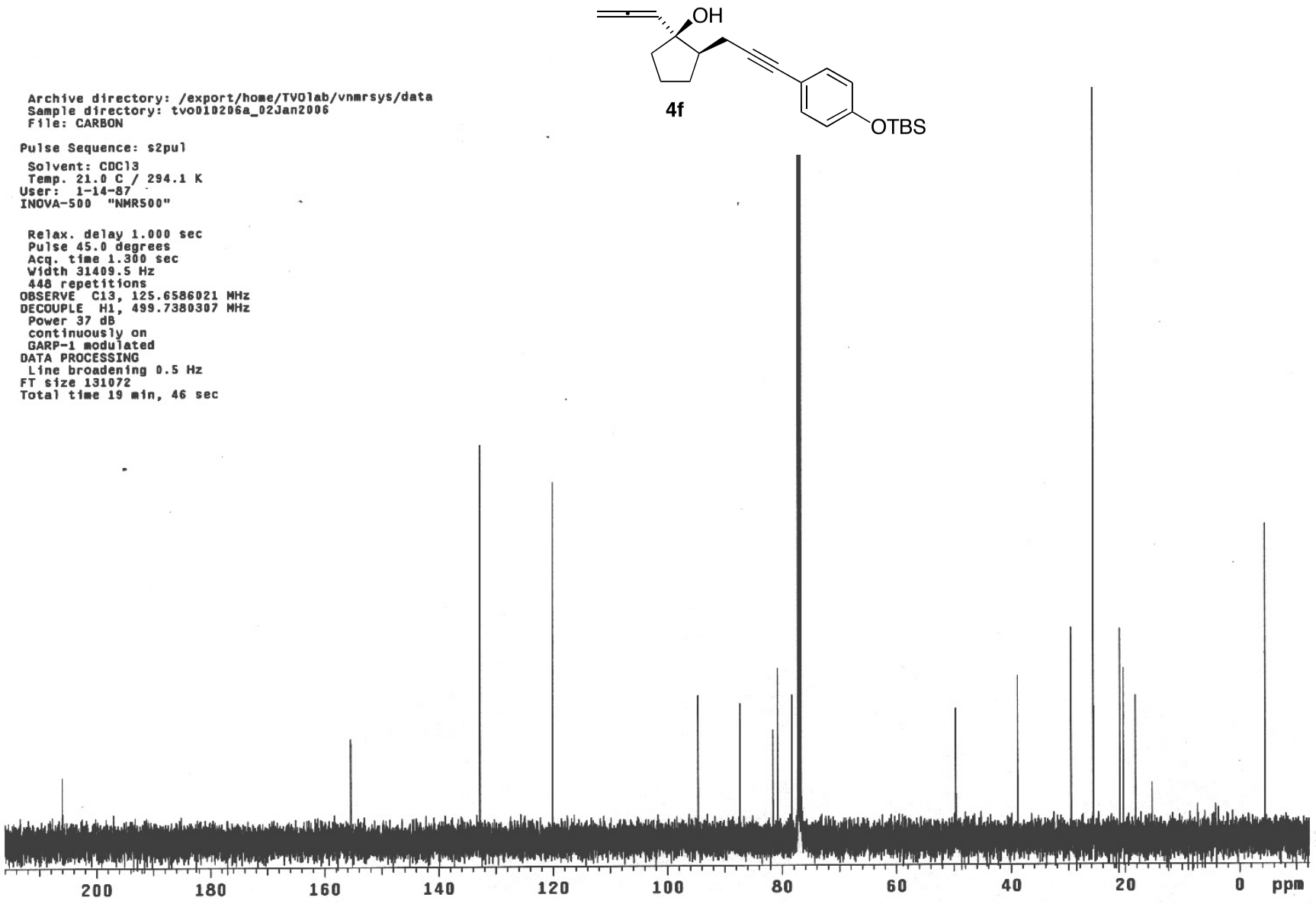
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 21.0 C / 294.1 K
File: PROTON
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7355526 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec

4f




OH
4f
OTBS
Archive directory: /export/home/TVOlab/vnmrsys/data
Sample directory: tvo010206a_02Jan2006
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 21.0 C / 294.1 K
User: 1-14-87
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
448 repetitions
OBSERVE C13, 125.6586021 MHz
DECOUPLE H1, 499.7380307 MHz
Power 37 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 46 sec
200
180
160
140
120
100
80
60
40
20
0
ppm

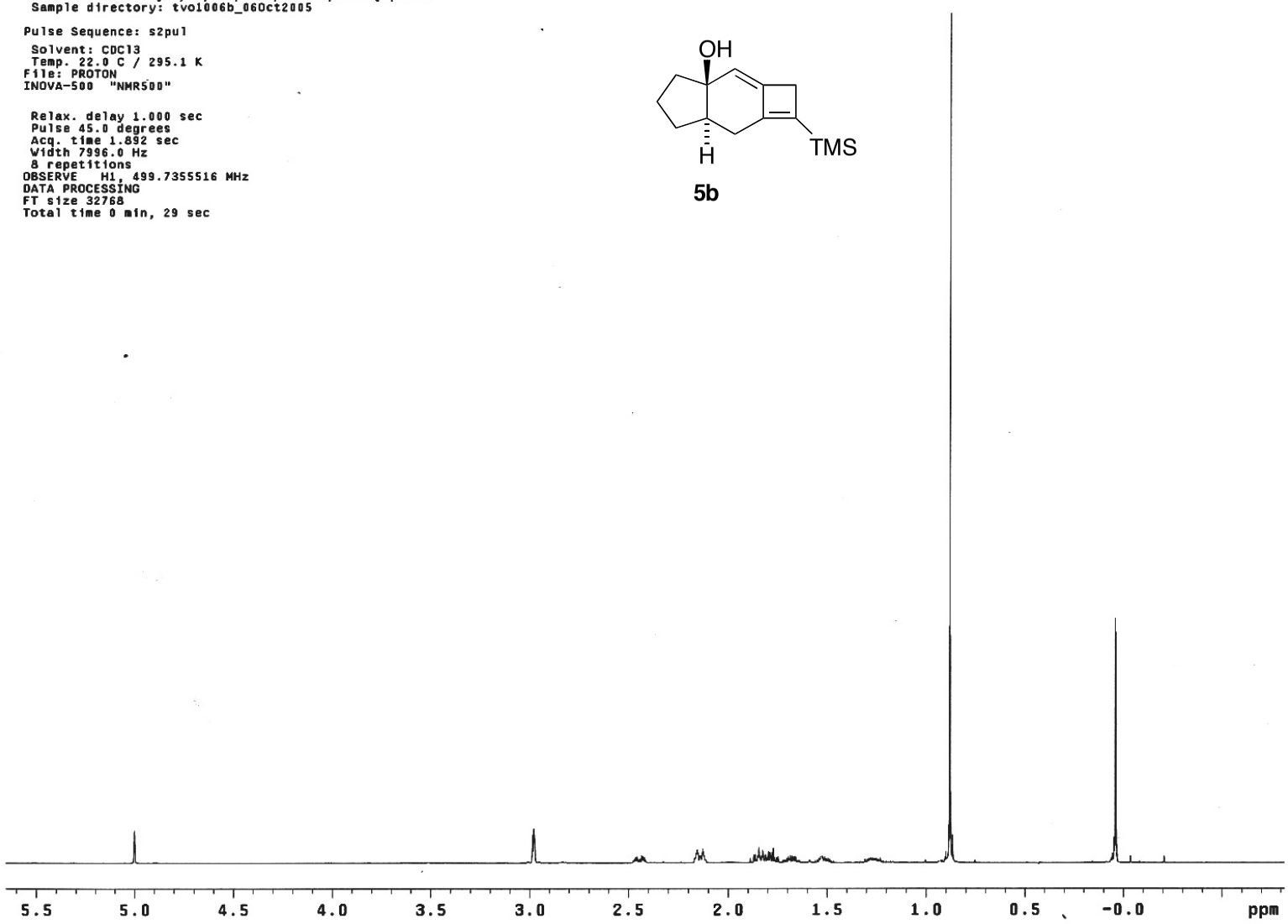
Archive directory: /export/home/TVOlab/vnmrsys/data
Sample directory: tvo1006b_06Oct2005

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: PROTON
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7355516 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec

5b



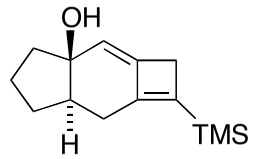
TMS derivative

Archive directory: /export/home/TVOlab/vnmrsys/data
Sample directory: tvo1007a_07Oct2005
File: CARBON

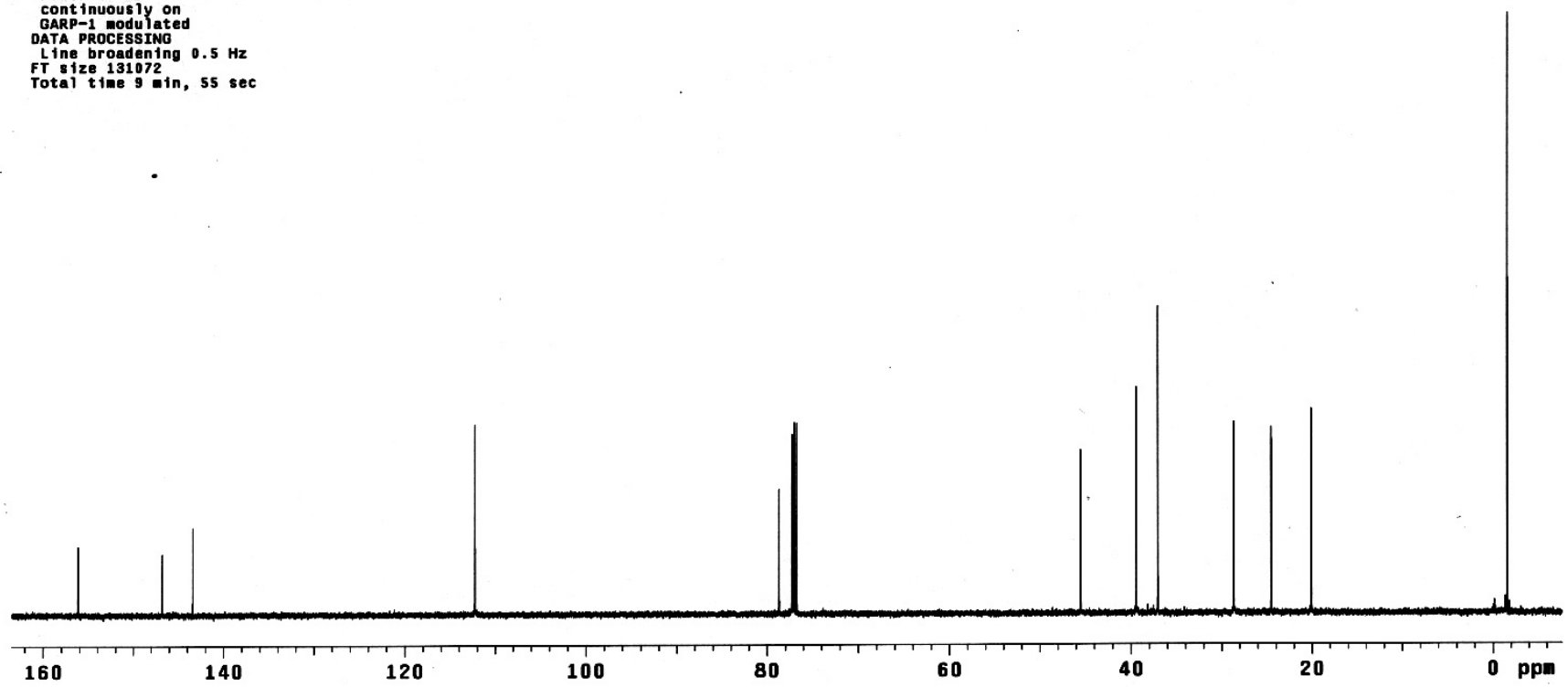
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 22.0 C / 295.1 K
User: 1-14-87
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31489.5 Hz
256 repetitions
OBSERVE C13, 125.6586031 MHz
DECOUPLE H1, 499.7380307 MHz
Power 40 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 9 min, 55 sec



5b



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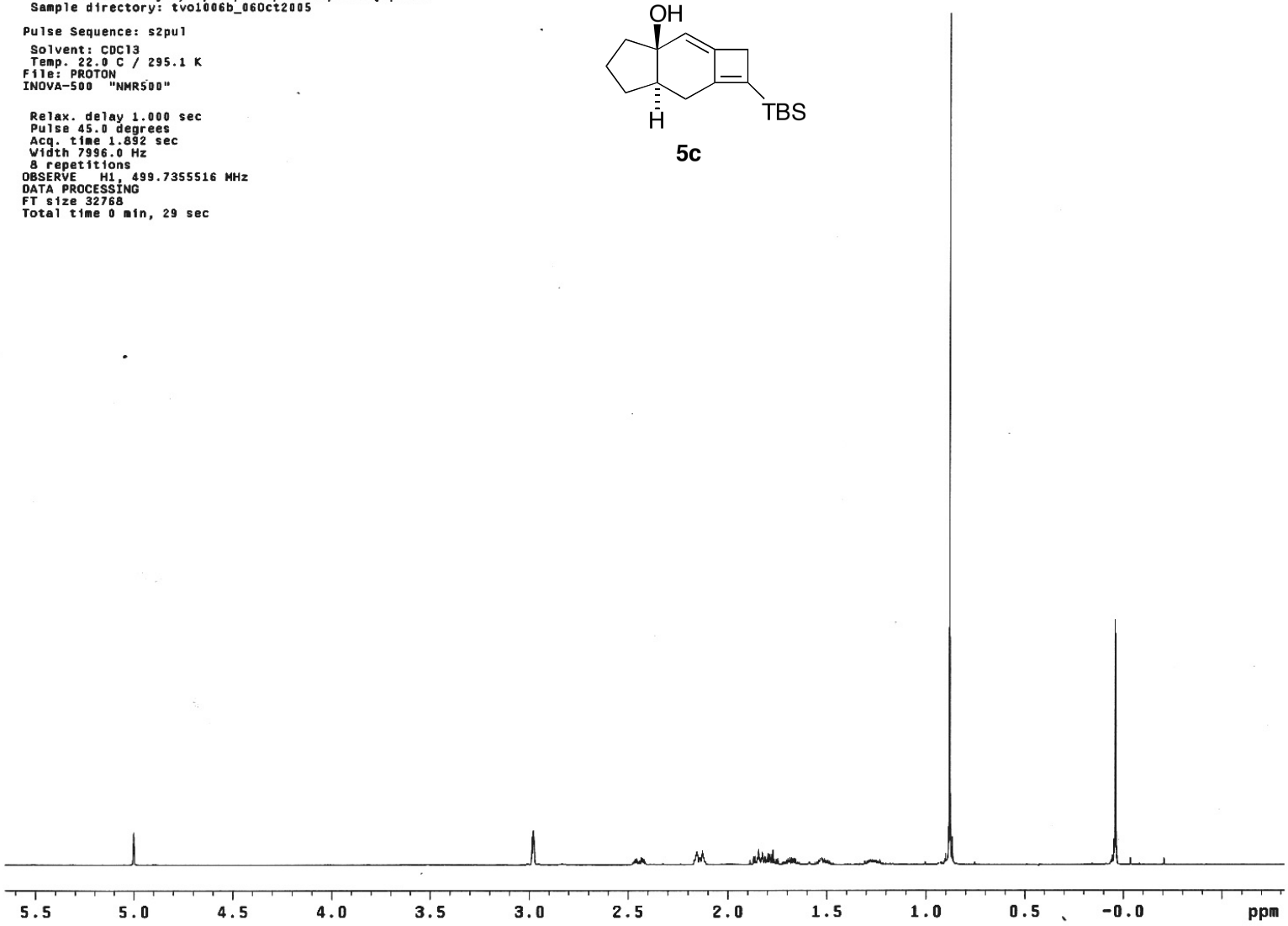
Sample directory: tvo1006b_06Oct2005

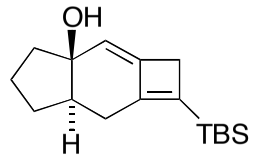
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: PROTON
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.0 Hz
8 repetitions
OBSERVE H1, 499.7355516 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec

5c

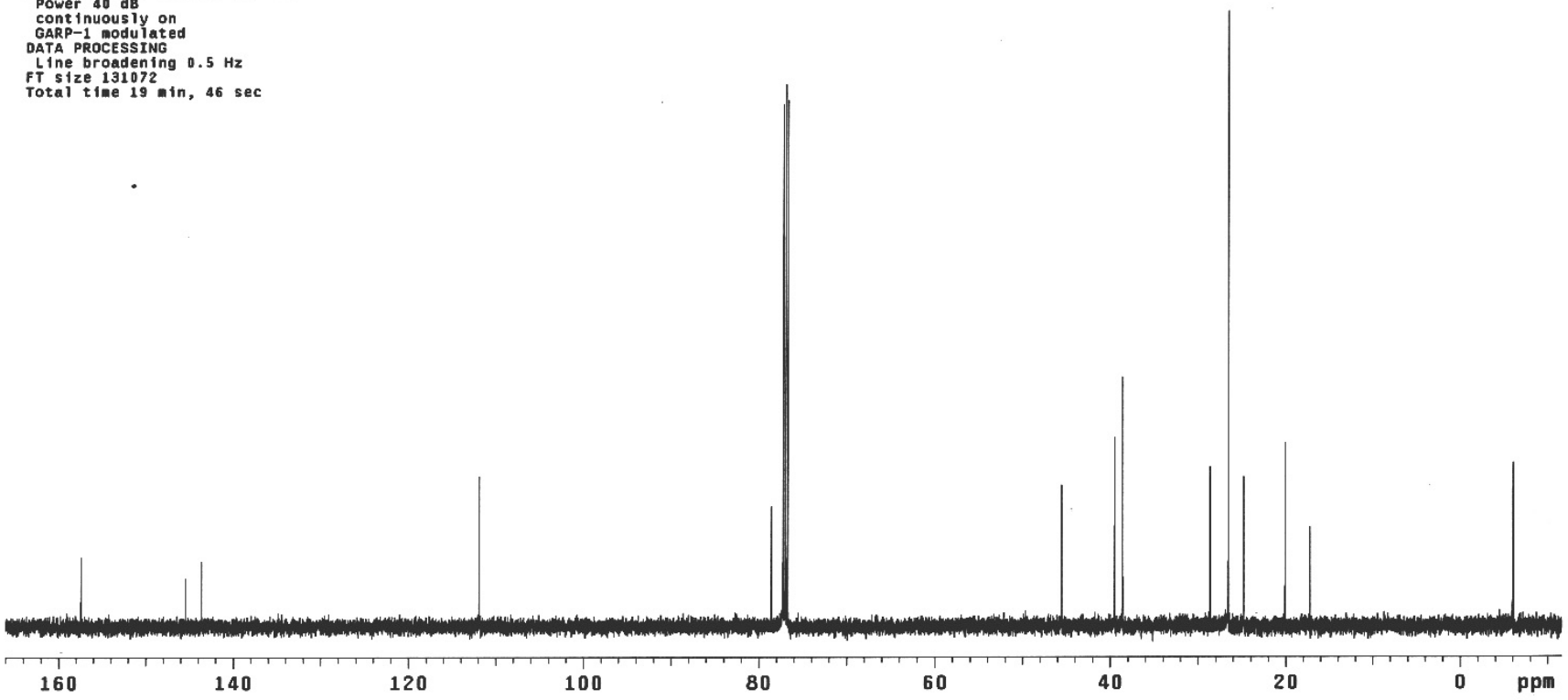


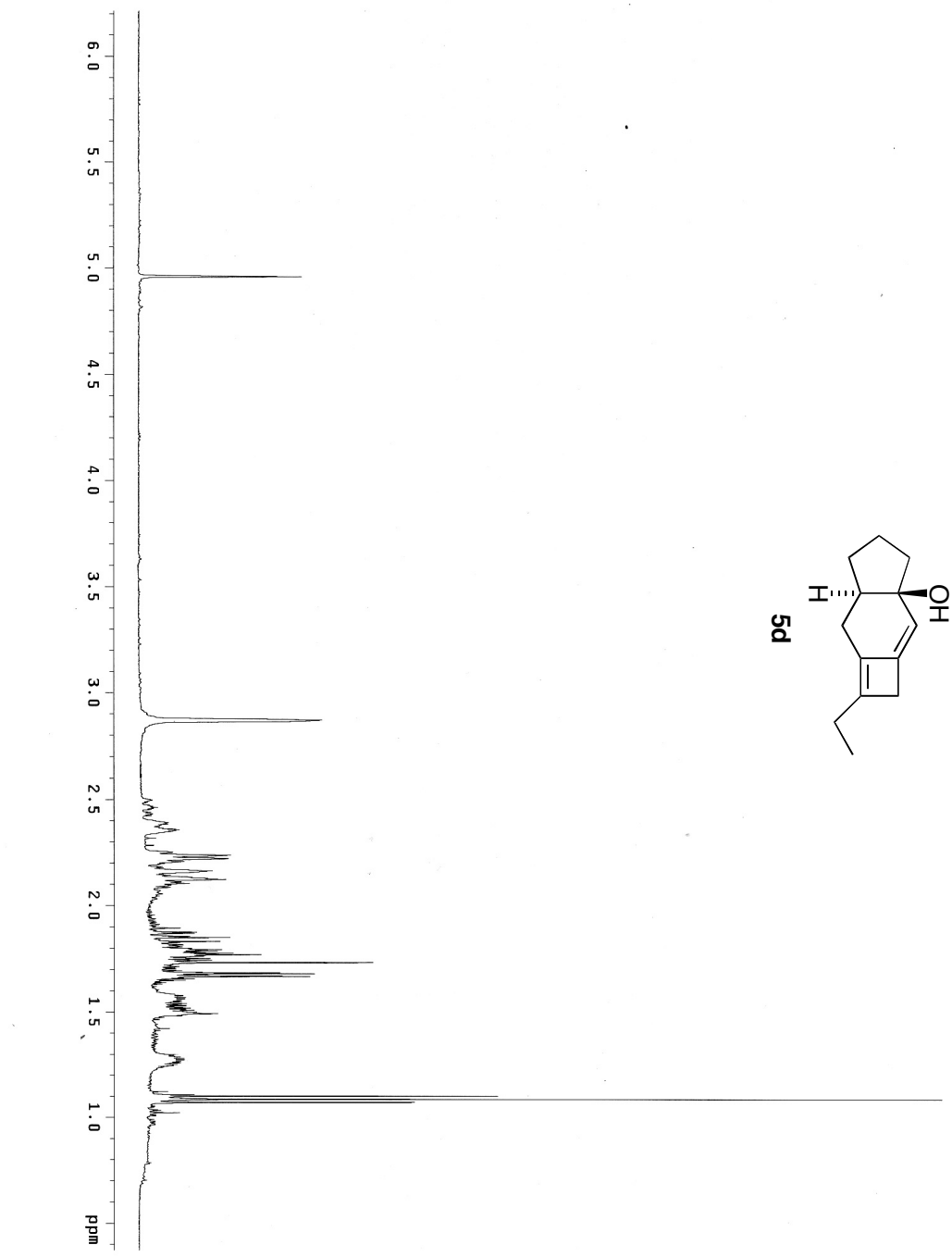


5c

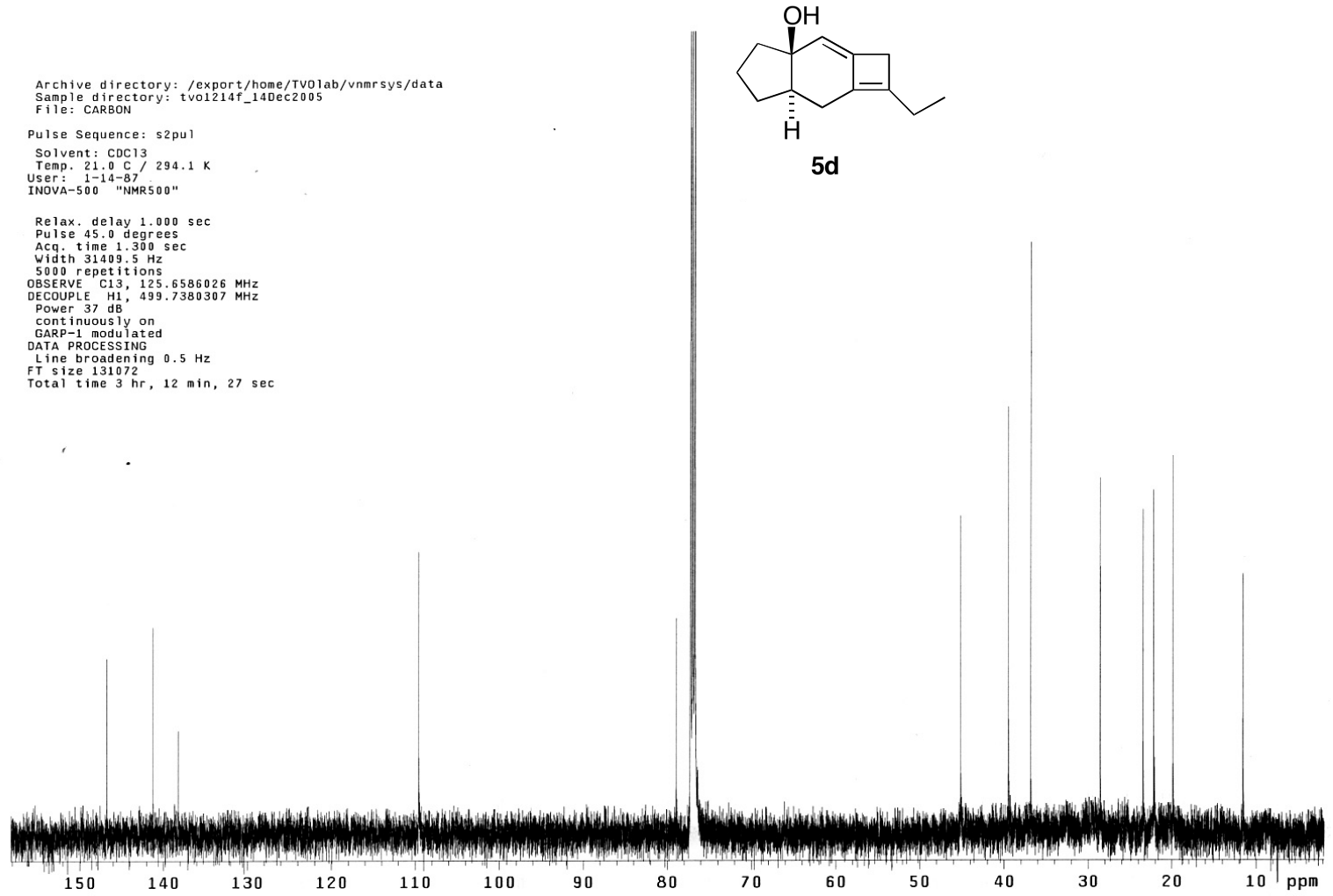
```
Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 22.0 C / 295.1 K
User:  1-14-87
INOVA-500  "NMR500"

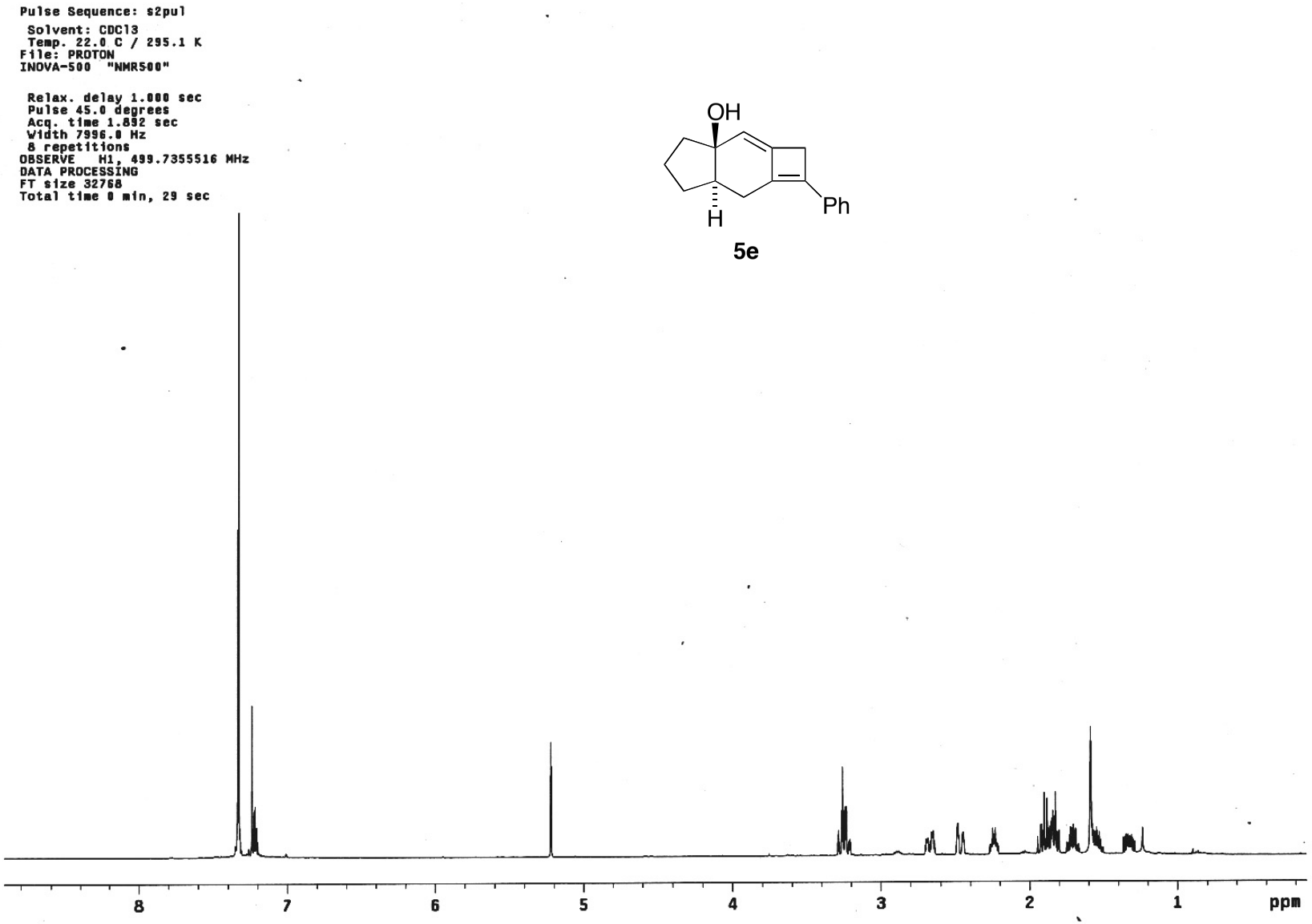
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 31409.5 Hz
 192 repetitions
OBSERVE  C13, 125.6586021 MHz
DECOUPLE  H1, 499.7380307 MHz
 Power 40 dB
 continuously on
 GARP-1 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 46 sec
```

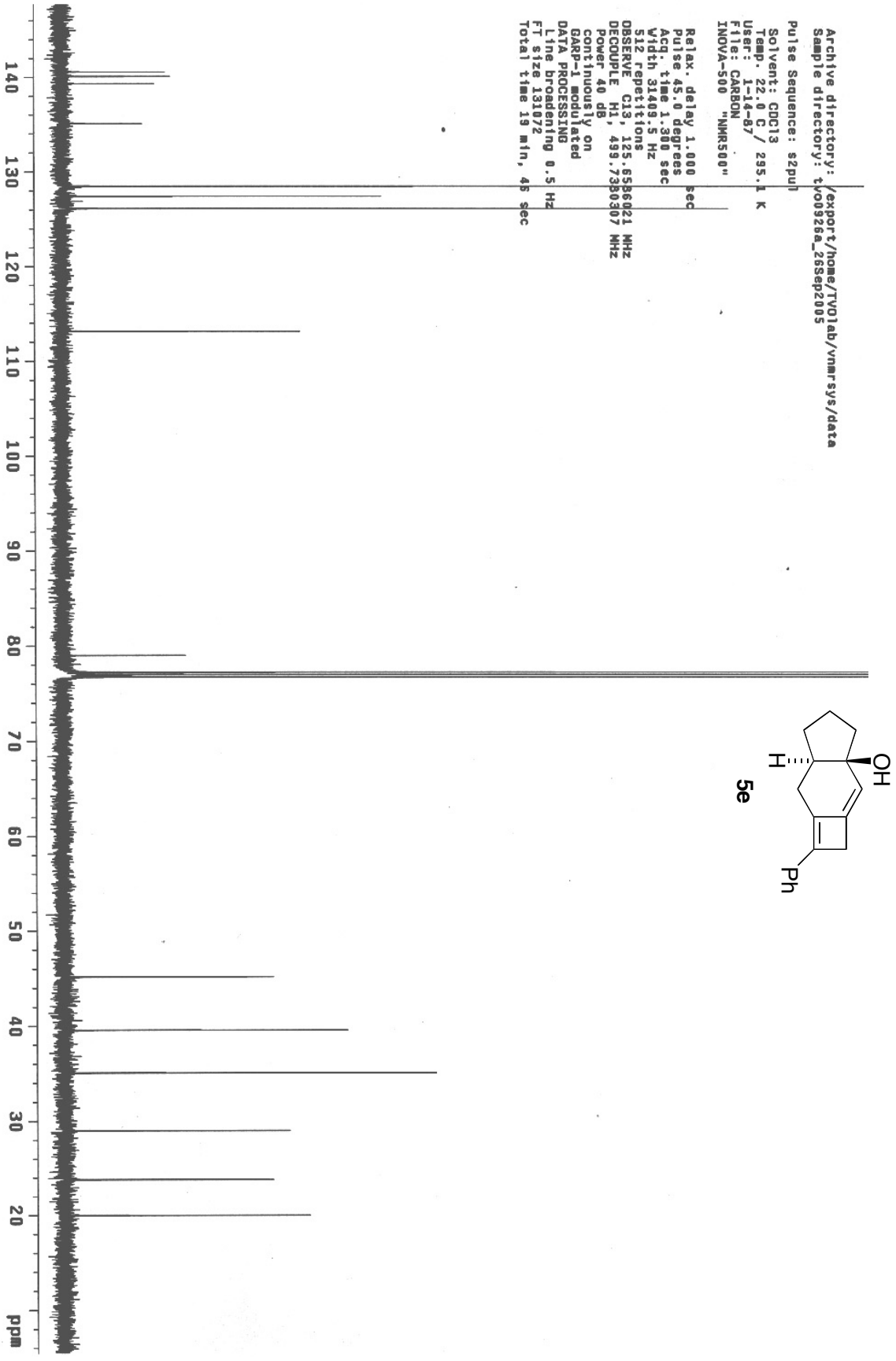




5d


Archive directory: /export/home/TVOlab/vnmrsys/data
Sample directory: tvol214f_14Dec2005
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 21.0 C / 294.1 K
User: 1-14-87
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
5000 repetitions
OBSERVE C13, 125.6586026 MHz
DECOUPLE H1, 499.7380307 MHz
Power 37 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 3 hr, 12 min, 27 sec
OH
H
5d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C / 295.1 K
File: PROTON
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.852 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.7355516 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 29 sec
OH
Ph
H
5e
8
7
6
5
4
3
2
1
ppm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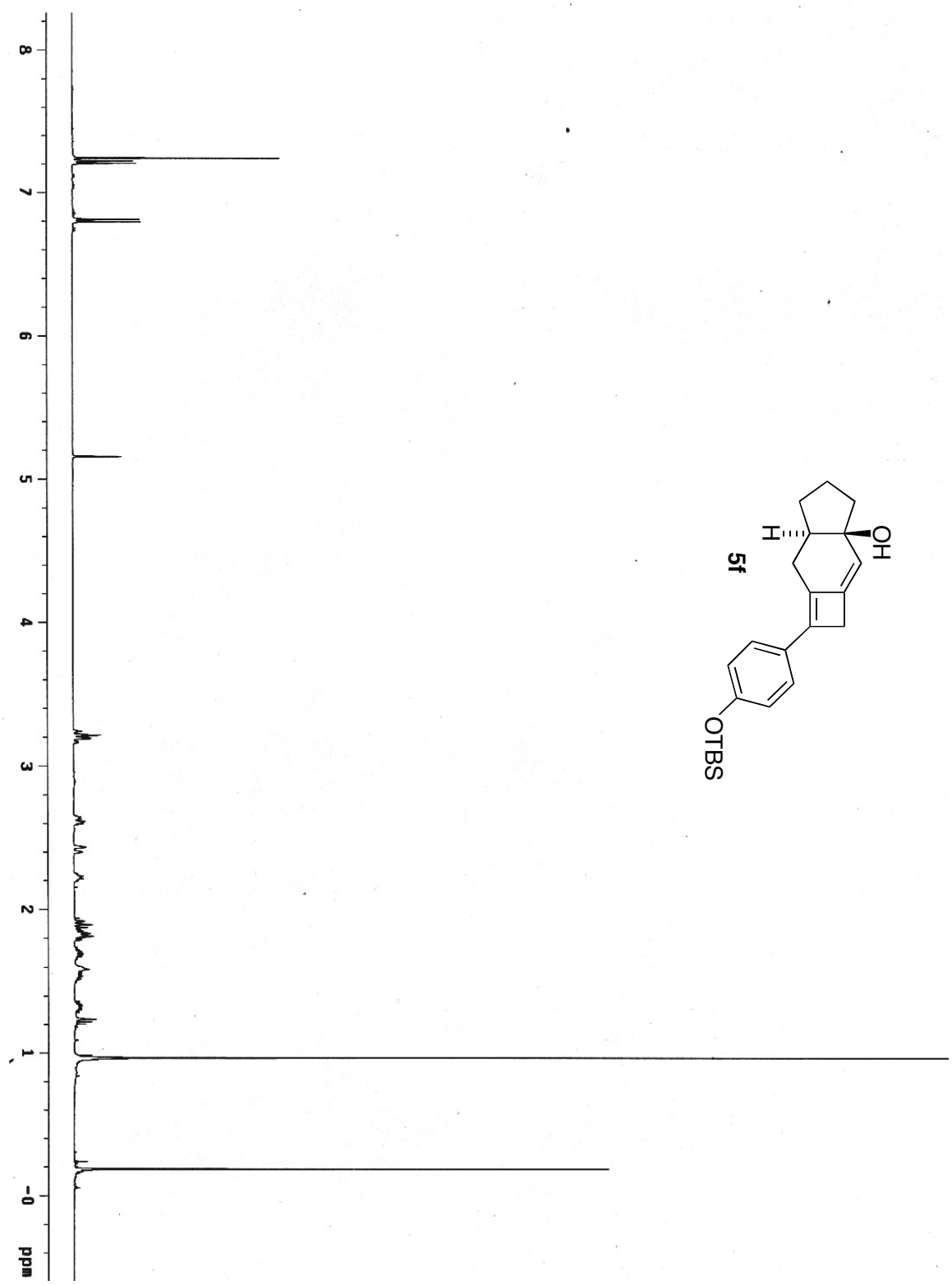
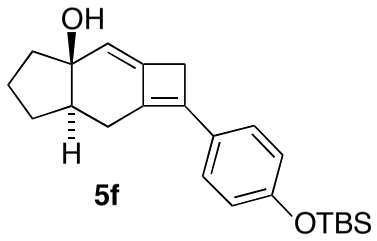
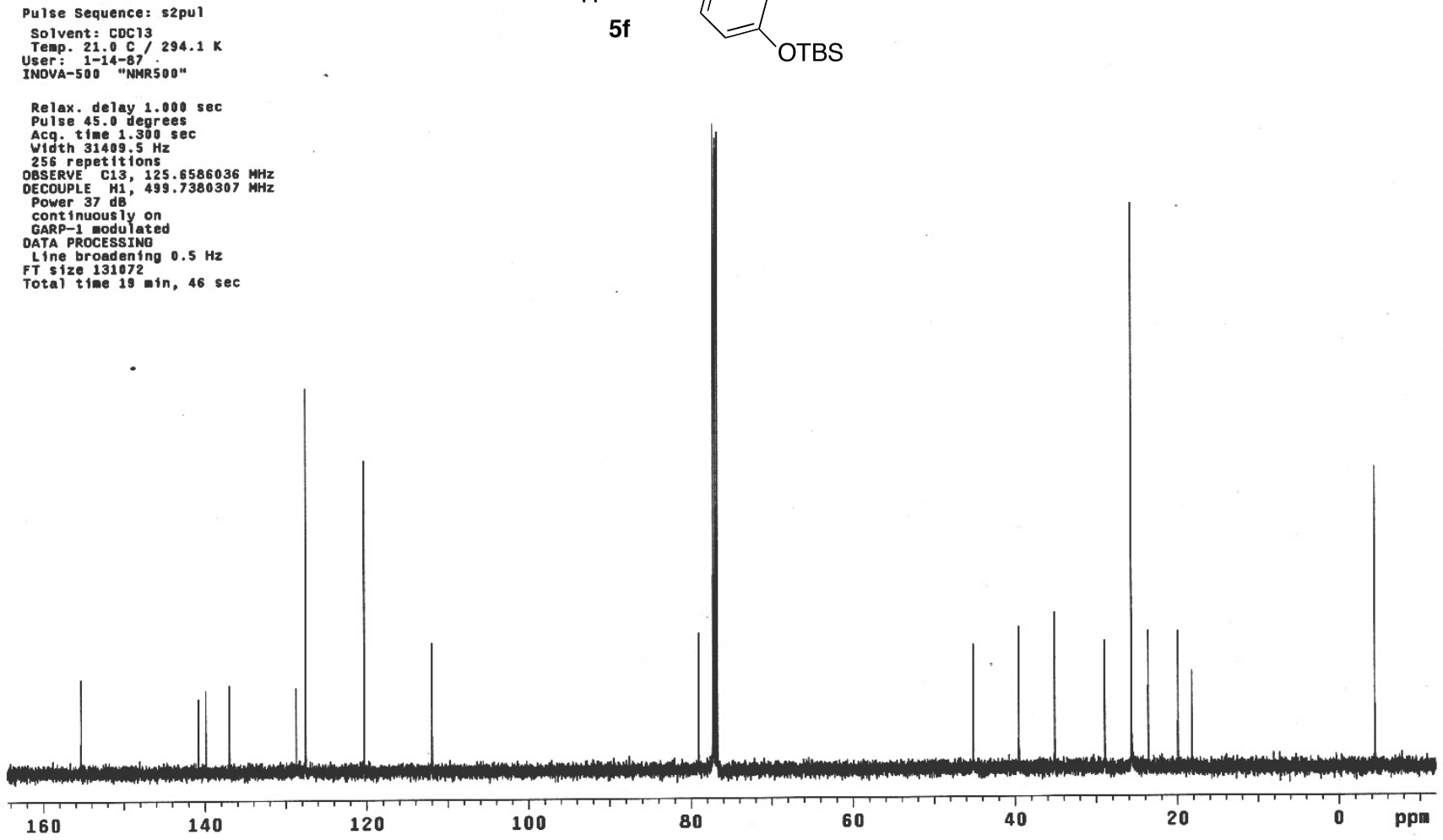
Sample directory: tvo0926a_26Sep2005
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 22.0 C./ 295.1 K
User: 1-14-87
File: CARBON
INOVA-500 "NMRS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
512 repetitions
OBSERVE C13, 125.6586021 MHz
DECOUPLE H1, 499.7380307 MHz
Power 40 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 45 sec
OH
H
Ph
5e
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OH
H
5f
OTBS
8
7
6
5
4
3
2
1
-0
ppm


OH
H
OTBS

5f


Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 21.0 C / 294.1 K
User: 1-14-87
INOVA-500 "NMR500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31409.5 Hz
256 repetitions
OBSERVE C13, 125.6586036 MHz
DECOUPLE H1, 499.7380307 MHz
Power 37 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min, 46 sec
160
140
120
100
80
60
40
20
0
ppm

Compound **4a**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.30 (t, J=6.59 Hz, 1 H), 4.88 (d, J=6.34 Hz, 2 H), 2.28 – 2.38 (m, 1 H), 2.22 – 2.27 (m, 1 H), 2.10 - 2.16 (m, 2 H), 1.98 - 2.04 (m, 1 H), 1.95 – 1.98 (m, 1 H), 1.90 - 1.95 (m, 1 H), 1.68 -1.82 (m, 2 H), 1.54 - 1.62 (m, 1 H), 1.32 – 1.40 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.00, 94.45, 83.45, 80.62, 78.33, 69.32, 49.28, 38.81, 29.34, 20.17, 19.88. HRMS calc'd for $C_{11}H_{13}O$ (M^+–1) 161.0966, found 161.0967.

Compound **4b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.30 (t, J=6.59 Hz, 1 H), 4.89 (d, J=6.34 Hz, 2 H), 2.58 (s, 1 H), 2.21 – 2.28 (m, 2 H), 2.08 – 2.16 (m, 1 H), 1.91 – 1.99 (m, 2 H), 1.77 – 1.84 (m, 1 H), 1.66 – 1.78 (m, 1 H), 1.52 – 1.62 (m, 1 H), 1.26 – 1.37 (m, 1 H), 0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.06, 106.19, 94.36, 86.36, 80.77, 78.20, 49.14, 38.68, 29.46, 21.22, 19.96, -0.03. HRMS calc'd for $C_{14}H_{21}OSi$ (M^+–1) 233.1362, found 233.1363.

Comopund **4c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.33 (t, J=6.59 Hz, 1 H), 4.90 (d, J=6.34 Hz, 2 H), 2.29 (dd, J=17.08, 8.30 Hz, 1 H), 2.23 (dd, J=16.59, 9.76 Hz, 1 H), 2.10 – 2.18 (m, 1 H), 1.90 – 2.05 (m, 2 H), 1.76 – 1.90 (m, 1 H), 1.68 – 1.76 (m, 1 H), 1.54 – 1.64 (m, 2 H), 1.30 – 1.40 (m, 1 H), 0.91 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.05, 106.72, 94.45, 84.41, 80.79, 78.24, 49.27, 38.74, 29.45, 26.06, 22.64, 21.27, 20.06, 16.47, -4.51. HRMS calc'd for $C_{17}H_{28}OSi$ 276.1910, found 276.1908.

Compound **4d**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.35 (t, J=6.83 Hz, 1 H), 4.87 (d, J=6.83 Hz, 2 H), 2.5 (br. s, 1 H), 2.02 - 2.21 (m, 5 H), 1.90 – 1.98 (m, 2 H), 1.75 – 1.83 (m, 1 H), 1.65 – 1.74 (m, 1 H), 1.52 - 1.60 (m, 1 H), 1.27 – 1.36 (m, 1 H), 1.09 (t, J=7.32 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.06, 94.45, 83.21, 80.78, 78.16, 78.01, 49.55, 38.66, 29.43, 20.07 (2 overlapping peaks), 14.19, 12.43. HRMS calc'd for $C_{13}H_{18}O$ 190.1358, found 190.1358.

Compound **4e**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 - 7.42 (m, 2 H), 7.26 - 7.31 (m, 3 H), 5.41 (t, J=6.59 Hz, 1 H), 4.91 (d, J=6.35 Hz, 2 H), 2.52 (dd, J=16.59, 7.32 Hz, 1 H), 2.39 (dd, J=17.08, 7.81 Hz, 1 H), 2.21 - 2.32 (m, 2 H), 2.06 - 2.15 (m, 1 H), 1.98 - 2.05 (m, 1 H), 1.74 - 1.91 (m, 2 H), 1.62 - 1.72 (m, 1 H), 1.43 - 1.53 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.02, 131.47, 128.21, 127.70, 123.61, 94.67, 88.88, 81.70, 80.77, 78.38, 49.61, 38.90, 29.51, 21.00, 20.39. HRMS calc'd for $C_{17}H_{16}$ (M^+–H_2O) 220.1252, found 220.1254.

Compound **4f**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (d, J=8.30 Hz, 2 H), 6.75 (d, J=8.30 Hz, 2 H), 5.41 (t, J=6.59 Hz, 1 H), 4.90 (d, J=6.83 Hz, 2 H), 2.48 (dd, J=16.6 Hz, 8.30 Hz, 1 H), 2.37 (dd, J=17.08, 6.83 Hz, 1 H), 2.32 (s, 1 H), 2.19 - 2.27 (m, 1 H), 2.08 (dddd, J=12.63, 8.66, 8.48, 3.90 Hz, 1 H), 1.96 – 2.04 (m, 1 H), 1.80 – 1.89 (m, 1 H), 1.73 – 1.81 (m, 1 H), 1.60 – 1.70 (m, 1 H), 1.39 – 1.51 (m, 1 H), 0.98 (s, 9 H), 0.19 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.04, 155.46, 132.79, 120.09, 94.67, 87.33, 81.59, 80.80, 78.33, 49.65, 38.87, 29.53, 29.49, 25.63, 20.96, 20.35, 18.20, -4.44. HRMS calc'd for $C_{23}H_{30}OSi$ (M^+–H_2O) 350.2066, found 350.2068.

Compound **5b**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.04 (s, 1 H), 2.92 - 3.00 (m, 2 H), 2.40 - 2.51 (m, 1 H), 2.11 - 2.21 (m, 2 H), 1.82 - 1.92 (m, 2 H), 1.75 - 1.82 (m, 1 H), 1.65 - 1.75 (m, 1 H), 1.61 (s, 1 H), 1.48 - 1.60 (m, 1 H), 1.23 - 1.35 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.17, 146.77, 143.38, 112.23, 78.69, 45.51, 39.41, 37.06, 28.67, 24.52, 20.10, -1.56. HRMS calc'd for $C_{14}H_{22}OSi$ 234.1440, found 234.1334.

Compound **5c**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.00 - 5.06 (m, 1 H), 2.96 - 3.06 (m, 2 H), 2.43 - 2.52 (m, 1 H), 2.13 - 2.21 (m, 2 H), 1.77 - 1.93 (m, 3 H), 1.66 - 1.76 (m, 1 H), 1.49 - 1.60 (m, 2 H), 1.25 - 1.35 (m, 1 H), 0.91 (s, 9 H), 0.07 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.45, 145.46, 143.63, 111.90, 78.60, 45.54, 39.49, 38.60, 28.63, 26.53, 24.80, 20.07, 17.24, -5.97, -6.06. HRMS calc'd for $C_{17}H_{22}Si$ (M^+–H_2O) 258.1804, found 258.1800.

Compound **5d**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.98 (s, 1 H), 2.84 - 2.94 (m, 2 H), 2.30 - 2.43 (m, 1 H), 2.13 – 2.29 (m, 3 H), 1.84 - 1.95 (m, 3 H), 1.73 - 1.84 (m, 1 H), 1.62 - 1.74 (m, 1 H), 1.44 - 1.61 (m, 2 H), 1.23 - 1.33 (m, 1 H), 1.10 (t, J=7.57 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.78, 141.23, 138.21, 109.58, 78.94, 45.13, 39.49, 36.82, 28.57, 23.45, 22.20, 19.87, 11.56.

Compound **5e**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 – 7.39 (m, 3 H), 7.20 - 7.30 (m, 2 H), 5.25 (s, 1 H), 3.17 - 3.37 (m, 2 H), 2.65 - 2.75 (m, 1 H), 2.45 - 2.54 (m, 1 H), 2.22 - 2.32 (m, 1 H), 1.81 - 2.00 (m, 3 H), 1.68 - 1.79 (m, 1 H), 1.52 - 1.66 (m, 2 H), 1.30 - 1.41 (m, 1 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.57, 140.11, 139.34, 135.06, 128.49, 127.43, 126.13, 113.15, 79.02, 45.20, 39.57, 35.06, 28.99, 23.82, 20.00. HRMS calc'd for $C_{17}H_{18}O$ 238.1356, found 238.1358.

Compound **5f**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (d, *J*=8.54 Hz, 2 H), 6.83 (d, *J*=8.54 Hz, 2 H), 5.19 (s, 1 H), 3.17 - 3.31 (m, 2 H), 2.60 - 2.70 (m, 1 H), 2.40 - 2.50 (m, 1 H), 2.20 - 2.30 (m, 1 H), 1.80 - 1.99 (m, 2 H), 1.67 - 1.78 (m, 1 H), 1.51-1.66 (m, 2 H), 1.30 - 1.40 (m, 1 H), 1.22 - 1.29 (m, 1 H), 0.97 (s, 9 H), 0.19 (s, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.32, 140.77, 139.90, 136.98, 128.68, 127.49, 120.27, 111.97, 79.05, 45.16, 39.55, 35.11, 28.95, 25.66, 23.60, 19.95, 18.24, -4.40. HRMS calc'd for $C_{23}H_{30}OSi$ (M^+–H_2O) 350.2066, found 350.2066