Supplementary Information

Enantioselective Synthesis of *Anomala Osakana* Pheromone and *Janus integer* Pheromone: A Flexible Approach to Chiral γ-Butyrolactones

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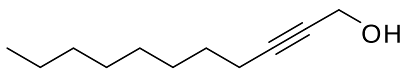
1. General Methods.

All reactions were carried out under an argon atmosphere and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC). Column chromatography purifications were carried out using silica gel. All solvents and reagents were freshly distilled before used. Diethylzinc was prepared from EtI with Zn, and then was diluted with toluene to 1.0 M. ^{1}H and ^{13}C NMR spectral measurements were measured on a 300-Bruker spectrometer with TMS as an internal standard. Optical rotations were recorded on a Perkin–Elmer 341 polarimeter. The ESI-MS was recorded on a Mariner biomassspectrometer. The ee value determination was carried out using chiral HPLC with a Daicel Chiracel OD-H column on Waters with a 996 UV-detector.

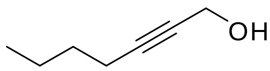
2. General preparation of propargylic alcohol 4:

To a solution of propargyl alcohol (**3**, 1.12 g, 20 mmol) in tetrahydrofuran (THF, 30 ml) and hexamethylphosphoric triamide (HMPA, 8 ml) was added *n*-BuLi (1.5 M in hexane, 26.7 ml, 40 mmol) at -78 °C. After the reaction temperature was warmed to -30 °C, 1-bromooctane or 1-bromobutane (15 mmol) was added to the mixture and stirred at room temperature overnight. The reaction mixture was treated with aqueous saturated NH_4Cl and extracted with EtOAc. The organic extract was washed with brine and dried over anhy. Na_2SO_4. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography (PE : EA = 9:1) to afford **4** as colorless oil.



4a

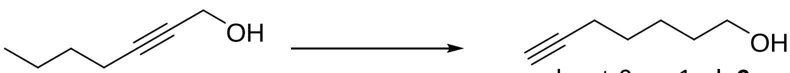
Undec-2-yn-1-ol (4a): 1.76g, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.25 (2H, t, *J* = 2.1 Hz), 2.21 (2H, tt, *J* = 2.1, 7.2 Hz), 1.67 (1H, bs), 1.51 (2H, m), 1.39-1.27 (10H, m), 0.88 (3H, t, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 86.6, 78.2, 51.4, 31.8, 29.2, 29.1, 28.9, 28.6, 22.6, 18.7, 14.1. EI-MS (*m*/*z*): 168 (M^+), 111 (M^+−57), 99 (M^+−69), 97 (M^+−71), 85 (M^+−83), 83 (M^+−85), 71 (M^+−97), 69 (M^+−99).



4b

Hept-2-yn-1-ol, 4b: 1.19g, 71% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.25 (2H, s), 2.22 (2H, tt, *J*= 2, 7 Hz), 1.69 (1H, br), 1.55-1.35 (4H, m), 0.91 (3H, t, *J*= 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 86.6, 78.2, 51.4, 30.6, 21.9, 18.4, 13.5. EI-MS (*m*/*z*): 112 (M^+), 111 (M^+−1), 95 (M^+−17), 81 (M^+−31), 67 (M^+−45).

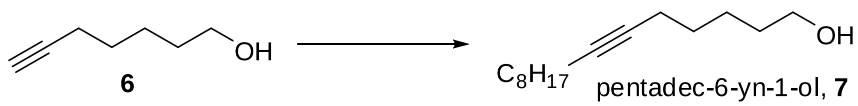
3. Zipper isomerization for the preparation of 6:



4b hept-6-yn-1-ol, **6**

The mixture of Li (0.56 g, 80 mmol) in 1,3-diaminopropane (30 ml) was stirred and heated in an oil bath at 70°C until the blue color discharges (1 h), affording a white suspension of the lithium amide. After cooling to room temperature, potassium tert-butoxide (5.3 g, 48 mmol,) was added to the mixture. The resultant pale yellow solution is stirred for 20 min at room temperature, and then **4b** (0.9 g, 8 mmol) was added. Residual **4b** was washed into the mixture with small portion of 1,3-diaminopropane. After stirring at room temperature for 3h, the reaction mixture was poured into plenty of ice-water and extracted with Et_2O for three times. The organic phase was combined and washed with 5% aqueous HCl and brine, then dried over anhy. Na_2SO_4. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography (PE : EA = 7:1) to afford **6** (0.82 g, 90%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.65 (2H, t, *J*= 6 Hz), 2.21 (2H, td, *J*= 3, 6.9 Hz), 1.96 (1H, t, *J*= 3 Hz), 1.64-1.55 (5H, m), 1.53-1.45 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 84.4, 68.3, 62.7, 32.1, 28.1, 24.8, 18.3. EI-MS (*m*/*z*): 112 (M^+), 111 (M^+−1), 97 (M^+−15), 95 (M^+−17), 83 (M^+−29), 81 (M^+−31), 69 (M^+−43), 57 (M^+−55), 55 (M^+−57).

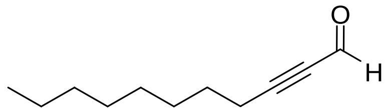
4. Coupling reaction of 6 with 1-bromooctane for the preparation of 7:



The ratio of **6**, 1-bromooctane and *n*-BuLi was 1:1:1. Using a similar producture as the preparation of **4** afforded **7** in 90% yield base on 40% of the recovered **6**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.65 (2H, t, *J*= 6 Hz), 2.19-2.10 (4H, m), 1.63-1.54 (2H, m), 1.52-1.42 (6H, m), 1.40-1.33 (3H, m), 1.27 (8H, m), 0.88 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 80.5, 79.8, 62.9, 32.3, 31.8, 29.2, 29.1, 28.7, 24.9, 24.1, 22.6, 18.71, 18.70, 14.1. ESI-MS: $[M+Na]^+$ 247.2.

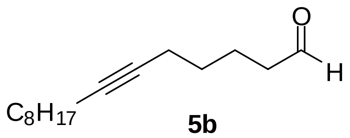
5. Swern oxidation for the preparation of 5:

Oxalyl chloride (0.52 ml, 6 mmol, 1.2 equiv) was added to dry DCM (20 mL) and cooled to −60°C under Ar. Dry DMSO (085 ml, 12 mmol, 2.4 equiv) was then added to the oxalyl chloride solution in drop wise. After stirring for 5mins, the solution of **4a** or **7** in 10 ml DCM was added to the mixture in 1min. The resulting cloudy white mixture was stirred for 15 min at −60°C. TEA 3.5 mL, 25 mol, 5.0 equiv) was added and the solution was stirred for 15 min at −60°C and 10 min at 0°C. Ice-water was added to quench the reaction and extracted with DCM for three times. The organic phase was combined and washed with 5% aqueous HCl and brine, then dried over anhy. Na_2SO_4. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography (PE : EA = 15:1) to afford **5**.



5a

Undec-2-ynal (5a): yellow oil, 0.63g, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.18 (1H, s), 2.41 (2H, t, *J* = 7.2 Hz), 1.65-1.55 (2H, m), 1.43-1.36 (2H, m), 1.28 (8H, m), 0.89 (3H, t, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.3, 99.4, 81.7, 31.8, 29.1, 29.0, 28.8, 27.5, 22.6, 19.1, 14.1. EI-MS (*m*/*z*): 166 (M^+), 165 (M^+−1), 137 (M^+−29), 123 (M^+−43), 109 (M^+−67), 95 (M^+−71), 81 (M^+−85), 71 (M^+−95), 67 (M^+−99).

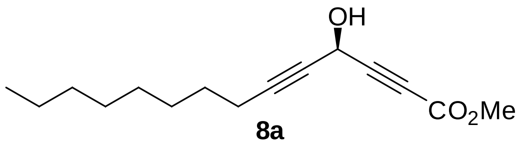


5b

Pentadec-6-ynal (5b): colorless oil, 0.81 g, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.78 (1H, t, *J*= 2 Hz), 2.46 (2H, td, *J*= 2, 7.2 Hz), 2.22-2.10 (4H, m) 1.75 (2H, q, *J*= 7.5 Hz), 1.57-1.42 (4H, m), 1.38-1.33 (2H, m), 1.27 (8H, m), 0.88 (3H, t, *J*= 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 202.5, 80.9, 79.2, 43.4, 31.8, 29.2, 29.1, 28.9, 28.4, 22.6, 21.2, 18.7, 18.5, 14.1. ESI-MS: $[M+Na]^+$ 245.2.

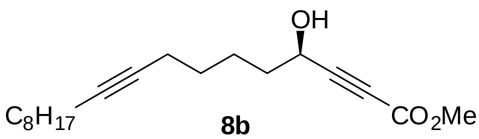
6. General procedure for the asymmetric addition of methyl propiolate to 5:

To a stirred solution of **L*** (21.6m g, 0.06 mmol, 30 mol %), DME (20.7 μL, 0.2 mmol) and Et_2Zn (0.4 mL, 0.4 mmol) in toluene (2 mL) under Ar, methyl propiolate (35.7 μL, 0.2 mmol) was added in one potion. After the solution has been stirred at 25℃ overnight, $Ti(O^iPr)_4$ (17.5 μL, 0.06 mmol, 30mol%) was added and stirred for 1h. Then, the aldehyde **5** (0.2 mmol) was added in one portion at 0°C. Ammonium chloride (saturated aq.) was added to quench the reaction until the reaction was complete (monitoring with TLC), and the mixture was extracted with methylene chloride and dried with sodium sulfate. After column chromatography on silica gel eluted with 10% ethyl acetate in hexanes, the optically active γ-hydroxy-α,β-acetylenic ester **8** was isolated. The enantiomeric purity of the product was determined by using HPLC.



8a

(*R*)-Methyl 4-hydroxytetradeca-2, 5-diynoate (8a): colorless oil, 80% yield. 84% ee was determined by HPLC analysis (OD column, 1.0mL/min, 3% i-PrOH in hexane); retention times: 17.5 min (major) and 19.4 min (minor). $[\alpha]^{20}_D$ = -4 (c = 1.31, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.21 (1H, bs), 3.80 (3H, s), 2.64 (1H, bs), 2.23 (2H, td, *J* = 2.1, 7.2 Hz), 1.57-1.47 (2H, m), 1.41-1.32 (2H, m), 1.27 (8H, m), 0.88 (3H, t, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.6, 87.5, 84.1, 75.2, 74.6, 52.9, 52.1, 31.8, 29.1, 29.0, 28.8, 28.1, 22.6, 18.6, 14.0. ESI-MS: $[M+Na]^+$ 273.1.



8b

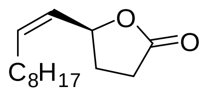
(*R*)-Methyl 4-hydroxyoctadeca-2, 9-diynoate (8b) colorless oil, 78% yield, 84% ee was determined by HPLC analysis (OD column, 1.0mL/min, 3% i-PrOH in hexane); retention times: 14.8 min (major) and 19.1 min (minor). $[\alpha]^{20}_D$ = -9 (c = 1.27, $CHCl_3$).^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.50 (1H, t, *J*= 6 Hz), 3.79 (3H, s), 2.20-2.10 (4H, m), 2.01 (1H, bs), 1.83-1.75 (2H, m), 1.63-1.53 (4H, m), 1.51-1.43 (2H, m), 1.38-1.33 (2H, m), 1.27 (8H, m), 0.88 (3H, t, *J*= 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 153.7, 88.0, 79.5, 76.3, 62.0, 52.8, 36.4, 31.8, 29.2, 29.1, 28.9, 28.6, 24.1, 22.6, 18.7, 18.6, 14.1. ESI-MS: $[M+Na]^+$ 329.2.

7. General procedure for the conversion of 8 to (4*S*, 5*Z*)-**1** or (4*R*, 9*Z*)-**2:**

Lindlar's Pd catalyst (5 wt.-% on $BaSO_4$, 20 mg) was added to a solution of **8** (0.2 mmol) in hexane (10 mL). The suspension was vigorously stirred under H_2 (1 atm) for 2h until the reaction completed (monitored by ^{1}H NMR). The catalyst was then removed by filtration through a small portion of Celite®, and washed with hexane. The hexane solution was concentrated in vacuo and used for the next step without purification.

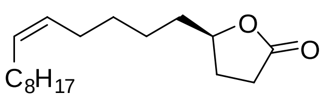
CuCl (21.9 mg, 1.1 equiv relative to the amount of **8** in the first) was added to the stirred solution of the above residue in 5 ml of MeOH. After cooling to 0℃. $NaBH_4$ (38 mg, 5 equiv) was added to the mixture in small portions until the reduction completed (monitored by TLC, 0.5 h). 1 ml 2M HCl was then added to quench the reaction. The mixture was extracted with EtOAc (5 ml × 3) and washed with brine, then dried over anhy. Na_2SO_4. The solvent was evaporated under vacuum to afford **10**.

The residue obtained from the above step was added 10 ml benzene and 3mg TsOH • H_2O. The mixture was heated at reflux for 2h. After the lactonization completed, benzene was evaporated under vacuum and diluted with Et_2O. The organic phase was washed with 5% aqueous $NaHCO_3$, 5% aqueous HCl and brine, then dried over anhy. Na_2SO_4. The solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography (PE : EA = 9:1), and afforded (4*S*, 5*Z*)-**1** or (4*R*, 9*Z*)-**2** as both colorless oil.



(4*S*, 5*Z*)-**1,** *Anomala Osakana* Pheromone

(4*S*, 5*Z*)-**1**: 87 % overall yield. $[\alpha]^{20}_D$ = +49 (c = 1.14, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.67 (1H, dtd, *J* = 0.9, 7.5, 10.8 Hz), 5.46 (1H, tt, *J* = 1.5, 10.8 Hz), 5.25 (1H, dtd, *J* = 0.9, 8.4, 6.6 Hz), 2.60-2.54 (2H, m), 2.43-2.33 (1H, m), 2.19-2.04 (2H, m), 2.01-1.88 (1H, m), 1.39-1.35 (1H, m), 1.39-1.26 (11H, m), 0.88 (3H, t, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.2, 135.9, 127.2, 76.4, 31.8, 29.4, 29.3, 29.2, 29.0, 27.8, 22.6, 14.1. HRMS (ESI): calcd. for C14H24O2 $[M+Na]^+$ 247.1699, found 247.1700, error = 0.4 ppm. Lit.[1]: $[\alpha]^{26}_D$ = +70.5 (c = 5.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ: 0.85 (t, *J* = 6.8 Hz, 3H), 1.20-1.30 (12H, m), 2.02-2.14 (2H, m), 2.31-2.39 (1H, m), 2.49–2.56 (2H, m), 5.22 (1H, tdd, *J* = 8.3, 6.6, 1.0 Hz), 5.42 (1H, ddt, *J* = 10.7, 8.6, 1.5 Hz), 5.64 (1H, dtd, *J* = 10.9, 7.7, 1.0 Hz). ^{13}C NMR ($CDCl_3$) d 14.48, 23.05, 28.23, 29.41, 29.60, 29.63, 29.71, 29.80, 29.82, 32.26, 76.83, 127.64, 136.25, 177.52.



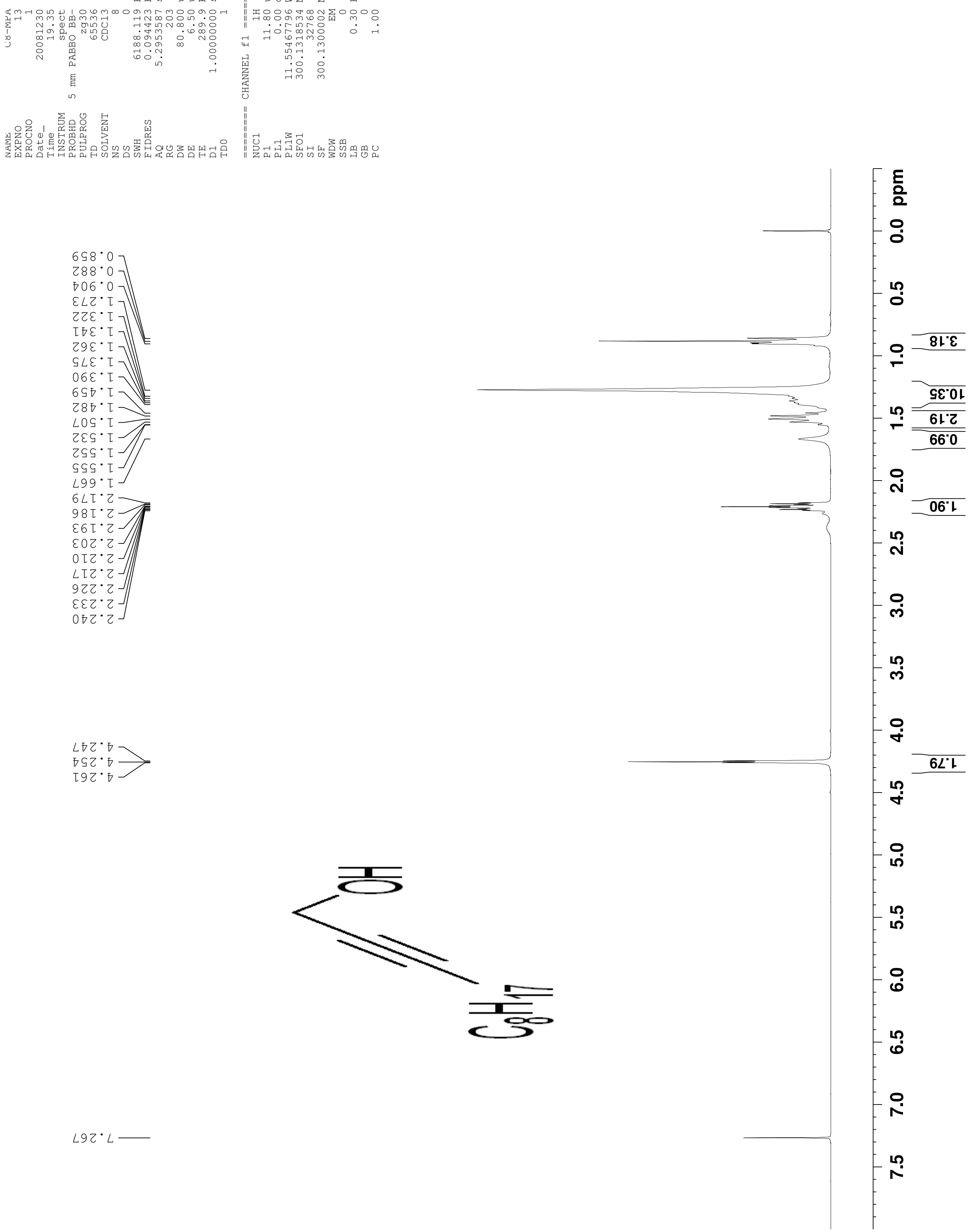
(4*R*, 9*Z*)-**2,** *Janus integer* Pheromone

(4*R*, 9*Z*)-**2**: 89% overall yield. $[\alpha]^{20}_D$ = +13 (c = 1.19, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.42-5.28 (2H, m), 4.53-4.44 (1H, m), 2.56-2.51 (2H, dd, *J*= 6.9, 9.6 Hz), 2.38-2.27 (1H, m), 2.08-1.98 (4H, m), 1.92-1.81 (1H, m), 1.80-1.69 (1H, m), 1.67-1.55 (1H, m), 1.53-1.37 (4H, m), 1.36-1.27 (13H, m), 0.88 (3H, t, *J*= 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 177.2, 130.4, 129.1,

(1) (a) J. H. Tumlinson, M. G. Klein, R. E. Doolittle, T. L. Ladd, A. T. Proveaux, *Science* **1977**, *197*, 789; (b) A. A. Dos Santos, W. Francke, *Tetrahedron: Asymmetry* **2006**, *17*, 2487

80.9, 35.5, 31.9, 29.7, 29.5, 29.4, 29.3, 28.8, 28.0, 27.2, 26.9, 24.8, 22.6, 14.1. HRMS (ESI): calcd. for C18H30O2 $[M+Na]^+$ 303.2295, found 303.2291, error = 1.3ppm. Lit.:[2] $[\alpha]^{26}_{D}$ = +24 (c = 0.50, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ : 0.88 (t, *J* = 7.0 Hz, 3H), 1.27-1.76 (m, 19 H), 1.81-1.89 (m, 1 H), 1.99-2.06 (m, 4 H), 2.32 (ddt, *J* = 6.5, 7.5, 13 Hz, 1 H), 2.53 (ddd, *J* = 1.3, 7.5, 9.2 Hz, 2 H), 4.48 (quint, *J* = 6.5 Hz, 1 H), 5.35 (dtt, *J* = 7.1, 12, 18 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ : 14.10, 14.11, 22.7, 24.9, 27.0, 27.2, 28.0, 28.9, 29.3, 29.4, 29.5, 29.7, 31.9, 35.5, 81.0, 129.1, 130.5, 177.3.

(2) C. Shibata, K.Mori, *Eur. J. Org. Chem.* **2004**, 1083.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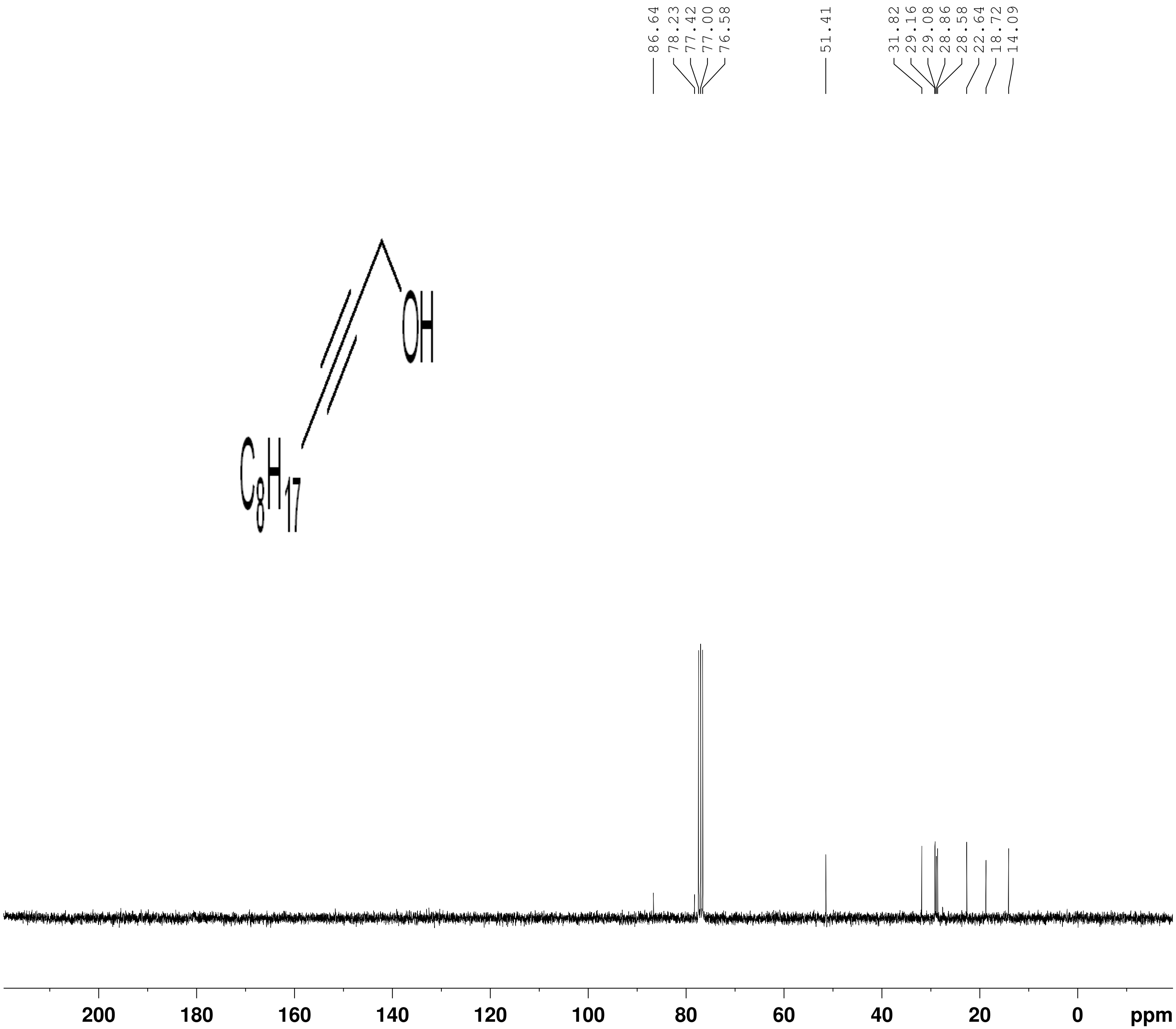

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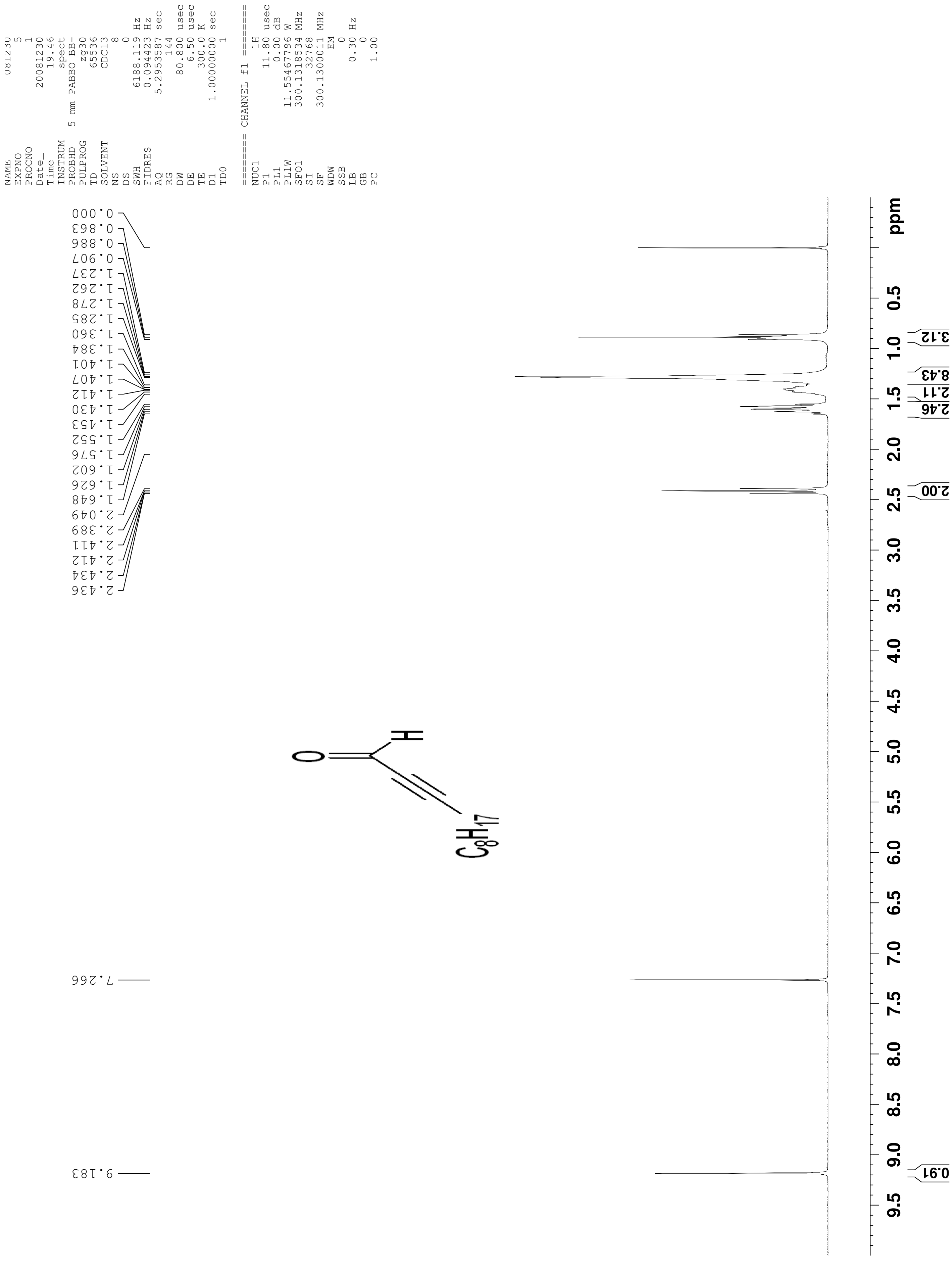
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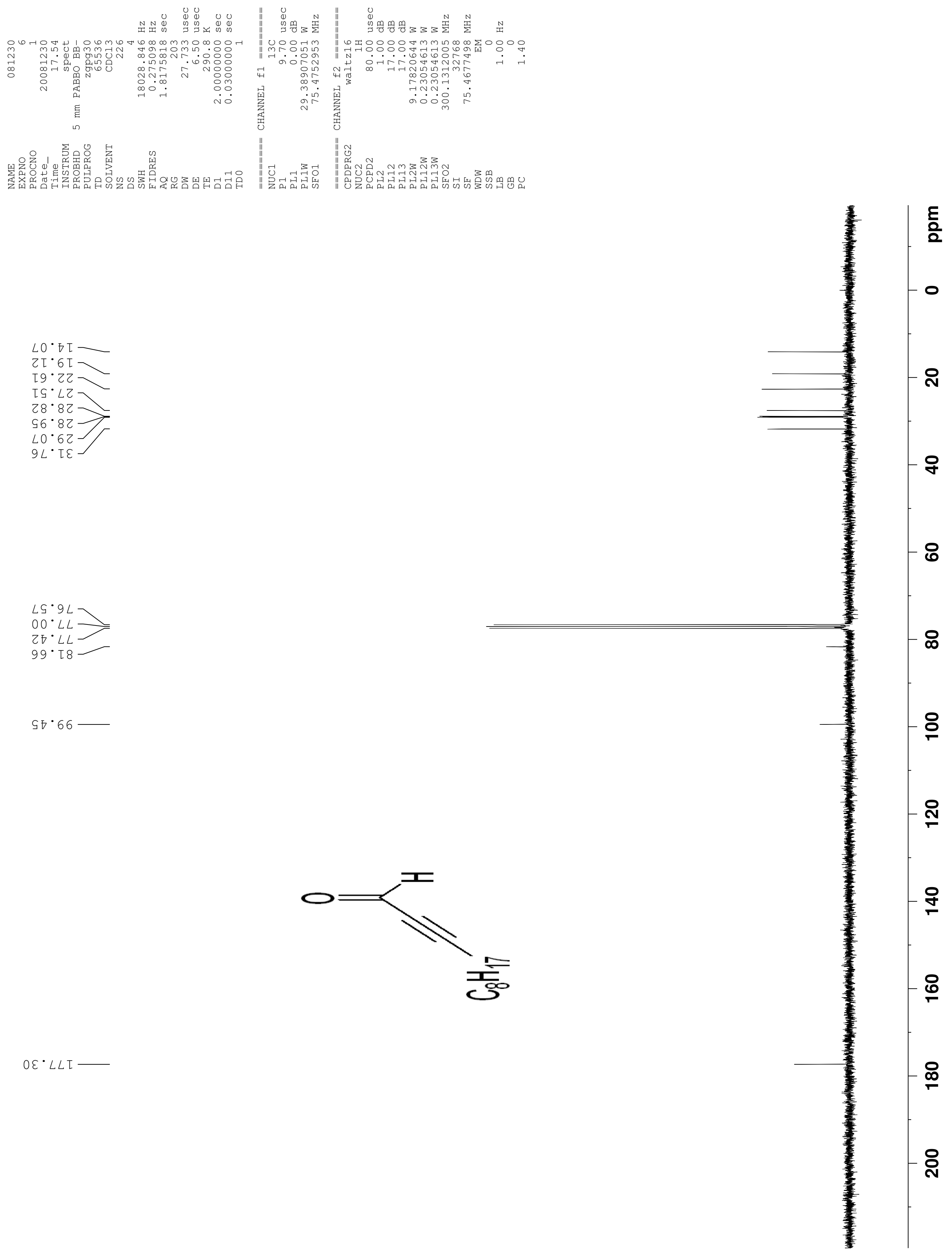
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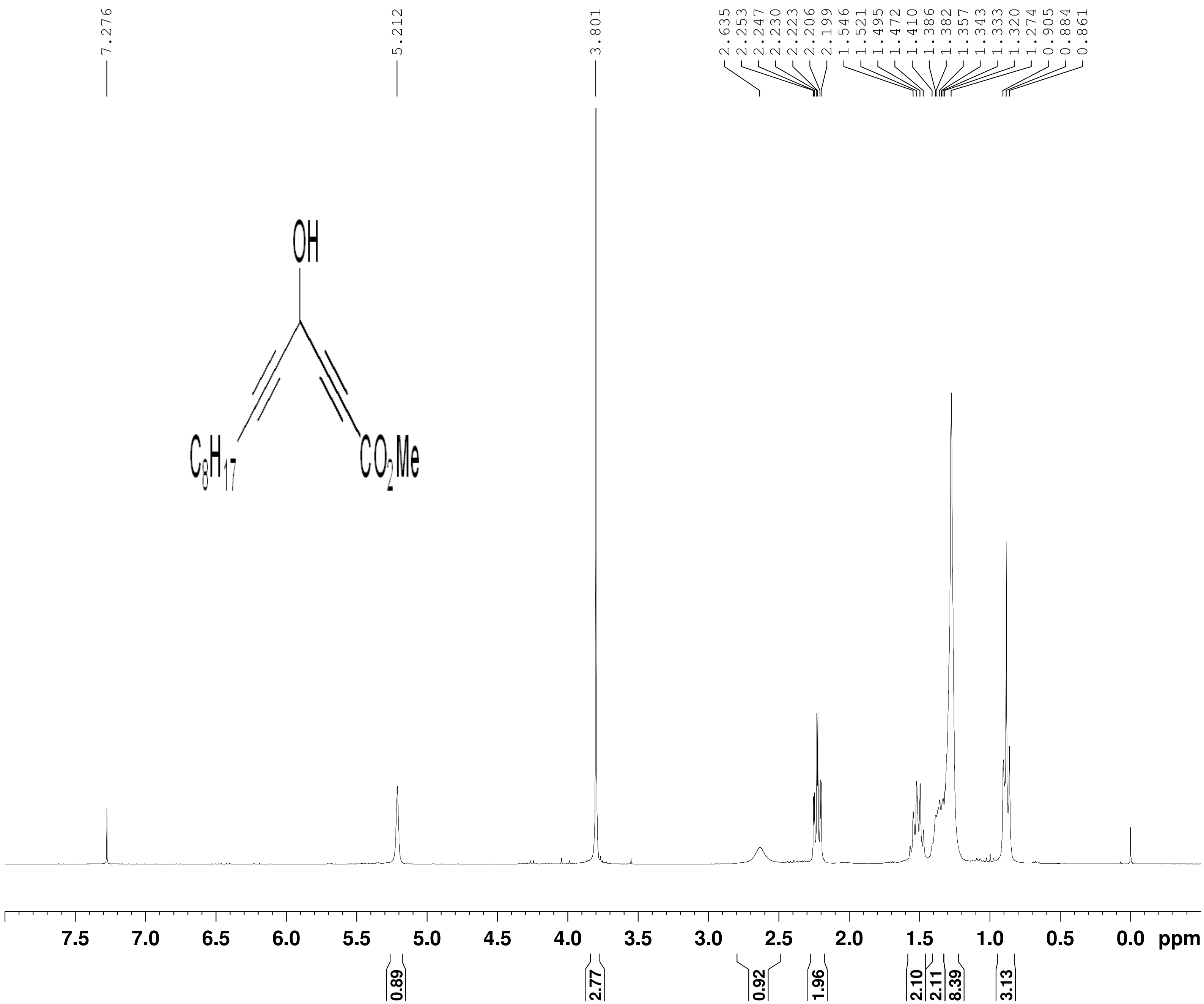
TD 65536
SOLVENT CDCl3
NS 226
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677498 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
14.07
19.12
22.61
27.51
28.82
28.95
29.07
31.76
76.57
77.00
77.42
81.66
99.45
177.30
O
H
C8H17
ppm
0
20
40
60
80
100
120
140
160
180
200



NAME	081230
EXPNO	3
PROCNO	1
Date_	20081230
Time	17.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 sec
RG	36
DW	80.800 usec
DE	6.50 usec
TE	290.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.80 usec
PL1	0.00 dB
PL1W	11.55467796 W
SFO1	300.1318534 MHz
SI	32768
SF	300.1299972 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

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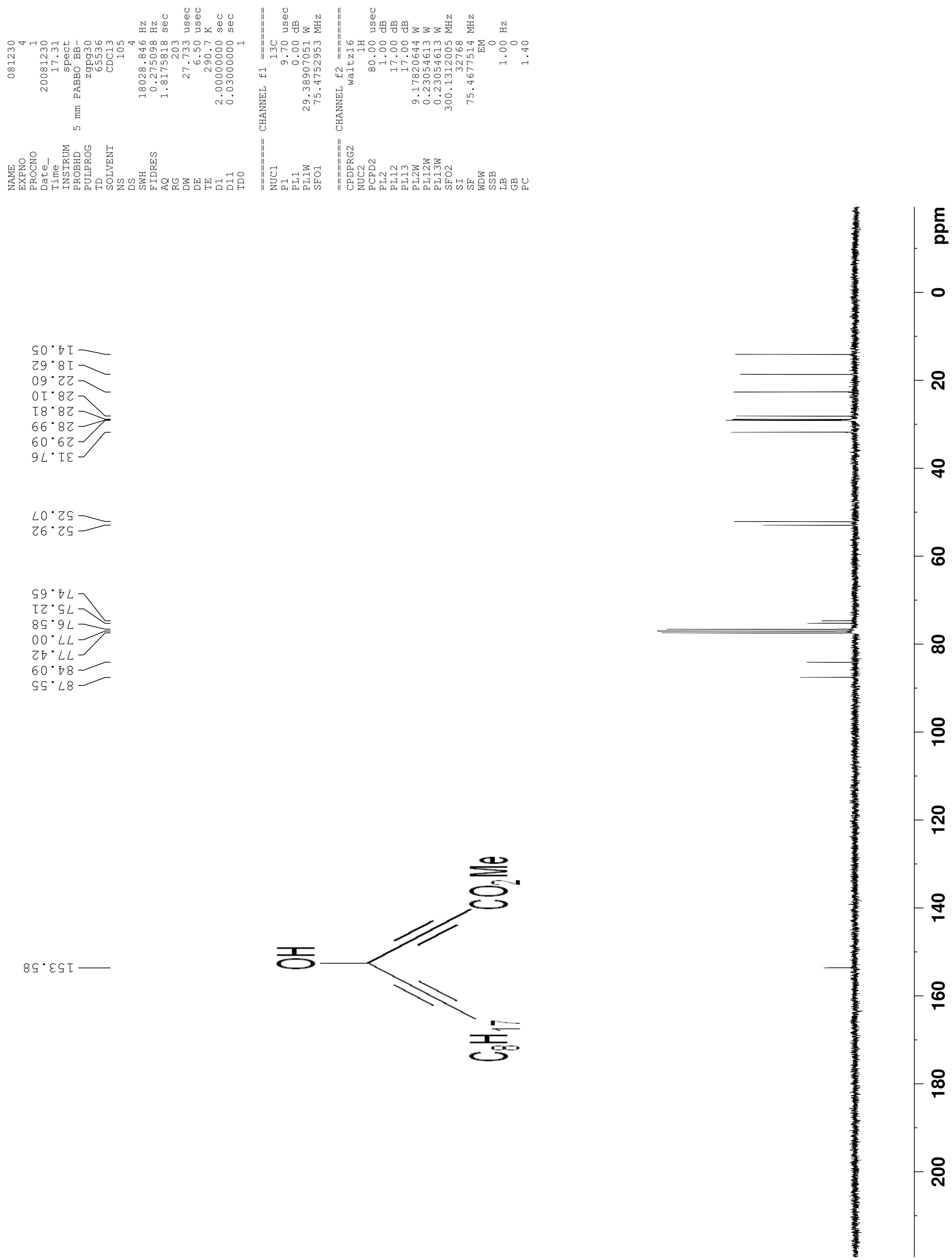
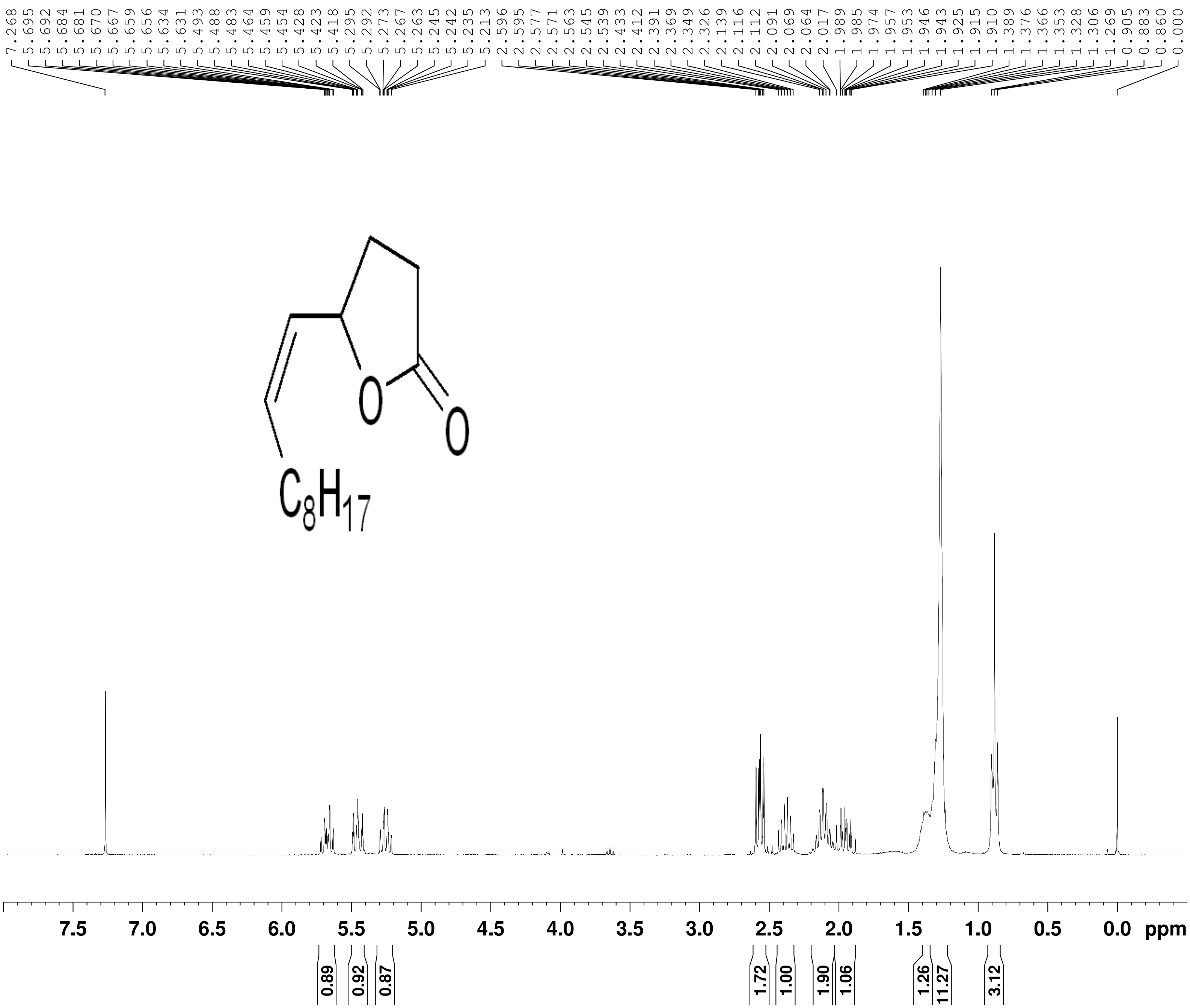
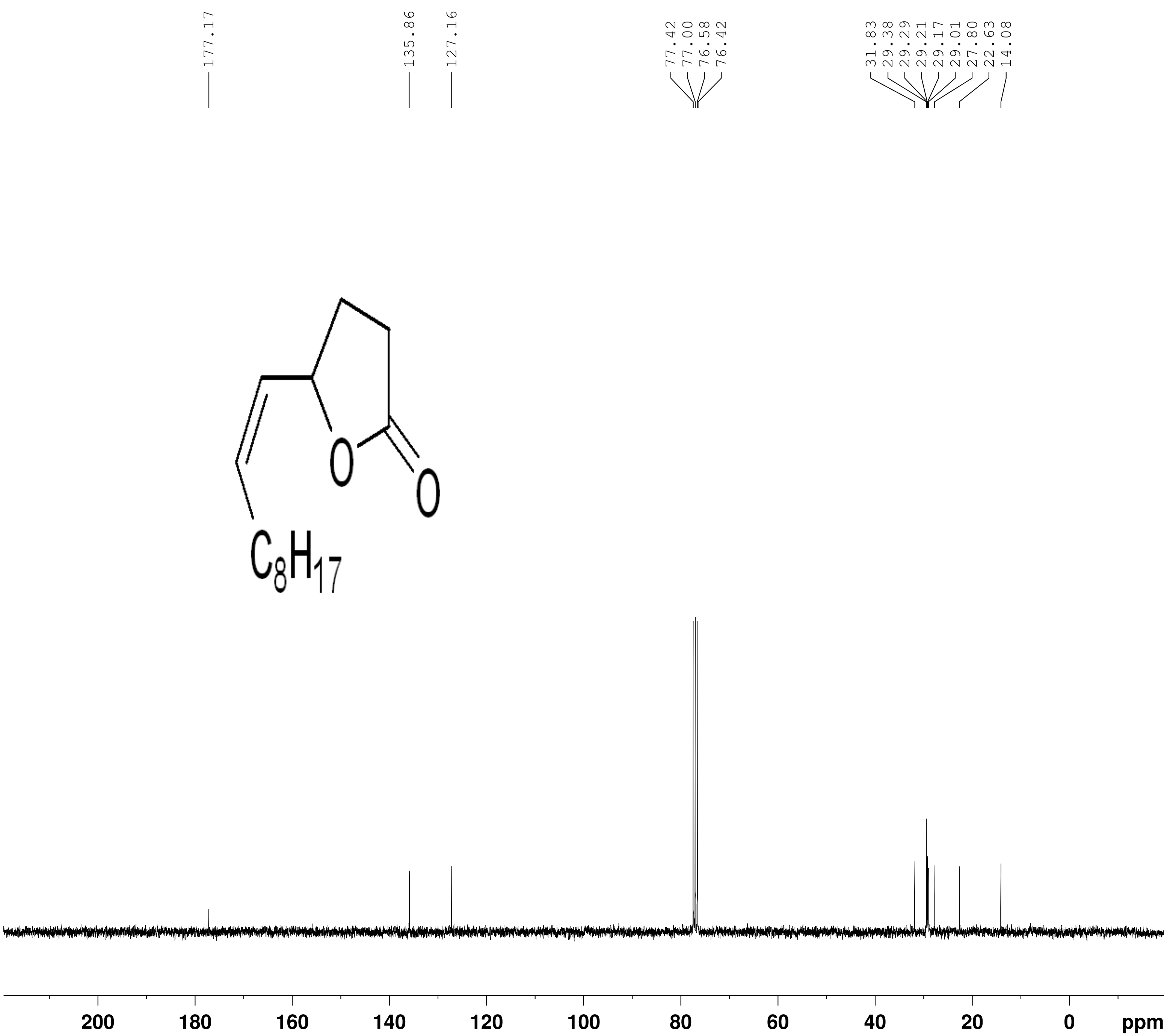




NAME	090108
EXPNO	6
PROCNO	1
Date_	20090108
Time	20.17
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 sec
RG	114
DW	80.800 usec
DE	6.50 usec
TE	289.8 K
D1	1.00000000 sec
TD0	1

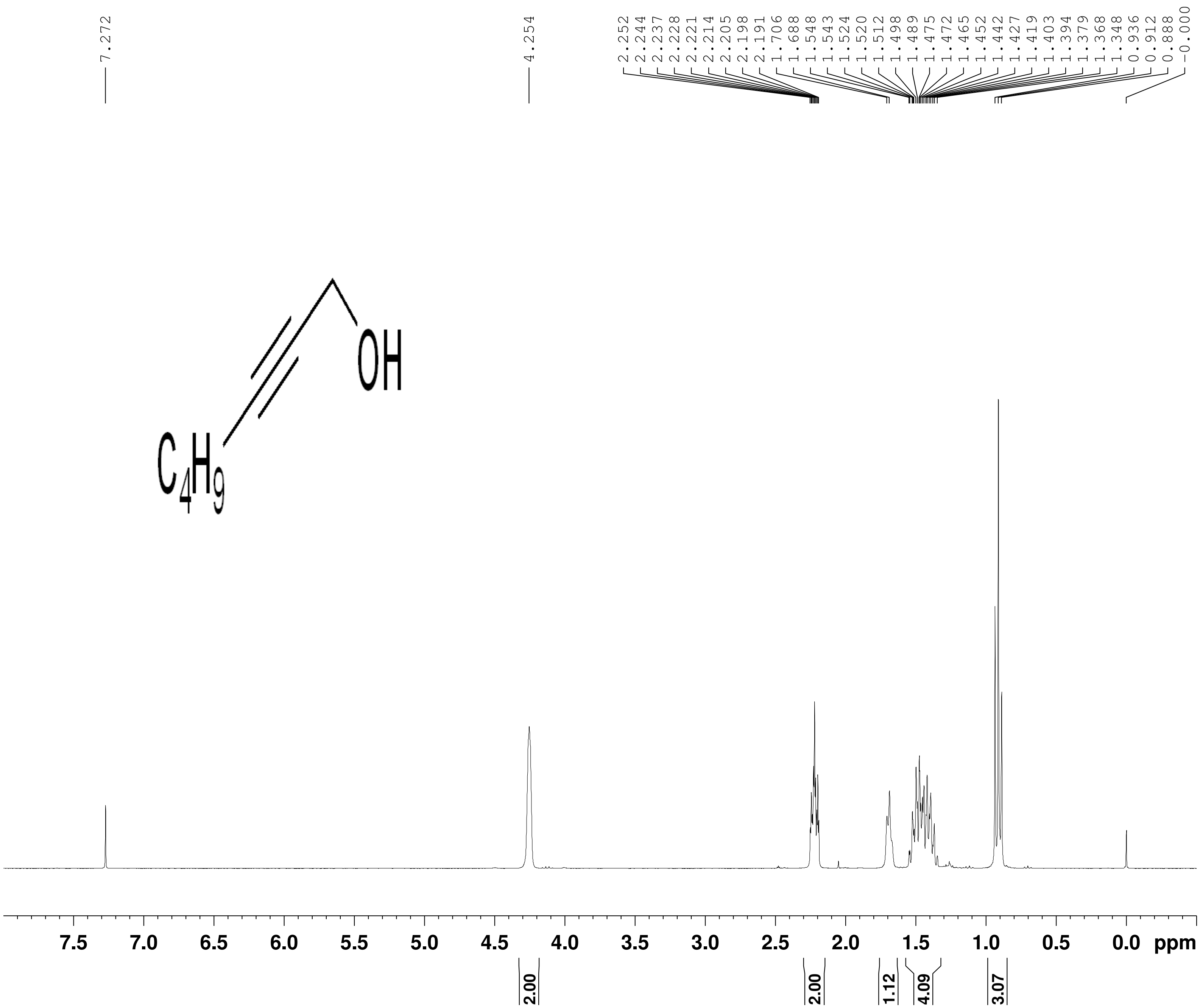
======== CHANNEL f1 ========

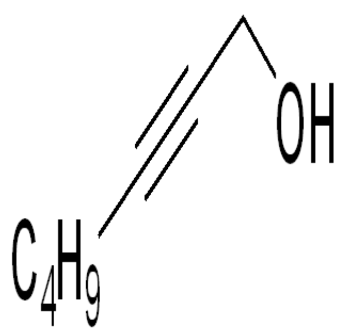
NUC1	1H
P1	11.80 usec
PL1	0.00 dB
PL1W	11.55467796 W
SFO1	300.1318534 MHz
SI	32768
SF	300.1299998 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

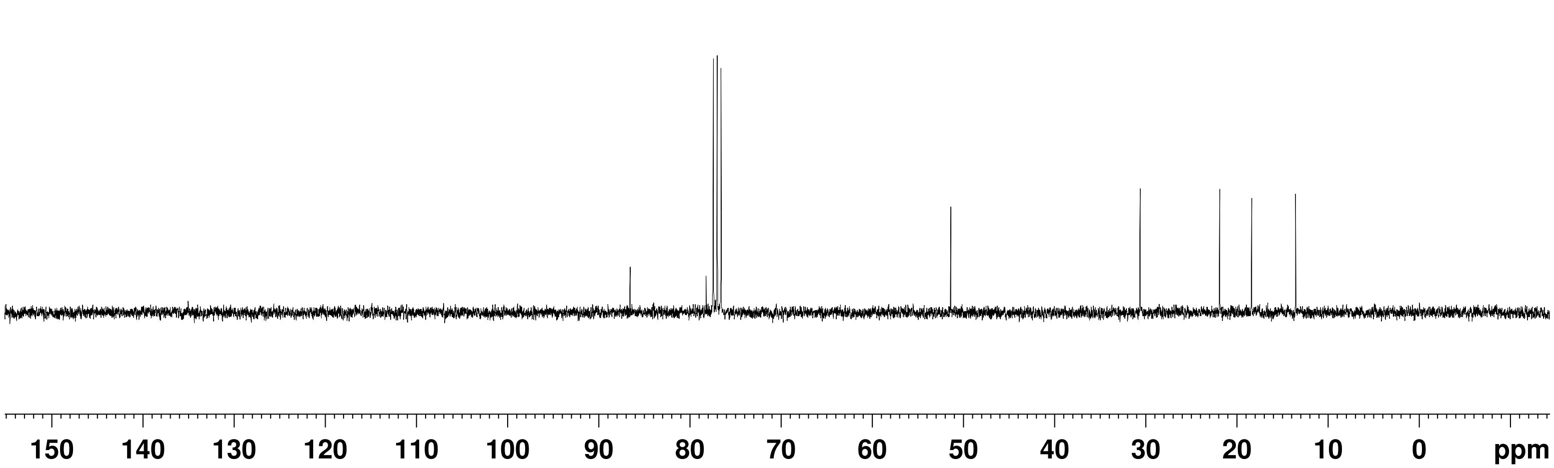


NAME	090108	
EXPNO	7	
PROCNO	1	
Date_	20090108	
Time	20.38	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	144	
DS	4	
SWH	18028.846	Hz
FIDRES	0.275098	Hz
AQ	1.8175818	sec
RG	203	
DW	27.733	usec
DE	6.50	usec
TE	290.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.70	usec
PL1	0.00	dB
PL1W	29.38907051	W
SFO1	75.4752953	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	1.00	dB
PL12	17.00	dB
PL13	17.00	dB
PL2W	9.17820644	W
PL12W	0.23054613	W
PL13W	0.23054613	W
SFO2	300.1312005	MHz
SI	32768	
SF	75.4677503	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

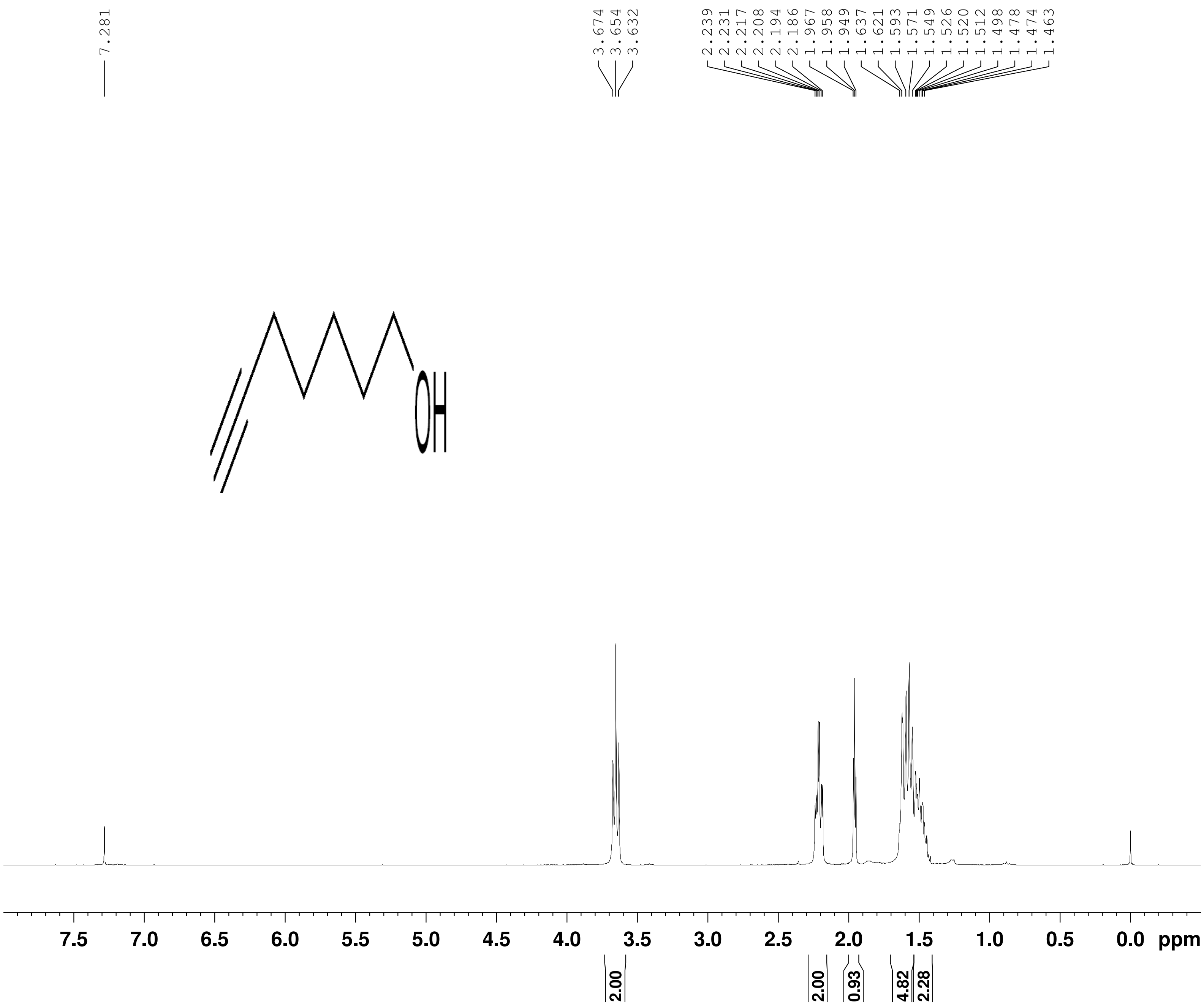
NAME	C4-C7-lactone
EXPNO	3
PROCNO	1
Date_	20081209
Time	21.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 sec
RG	80.6
DW	80.800 usec
DE	6.50 usec
TE	290.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.80 usec
PL1	0.00 dB
PL1W	11.55467796 W
SFO1	300.1318534 MHz
SI	32768
SF	300.1299985 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



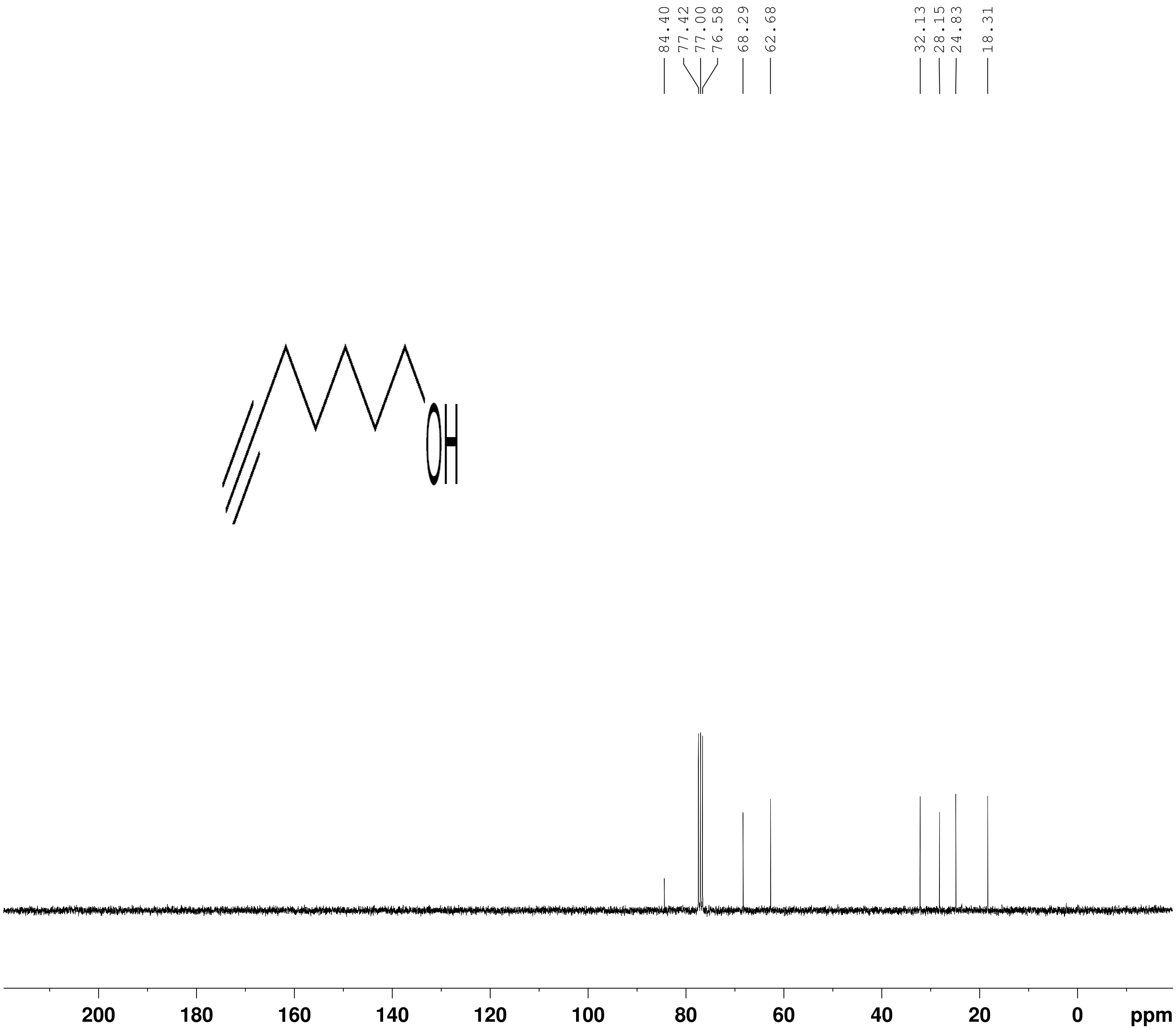




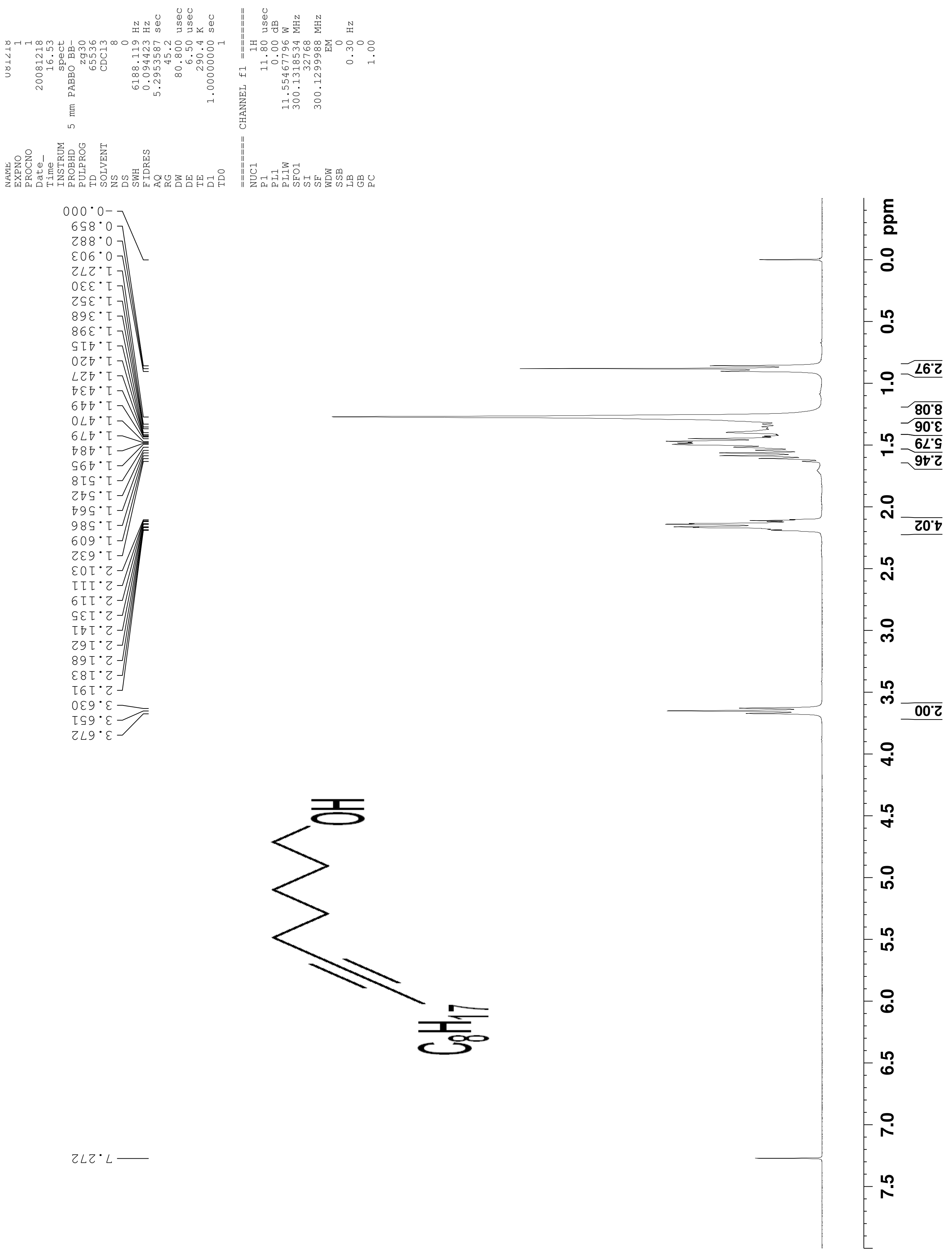

```
NAME          C4-C7-lactone
EXPNO                     4
PROCNO                    1
Date_              20081209
Time                  21.09
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       38
DS                        0
SWH              18028.846 Hz
FIDRES            0.275098 Hz
AQ               1.8175818 sec
RG                      203
DW                   27.733 usec
DE                     6.50 usec
TE                    290.7 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.70 usec
PL1                    0.00 dB
PL1W            29.38907051 W
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    1.00 dB
PL12                  17.00 dB
PL13                  17.00 dB
PL2W             9.17820644 W
PL12W            0.23054613 W
PL13W            0.23054613 W
SFO2           300.1312005 MHz
SI                    32768
SF              75.4677509 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

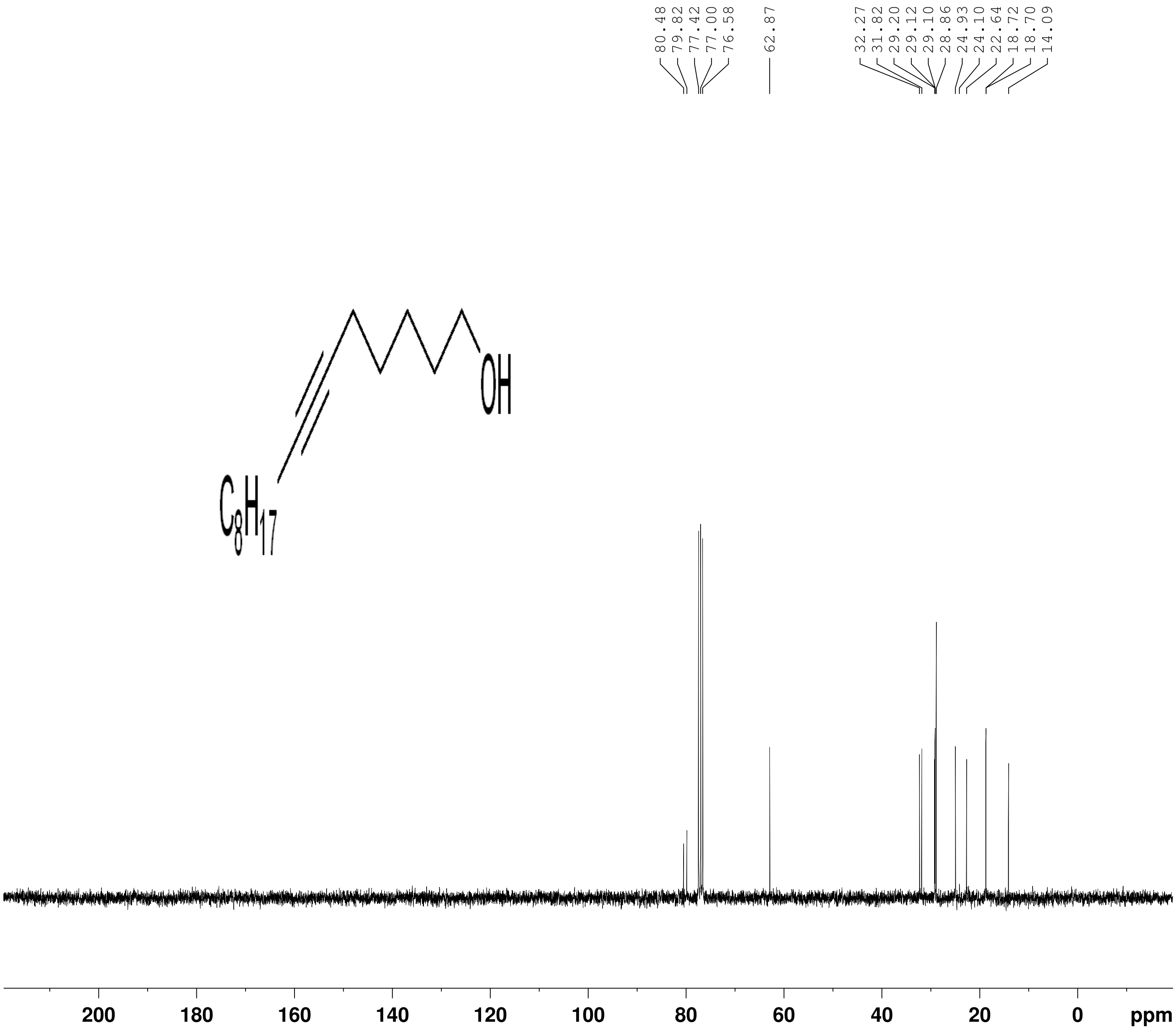



```
NAME        C4-C7-lactone
EXPNO                  10
PROCNO                  1
Date_            20081219
Time                10.47
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              6188.119 Hz
FIDRES           0.094423 Hz
AQ              5.2953587 sec
RG                     57
DW                 80.800 usec
DE                   6.50 usec
TE                  289.7 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                  0.00 dB
PL1W          11.55467796 W
SFO1          300.1318534 MHz
SI                  32768
SF            300.1299962 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



NAME	C4-C7-lactone
EXPNO	11
PROCNO	1
Date_	20081219
Time	10.47
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	40
DS	0
SWH	18028.846 Hz
FIDRES	0.275098 Hz
AQ	1.8175818 sec
RG	203
DW	27.733 usec
DE	6.50 usec
TE	289.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.70 usec
PL1	0.00 dB
PL1W	29.38907051 W
SFO1	75.4752953 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	17.00 dB
PL13	17.00 dB
PL2W	9.17820644 W
PL12W	0.23054613 W
PL13W	0.23054613 W
SFO2	300.1312005 MHz
SI	32768
SF	75.4677520 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


NAME 081218
EXPNO 1
PROCNO 1
Date_ 20081218
Time 16.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 45.2
DW 80.800 usec
DE 6.50 usec
TE 290.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.80 usec
PL1 0.00 dB
PL1W 11.55467796 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1299988 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-0.000
0.859
0.882
0.903
1.272
1.330
1.352
1.368
1.398
1.415
1.420
1.427
1.434
1.449
1.470
1.479
1.484
1.495
1.518
1.542
1.564
1.586
1.609
1.632
2.103
2.111
2.119
2.135
2.141
2.162
2.168
2.183
2.191
3.630
3.651
3.672
7.272
2.97
8.08
3.06
5.79
2.46
4.02
2.00
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
OH
C_8H_{17}



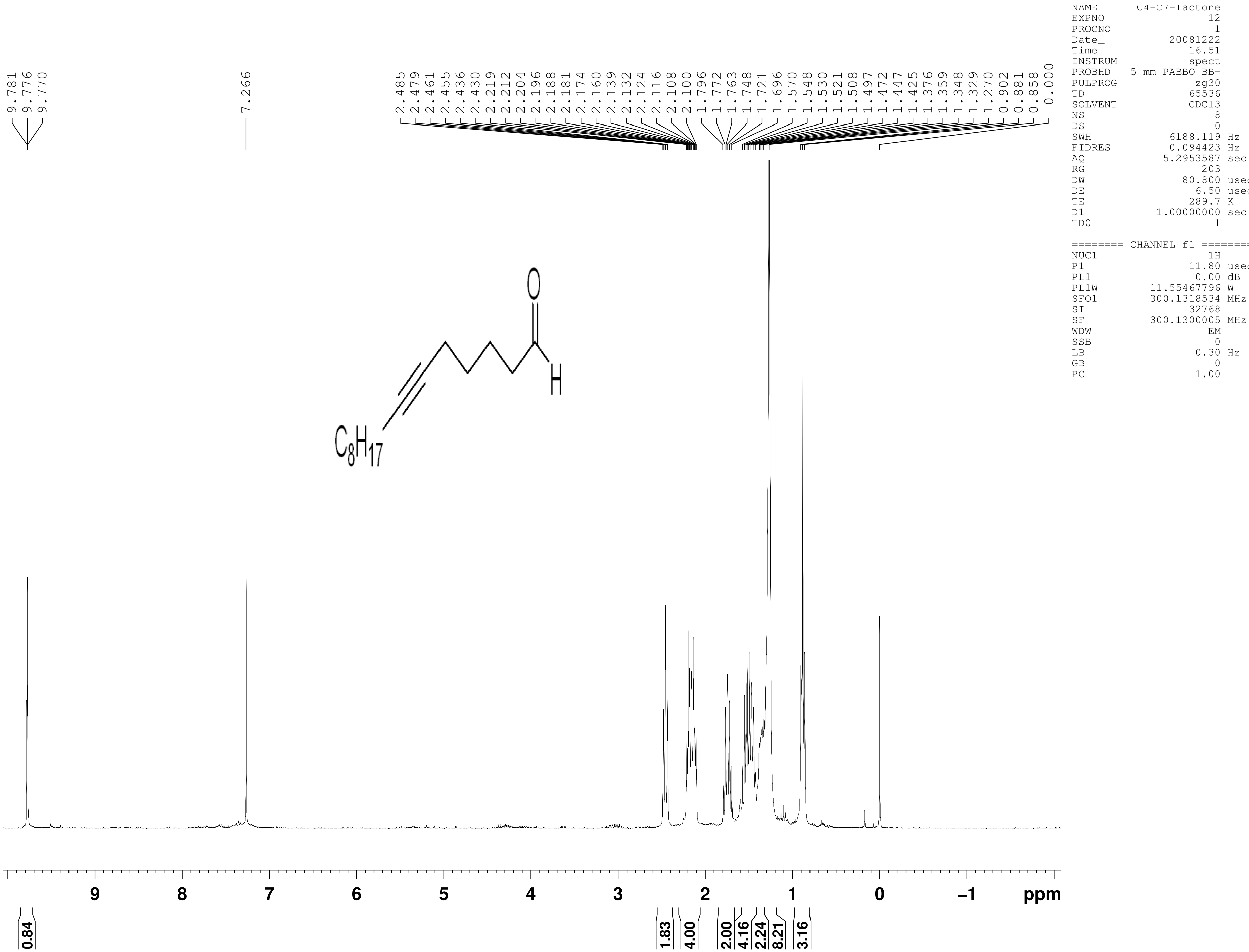
NAME	081218	
EXPNO	2	
PROCNO	1	
Date_	20081218	
Time	16.56	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	65	
DS	0	
SWH	18028.846	Hz
FIDRES	0.275098	Hz
AQ	1.8175818	sec
RG	203	
DW	27.733	usec
DE	6.50	usec
TE	290.4	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	

======== CHANNEL f1 ========

NUC1	13C	
P1	9.70	usec
PL1	0.00	dB
PL1W	29.38907051	W
SFO1	75.4752953	MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	1.00	dB
PL12	17.00	dB
PL13	17.00	dB
PL2W	9.17820644	W
PL12W	0.23054613	W
PL13W	0.23054613	W
SFO2	300.1312005	MHz
SI	32768	
SF	75.4677503	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.10	


NAME C4-C7-lactone
EXPNO 12
PROCNO 1
Date_ 20081222
Time 16.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 203
DW 80.800 usec
DE 6.50 usec
TE 289.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.80 usec
PL1 0.00 dB
PL1W 11.55467796 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300005 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.781
9.776
9.770
7.266
2.485
2.479
2.461
2.455
2.436
2.430
2.219
2.212
2.204
2.196
2.188
2.181
2.174
2.160
2.139
2.132
2.124
2.116
2.108
2.100
1.796
1.772
1.763
1.748
1.721
1.696
1.570
1.548
1.530
1.521
1.508
1.497
1.472
1.447
1.425
1.376
1.359
1.348
1.329
1.270
0.902
0.881
0.858
-0.000
O
H
C8H17
9
8
7
6
5
4
3
2
1
0
–1
ppm
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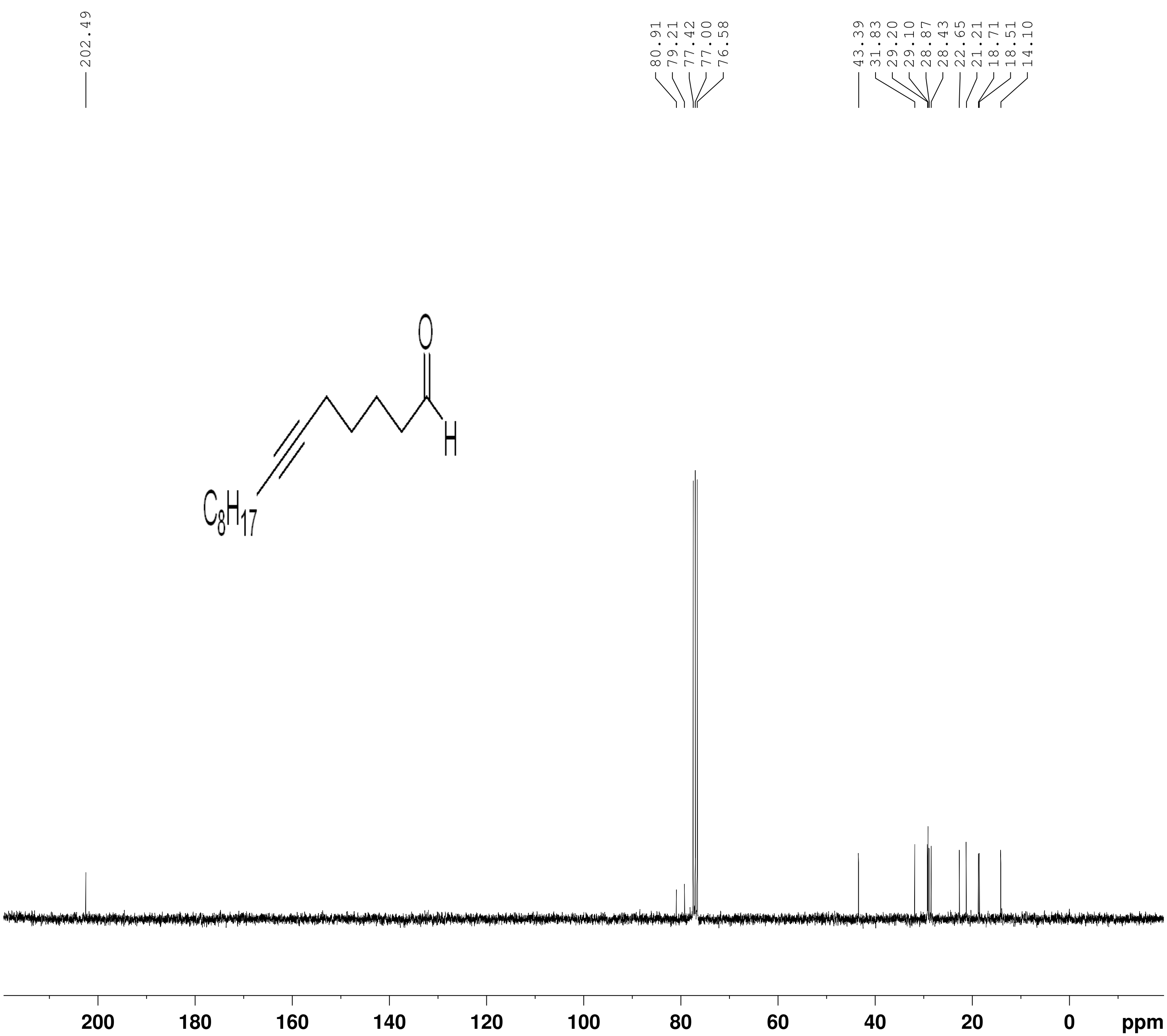
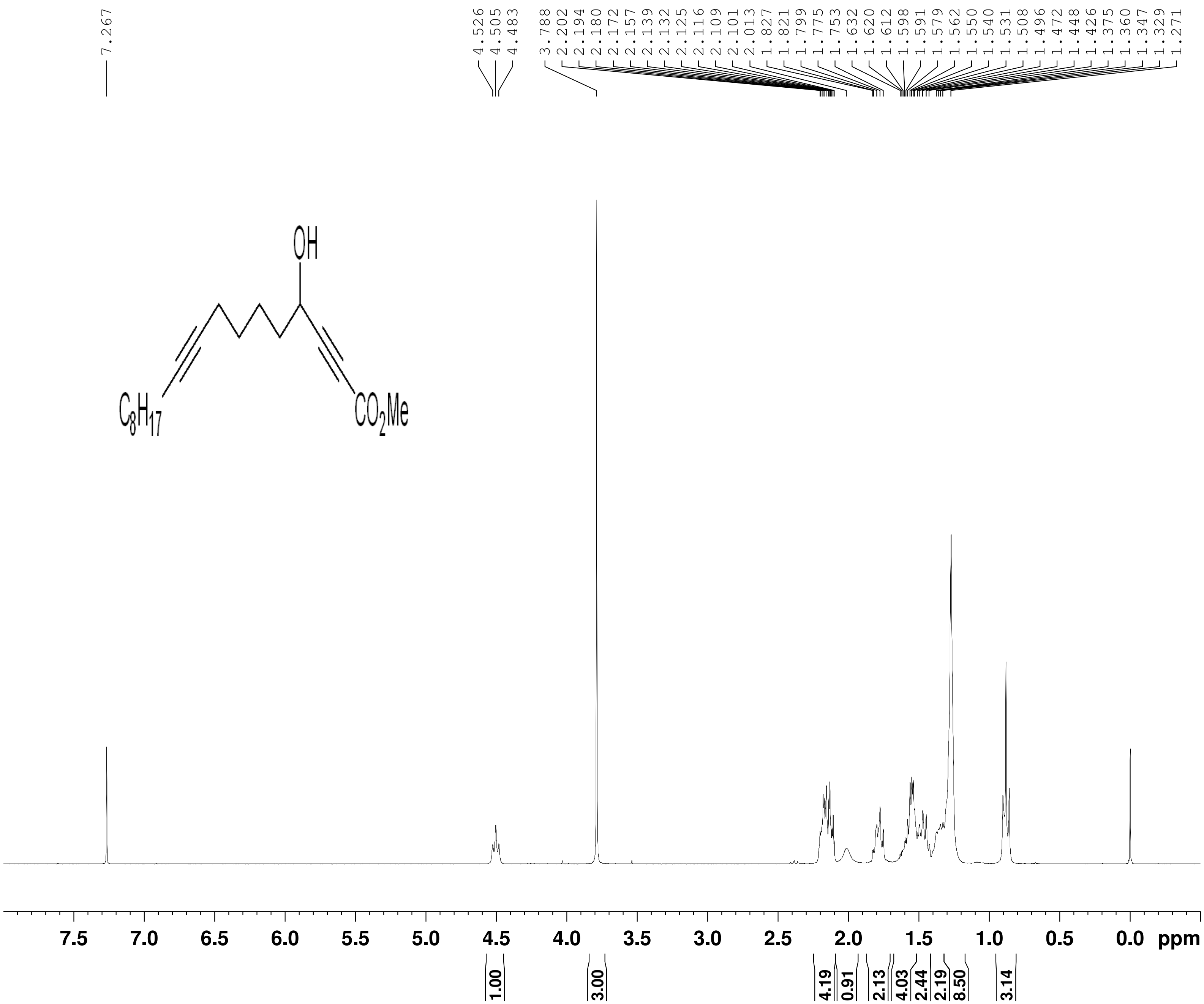
2.00
4.16
2.24
8.21
3.16

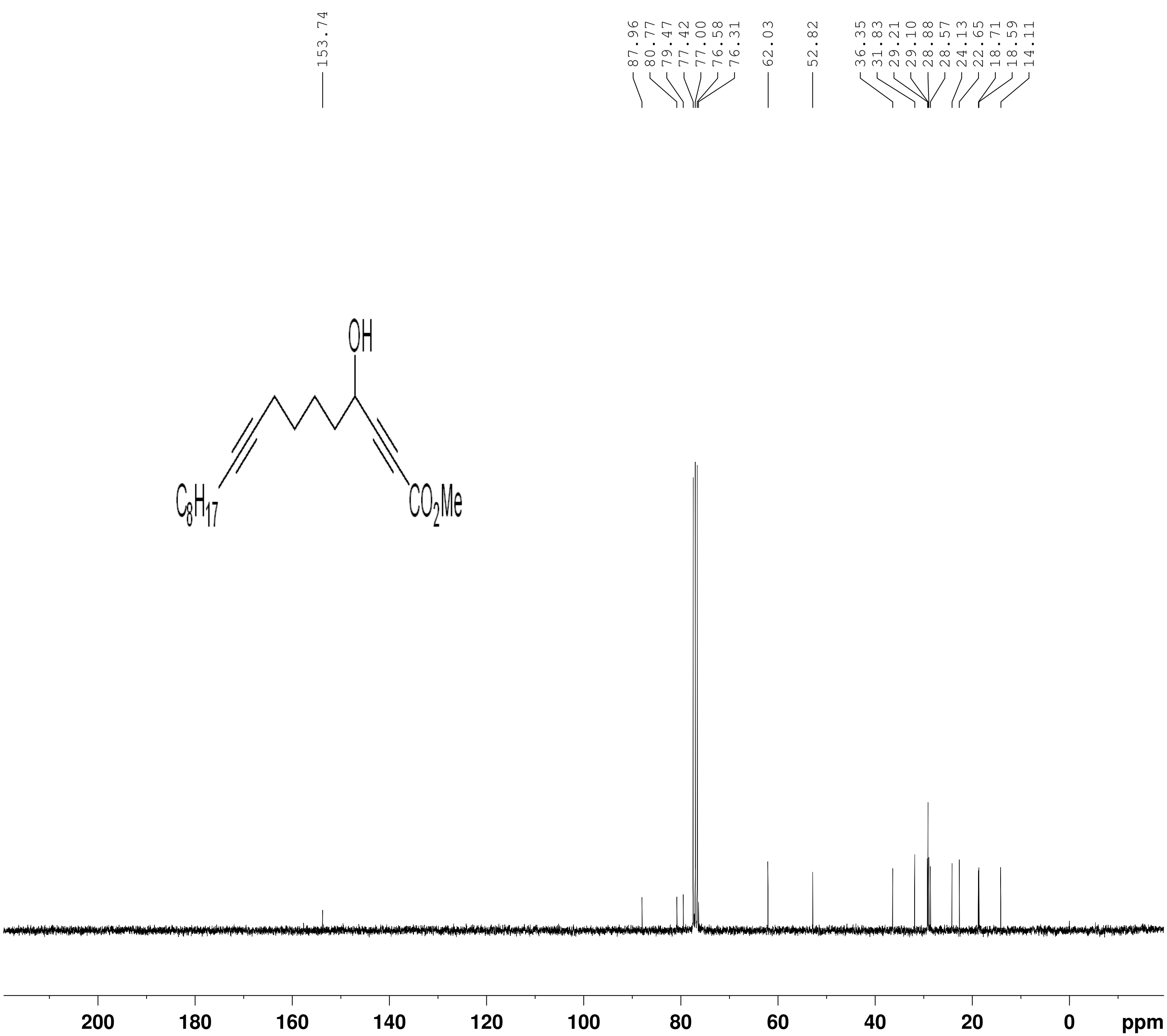


NAME	C4-C7-lactone	
EXPNO	13	
PROCNO	1	
Date_	20081222	
Time	16.55	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	187	
DS	0	
SWH	18028.846	Hz
FIDRES	0.275098	Hz
AQ	1.8175818	sec
RG	203	
DW	27.733	usec
DE	6.50	usec
TE	290.4	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.70	usec
PL1	0.00	dB
PL1W	29.38907051	W
SFO1	75.4752953	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	1.00	dB
PL12	17.00	dB
PL13	17.00	dB
PL2W	9.17820644	W
PL12W	0.23054613	W
PL13W	0.23054613	W
SFO2	300.1312005	MHz
SI	32768	
SF	75.4677498	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	




```
NAME       C4-C7-lactone
EXPNO                 14
PROCNO                 1
Date_           20081224
Time               15.09
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            6188.119 Hz
FIDRES         0.094423 Hz
AQ            5.2953587 sec
RG                  80.6
DW                80.800 usec
DE                  6.50 usec
TE                 290.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.80 usec
PL1                 0.00 dB
PL1W         11.55467796 W
SFO1         300.1318534 MHz
SI                 32768
SF           300.1300002 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



NAME	C4-C7-lactone	
EXPNO	15	
PROCNO	1	
Date_	20081224	
Time	15.13	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	240	
DS	0	
SWH	18028.846	Hz
FIDRES	0.275098	Hz
AQ	1.8175818	sec
RG	203	
DW	27.733	usec
DE	6.50	usec
TE	290.9	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	

======== CHANNEL f1 ========

NUC1	13C	
P1	9.70	usec
PL1	0.00	dB
PL1W	29.38907051	W
SFO1	75.4752953	MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	1.00	dB
PL12	17.00	dB
PL13	17.00	dB
PL2W	9.17820644	W
PL12W	0.23054613	W
PL13W	0.23054613	W
SFO2	300.1312005	MHz
SI	32768	
SF	75.4677499	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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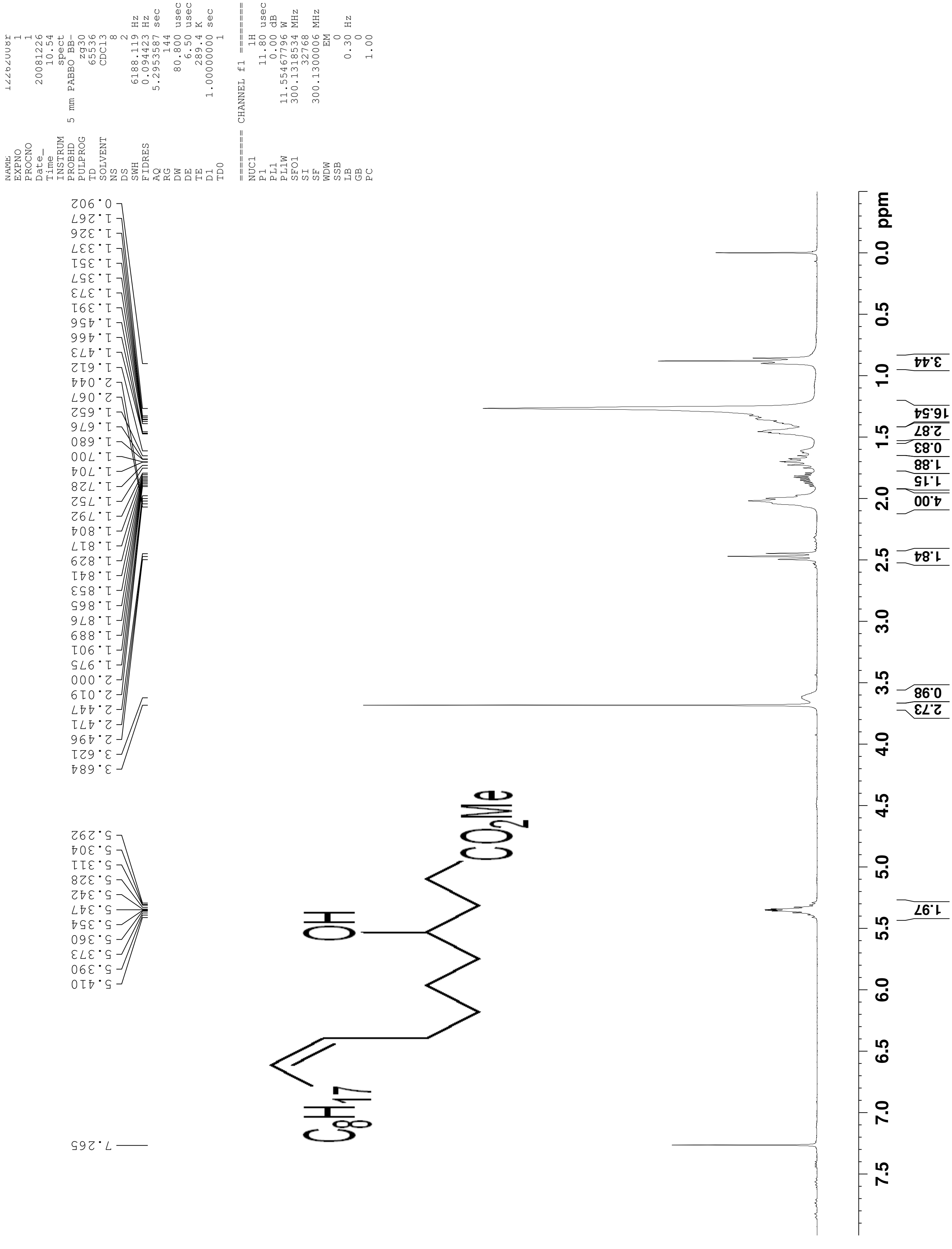
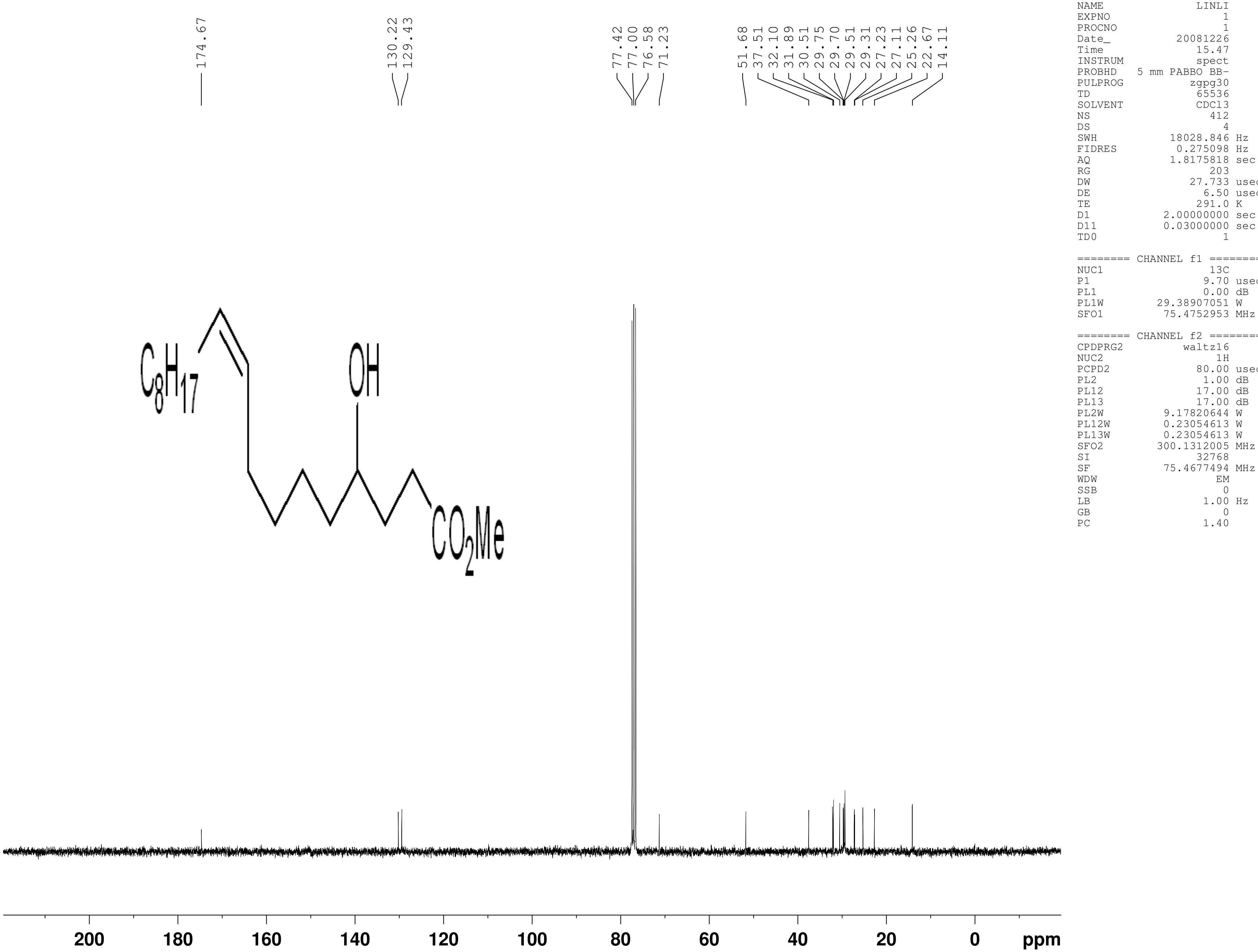
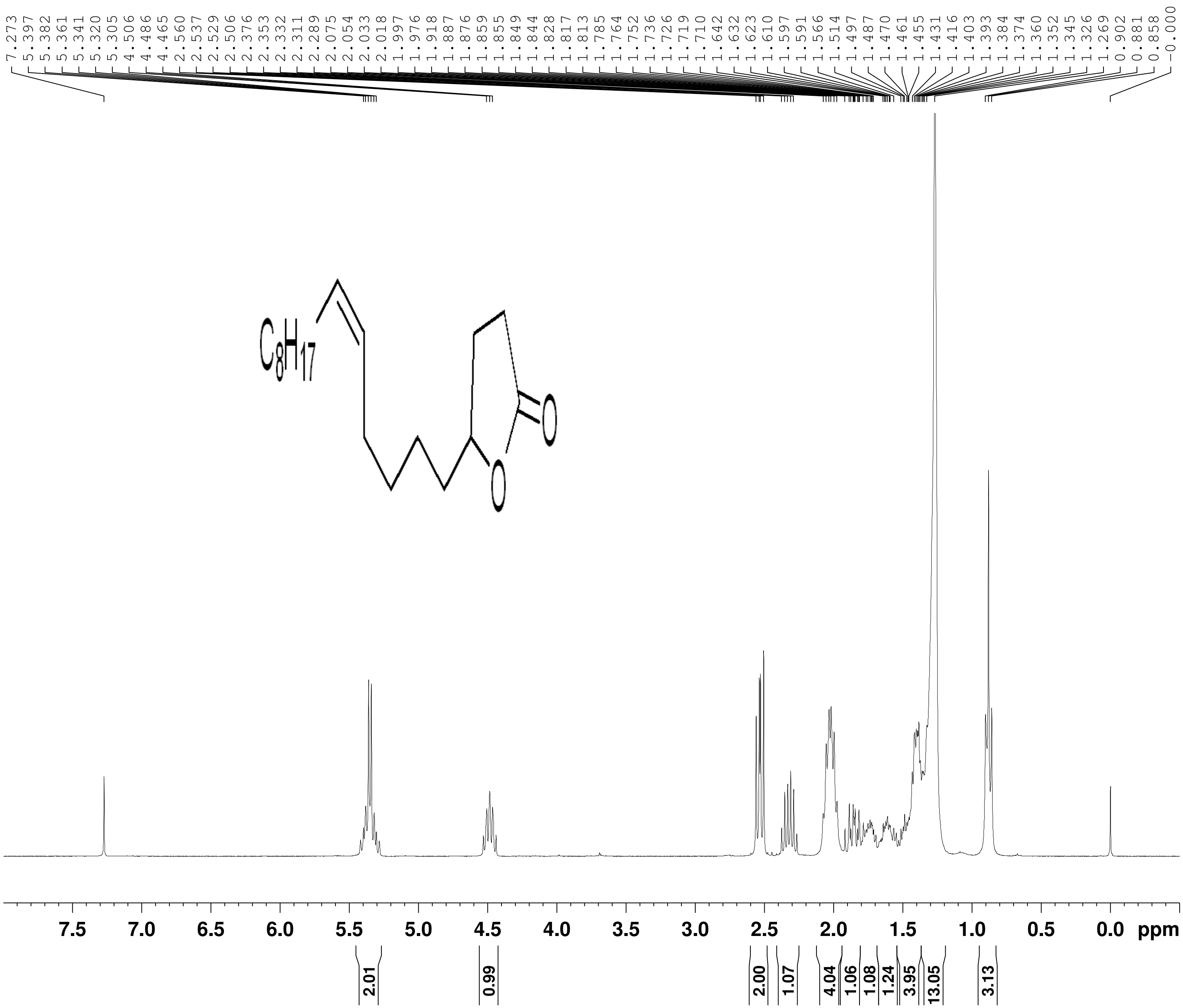
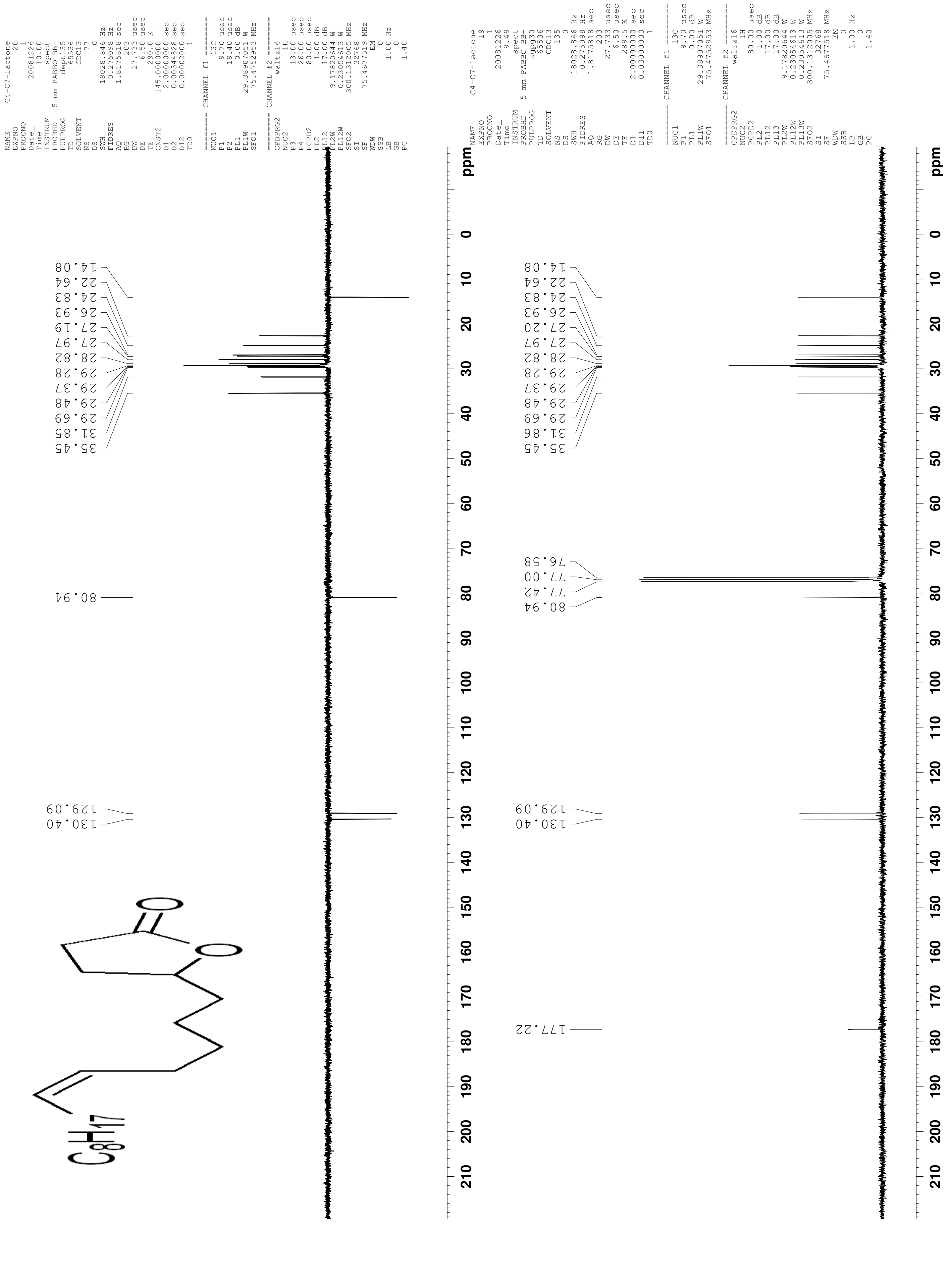



174.67
130.22
129.43
77.42
77.00
76.58
71.23
51.68
37.51
32.10
31.89
30.51
29.75
29.70
29.51
29.31
27.23
27.11
25.26
22.67
14.11
C8H17
OH
CO2Me
200
180
160
140
120
100
80
60
40
20
0
ppm
NAME LINLI
EXPNO 1
PROCNO 1
Date_ 20081226
Time 15.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 412
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 291.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677494 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




```
NAME        C4-C7-lactone
EXPNO                  18
PROCNO                  1
Date_            20081226
Time                 9.48
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              6188.119 Hz
FIDRES           0.094423 Hz
AQ              5.2953587 sec
RG                   40.3
DW                 80.800 usec
DE                   6.50 usec
TE                  289.5 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.80 usec
PL1                  0.00 dB
PL1W          11.55467796 W
SFO1          300.1318534 MHz
SI                  32768
SF            300.1299986 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```


NAME C4-C7-lactone
EXPNO 20
PROCNO 1
Date_ 20081226
Time 10.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG dept135
TD 65536
SOLVENT CDCl3
NS 77
DS 0
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.0 K
CNST2 145.0000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
P2 19.40 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P3 13.00 usec
P4 26.00 usec
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677519 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
14.08
22.64
24.83
26.93
27.19
27.97
28.82
29.28
29.37
29.48
29.69
31.85
35.45
80.94
129.09
130.40
ppm
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
C8H17
O
O
NAME C4-C7-lactone
EXPNO 19
PROCNO 1
Date_ 20081226
Time 9.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 135
DS 0
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 289.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677518 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
14.08
22.64
24.83
26.93
27.20
27.97
28.82
29.28
29.37
29.48
29.69
31.86
35.45
76.58
77.00
77.42
80.94
129.09
130.40
177.22
ppm
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210