Cyclization of Oxa-Bicyclic Alkenes with β-Iodo-(Z)-propenoates and *o*-Iodobenzoate Catalyzed by Nickel Complexes: A Simple Efficient Route to Annulated Coumarins

Dinesh Kumar Rayabarapu, Paritosh Shukla and Chien-Hong Cheng*

Department of Chemistry, Tsing Hua University, Hsinchu, Taiwan, 300 ROC

Supporting Information

General Procedure for the Cyclization of 7-Oxabenzonorbornadienes (1) with Methyl 2-Iodobenzoate (2). A round-bottom side-arm flask (25 mL) containing **1** (2.00 mmol), $NiBr_2$(dppe) (0.0500 mmol) and zinc powder (0.180 g, 2.75 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled CH_3CN (3.0 mL) and **2** (1.0 mmol) were added. The system was heated with stirring at 80 $^{\circ}$C for 12 h and was then cooled to ambient temperature. After dilution with dichloromethane (15 mL), the reaction mixture was stirred in the air for 15 min, filtered through a thin Celite and silica gel pad and washed with dichloromethane several times. The filtrate was concentrated and the residue was purified on a silica gel column using hexane-ethyl acetate as eluent to afford the desired cyclization products **3**. Important spectral data of these products are listed below.

6*H*-Dibenzo[*c*,*h*]chromen-6-one (3a). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52-7.58 (3 H, m), 7.67 (1 H, d, *J* = 9 Hz), 7.78 (1 H, d, *J* = 6 Hz), 7.79 (1 H, d, *J* = 7.5 Hz), 7.95 (1 H, d, *J* = 9 Hz), 8.08 (1H, d, *J* = 8 Hz), 8.38 (1H, d, *J* = 7.5 Hz), 8.49 (1H, d, J = 7.5 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ =112.8, 119.0, 121.0, 121.9, 122.1, 123.7, 124.3, 126.9, 127.5, 127.7, 128.4, 130.4, 134.1, 134.8, 135.2, 147.0, 161.1; HRMS (m/e): calcd for $C_{17}H_{10}O_2$ 246.0681, found 246.0678

2,3-Dimethoxy-6*H*-dibenzo[*c*,*h*]chromen-6-one (3b). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.01 (3H, s), 4.08 (3H, s), 7.13 (1H, s), 7.55 (1H, td, *J* = 7 Hz, *J* = 1 Hz), 7.60 (1H, d, *J* = 8.5 Hz), 7.78 (1H, s), 7.84 (1H, td, *J* = 8 Hz, J=1 Hz), 7.89 (1H, d, *J* = 8.5 Hz), 8.14 (1H, d, *J* = 7.5 Hz), 8.43 (1H, dd, *J* = 4Hz, *J* = 1 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 55.9, 56.3, 101.0, 106.4, 111.9, 117.5, 119.0 120.6, 121.7, 122.9, 128.1, 130.4, 130.5, 134.7, 146.4, 150.2, 150.9, 161.5; HRMS (m/e): calcd for $C_{19}H_{14}O_4$ 306.0892, found 306.0894.

12-Methyl-6*H*-dibenzo[*c*,*h*]chromen-6-one (3c). ^{1}H NMR (500 MHz, $CDCl_3$): δ

= 2.64 (3H, s), 7.50 (1H, td, *J* = 1.0 Hz, *J* = 8.5 Hz), 7.54-7.58 (2H, m), 7.70 (1H, s), 7.76 (1H, td, *J* = 1.0 Hz, *J* = 8.0 Hz), 7.86-7.89 (1H, m), 8.04 (1H, d, *J* = 8.5 Hz), 8.35 (1H, dd, *J* = 1.0 Hz, *J* = 7.5 Hz), 8.47-8.50 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 19.3, 112.2, 119.0, 121.0, 121.7, 122.5, 123.7, 124.0, 126.5, 127.5, 128.3, 130.4, 130.6, 133.2, 134.7, 135.1, 145.7, 161.2; HRMS (m/e): calcd for $C_{18}H_{12}O_2$ 260.0837, found 260.0832.

14*H*-Benzo[*c*]naphtho[2,3-*h*]chromen-14-one (3e). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.52 (2H, m), 7.60 (1H, *t*, *J* = 7.2 Hz), 7.91-7.85 (2H, m), 8.00 (2H, t, *J* = 7 Hz), 8.12-8.09 (1H, m), 8.18 (1H, d, *J* = 8 Hz), 8.41 (1H, s), 8.48 (1H, d, *J* = 7.6 Hz), 9.16 (1H, s); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 111.4, 118.3, 121.0, 121.7, 121.9, 122.3, 124.9, 126.1, 126.5, 127.9, 128.4, 128.8, 130.5, 131.4, 131.9, 132.5, 134.9, 135.3, 147.3, 161.3; HRMS (m/e): calcd for $C_{21}H_{12}O_2$ 296.0837, found 296.0841.

2*H*-Benzo[*h*]chromen-2-one (3g). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.45 (1H, d, *J* = 9 Hz), 7.38 (1H, d, *J* = 8 Hz), 7.62-7.57 (3H, m), 7.75 (1H, *J* = 8 Hz), 7.81 (1H, dd, *J* = 4.5 Hz, *J* = 1 Hz), 8.46 (1H, dd, *J* = 4.5 Hz, J = *1* Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 114.1, 11.5, 122.7, 122.9, 123.4,127.0, 127.7, 128.6, 134.7, 144.1, 151.1, 160.8; HRMS (m/e): calcd for $C_{13}H_8O_2$ 196.0524, found 196.0521

8,9-Di(methyloxy)-2*H*-benzo[*h*]chromen-2-one (3h). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.01 (3H, s), 4.05 (3H, s), 6.42 (1H, d, *J* = 10.0 Hz), 7.13 (1H, s), 7.30 (1H, d, *J* = 8.0 Hz), 7.51 (1H, d, *J* = 8.0 Hz) 7.74 (1H, s), 7.78(1H, d, *J* = 9.0 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 56.0, 56.3, 100.9, 106.5, 113.3, 114.5, 118.2, 122.0, 122.8, 131.3, 144.6, 150.3, 150.4, 151.5, 161.4; HRMS (m/e): calcd for $C_{15}H_{12}O_4$ 256.0736, found 256.0735.

4-Methyl-2*H*-benzo[*h*]chromen-2-one (3i). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (3H, d, *J* = 1.6 Hz), 6.39(1H, d, *J* = 1.2 Hz), 7.62-7.66(4H, m), 7.87(1H, dd, *J* = 2.4

Hz, J = 4.4 Hz), 8.58 (1H, dd, J = 2.0 Hz, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 19.13, 114.27, 115.10, 120.22, 122.57, 123.09, 124.04, 127.04, 127.56, 128.51, 134.70, 150.52, 153.29, 160.76; HRMS (m/e): calcd for $C_{14}H_{10}O_2$ 210.0680, found 210.0679.

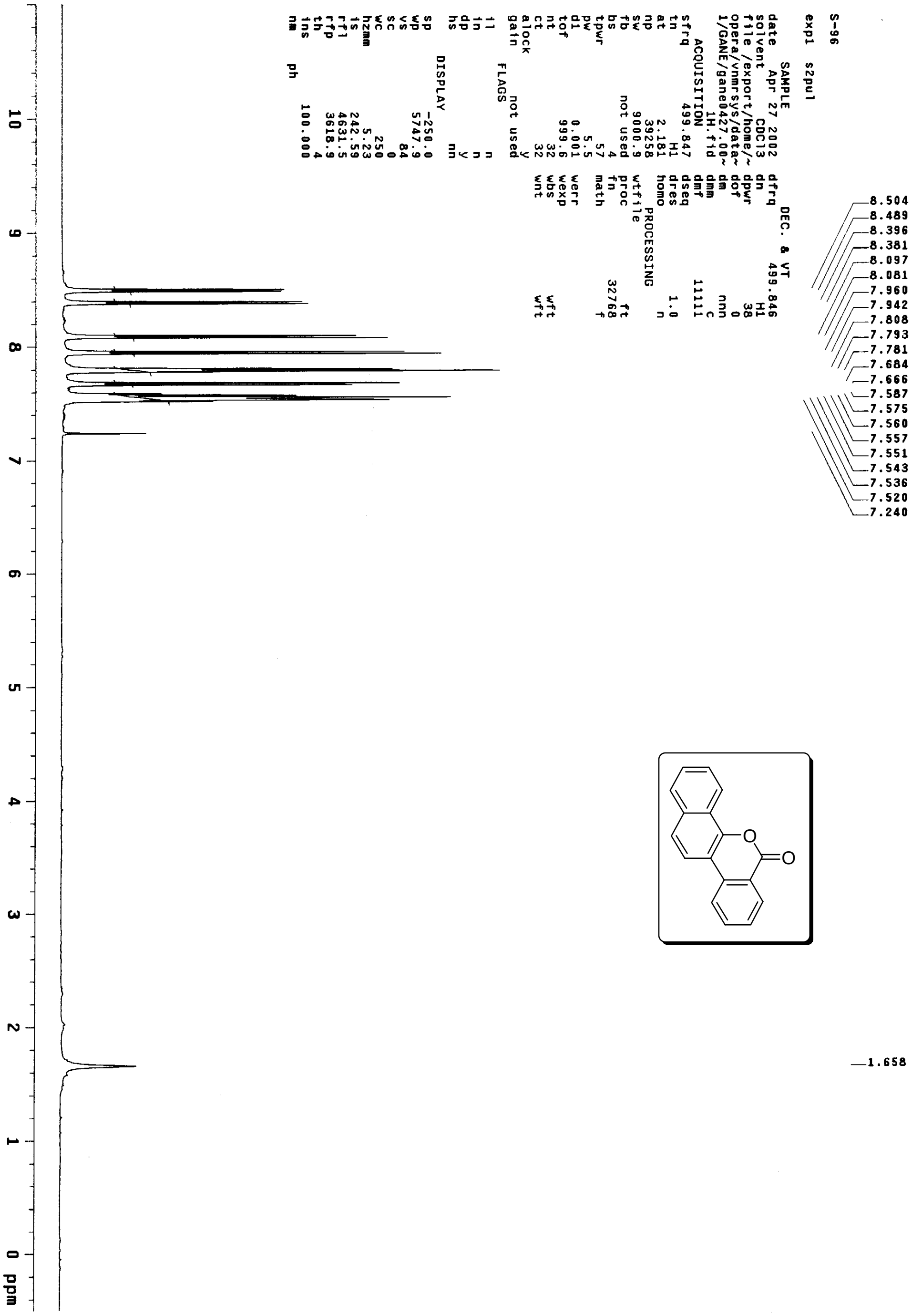
8,9-Dimethoxy-4-methyl-2*H*-benzo[*h*]chromen-2-one (3j). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (3H, d, J = 1.2 Hz,), 4.00 (3H, s), 4.04 (3H, s), 6.27 (1H, d, J = 1.6 Hz,), 7.10 (1H, s), 7.41 (1H, d, J = 8.4 Hz,), 7.50 (1H, d, J = 8.4 Hz,), 7.72 (1H, s); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 19.09, 55.93, 56.28, 101.26, 106.31, 113.15, 114.16, 118.28, 118.71, 122.50, 131.17, 149.68, 150.29, 151.50, 153.67, 161.22; HRMS (m/e): calcd for $C_{16}H_{14}O_4$ 270.0892, found 270.0893.

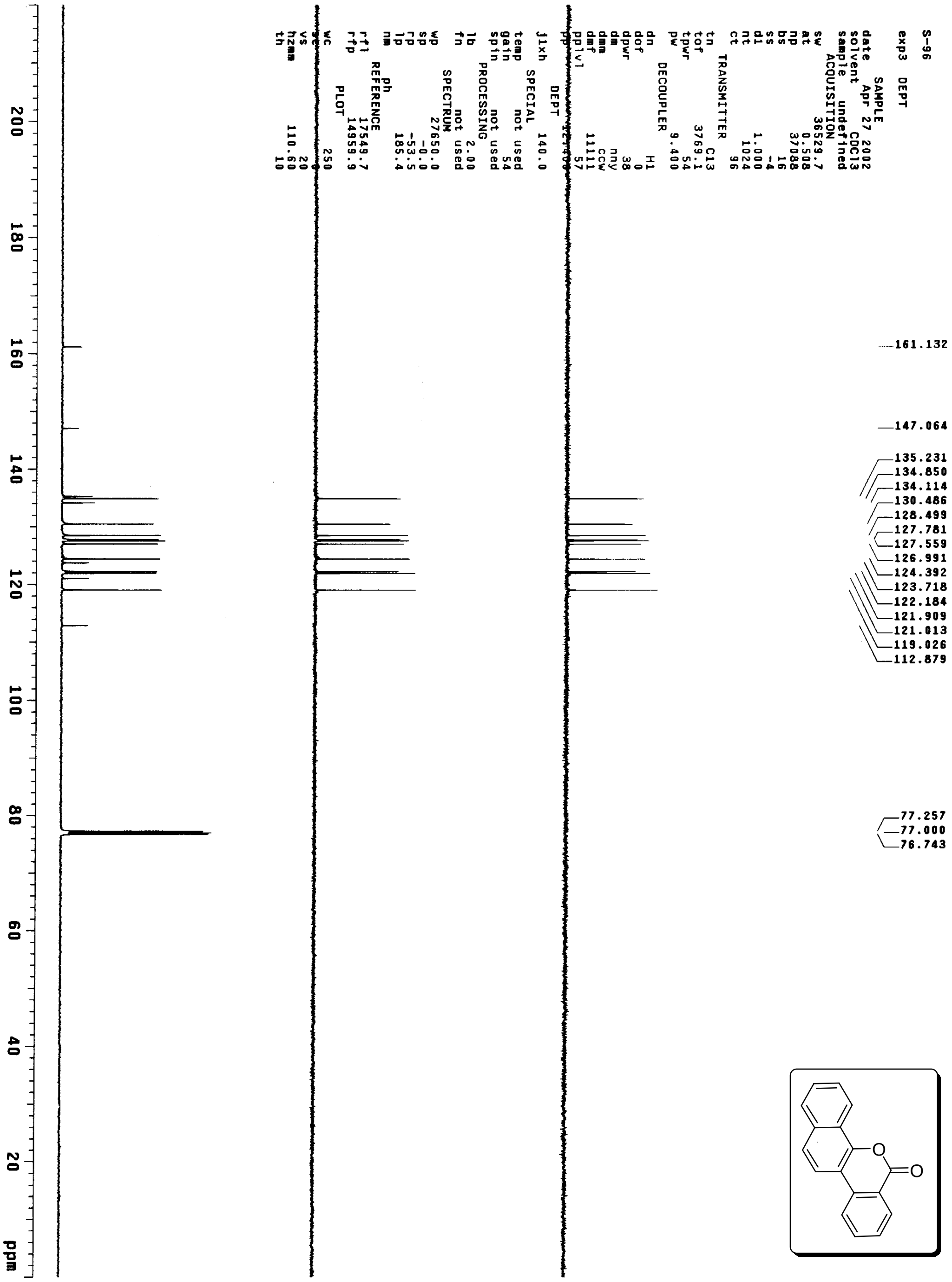
9-Methyl-6-oxaheptacyclo[14.6.6.0^{2,15}.0^{4,13}.0^{5,10}.0^{17,22}.0^{23,28}]octacosa-2(15),3,5(10), 8,11,13,17(22),18,20,23(28),24,26-dodecaen-7-one (3l). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (3H, d, J = 0.8 Hz), 5.55 (1H, s), 5.60 (1H, s), 6.28 (1H, d, J = 0.8 Hz), 7.00-7.05 (4H, m), 7.41-7.47 (5H, m), 7.53 (1H, d, J = 8.8 Hz), 7.76 (1H, s), 8.50 (1H, s); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 18.8, 53.6, 53.7, 113.6, 114.9, 116.3, 119.9, 120.7, 121.4, 123.4, 123.7, 123.9, 125.6, 125.7, 133.1, 143.4, 143.9, 144.1, 144.9, 150.0, 153.3, 160.7; HRMS (m/e): calcd for $C_{28}H_{18}O_2$ 386.1307, found 386.1302.

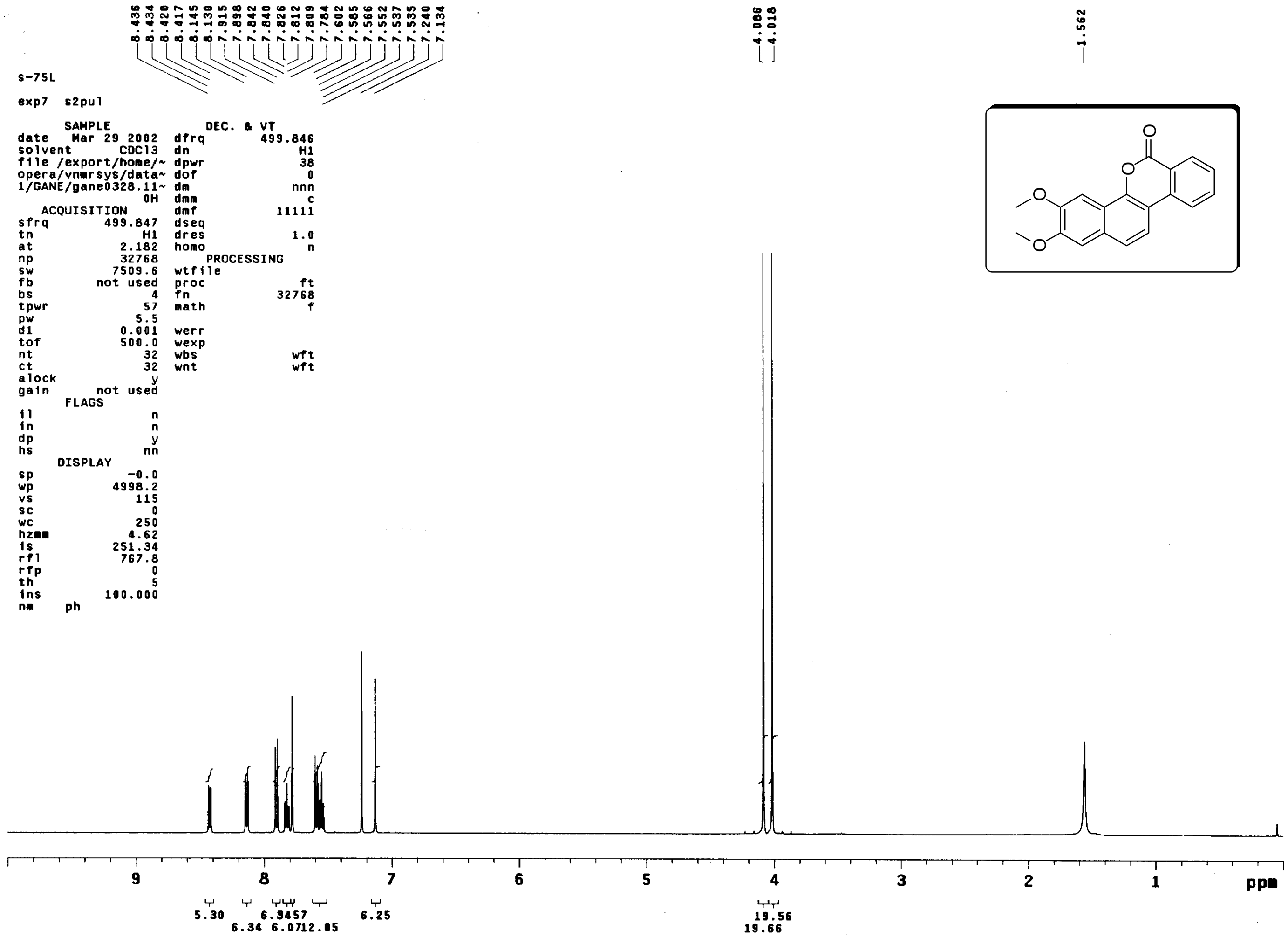
5,6-Dihydrobenzo[*c*]phenanthridin-6-one (4). ^1H NMR (500 MHz, $CDCl_3$): δ = 3.89-3.87 (1H, m), 4.86(1H, d, J = 6 Hz), 5.50 (1H, s), 5.77-5.50 (1H, m), 7.16 (1H, d, J = 7.5 Hz), 7.26-7.24 (2H, m), 7.34-7.30 (2H, m), 7.39 (1H, td, J = 7 Hz, J = 1 Hz), 7.52 (1H, td, J = 7 Hz, J = 1 Hz), 8.09 (1H, d, J = 7.5 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 38.8, 52.2, 127.1, 127.2, 127.6, 127.7, 128.0, 128.3, 128.6, 129.3, 131.7, 132.7, 133.0, 139.6; HRMS (m/e): calcd for $C_{17}H_{13}NO$ 247.0997, found 247.0997.

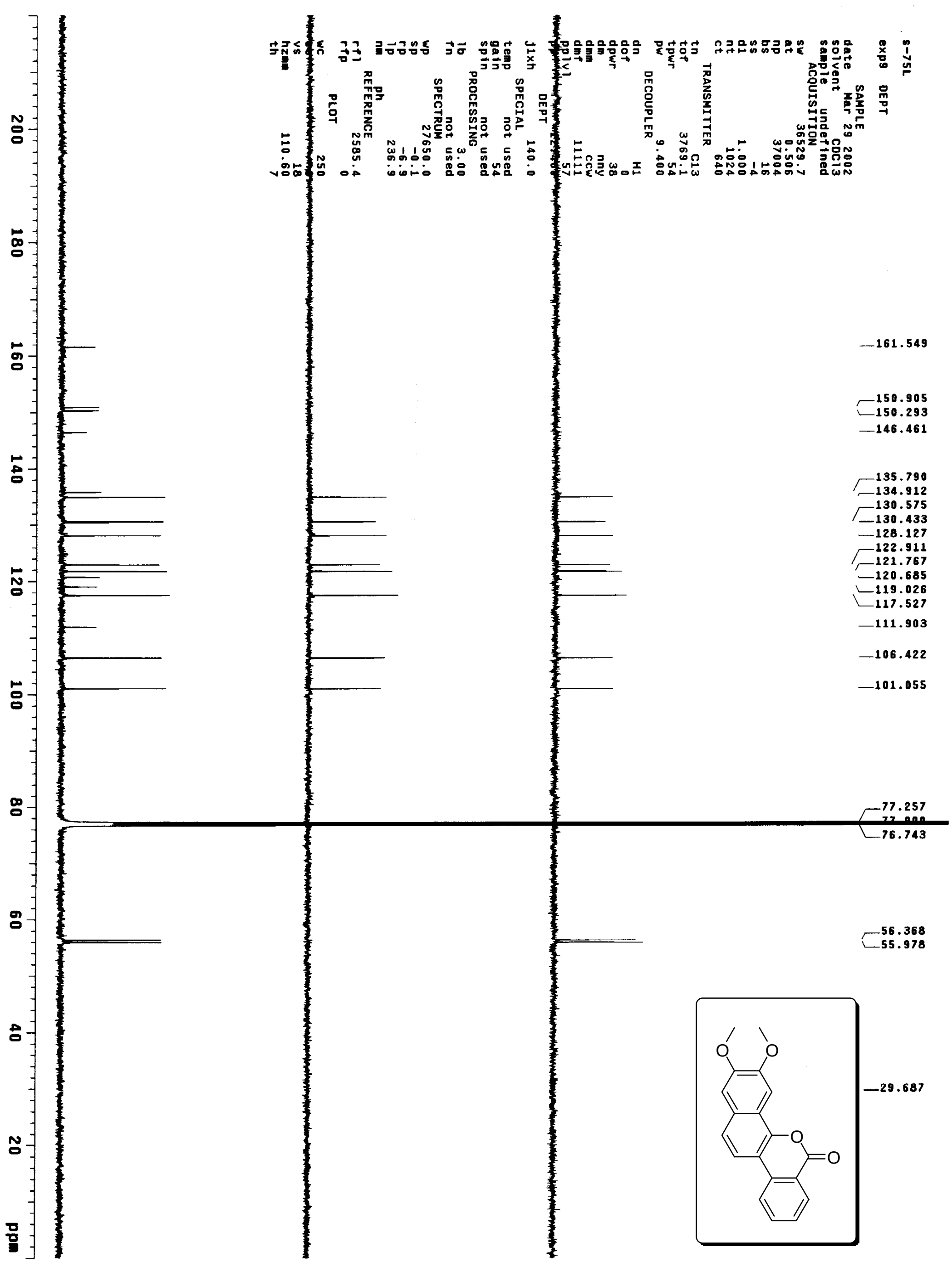
(3*R,4*S**,4a*S**,10b*R**)-3,4-Di((methyloxy)methyl)-4,4a,6,10b-tetrahydro-3*H*-b**

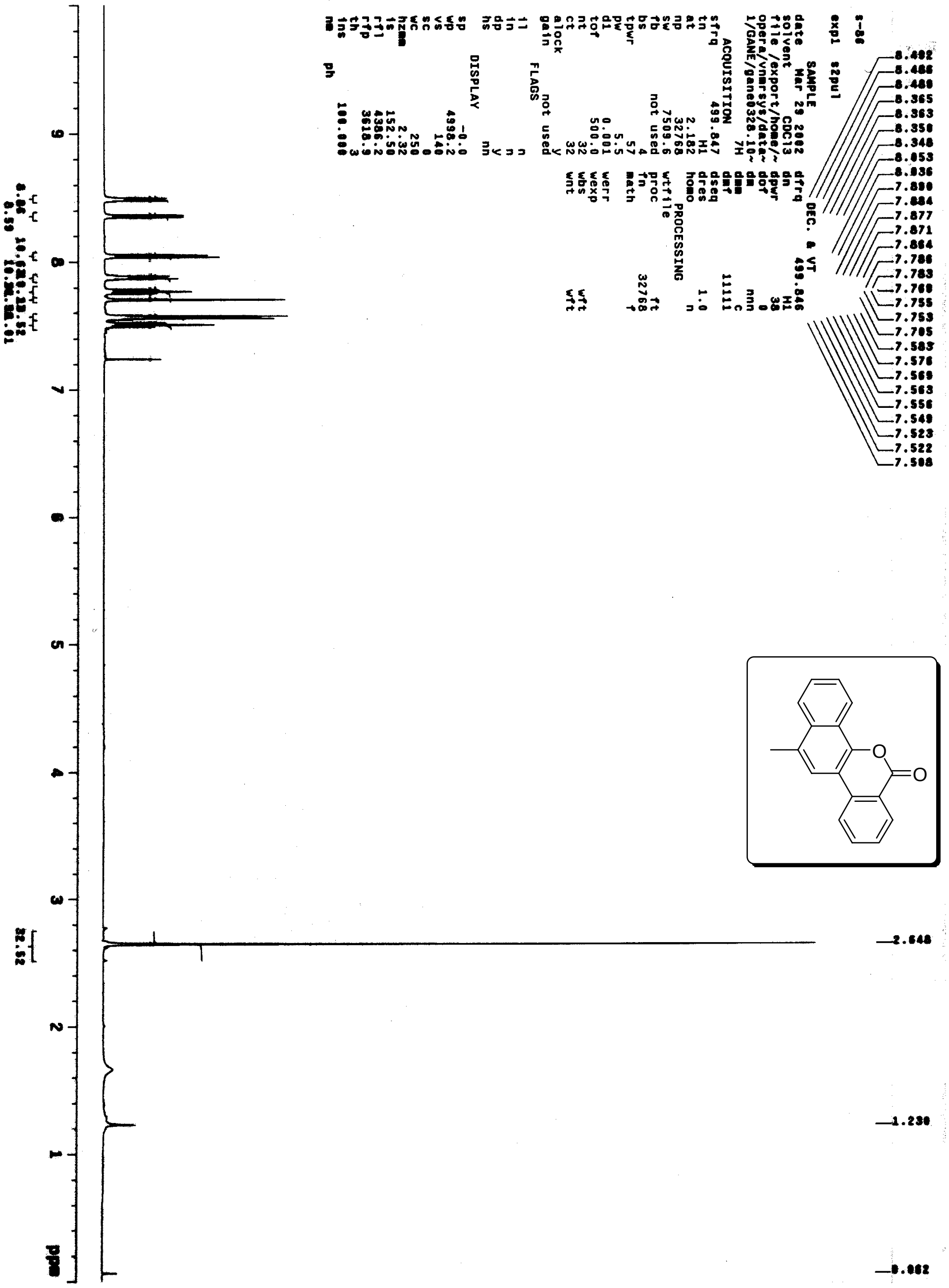
enzo[*c*]chromen-6-one (6). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.07-3.10 (1H, m), 3.18-3.19 (1H, m), 3.29 (3H, s), 3.34-3.35 (1H, m), 3.37 (1H, s), 3.52 (1H, d, *J* = 6.0 Hz), 3.53-3.57 (2H, m), 3.63-3.68 (2H, m), 5.80 (1H, dd, *J* = 2.8 Hz, *J* = 9.2 Hz), 6.59 (1H, dd, *J* = 2.8 Hz, *J* = 9.2 Hz), 7.47 (1H, t, *J* = 7.6 Hz), 7.58 (1H, d, *J* = 8.0 Hz), 7.73 (1H, t, *J* = 7.6 Hz), 8.30 (1H, d, *J* = 8.0 Hz); HRMS (m/e): calcd for $C_{17}H_{20}O_4$ 288.1362, found 288.1359.

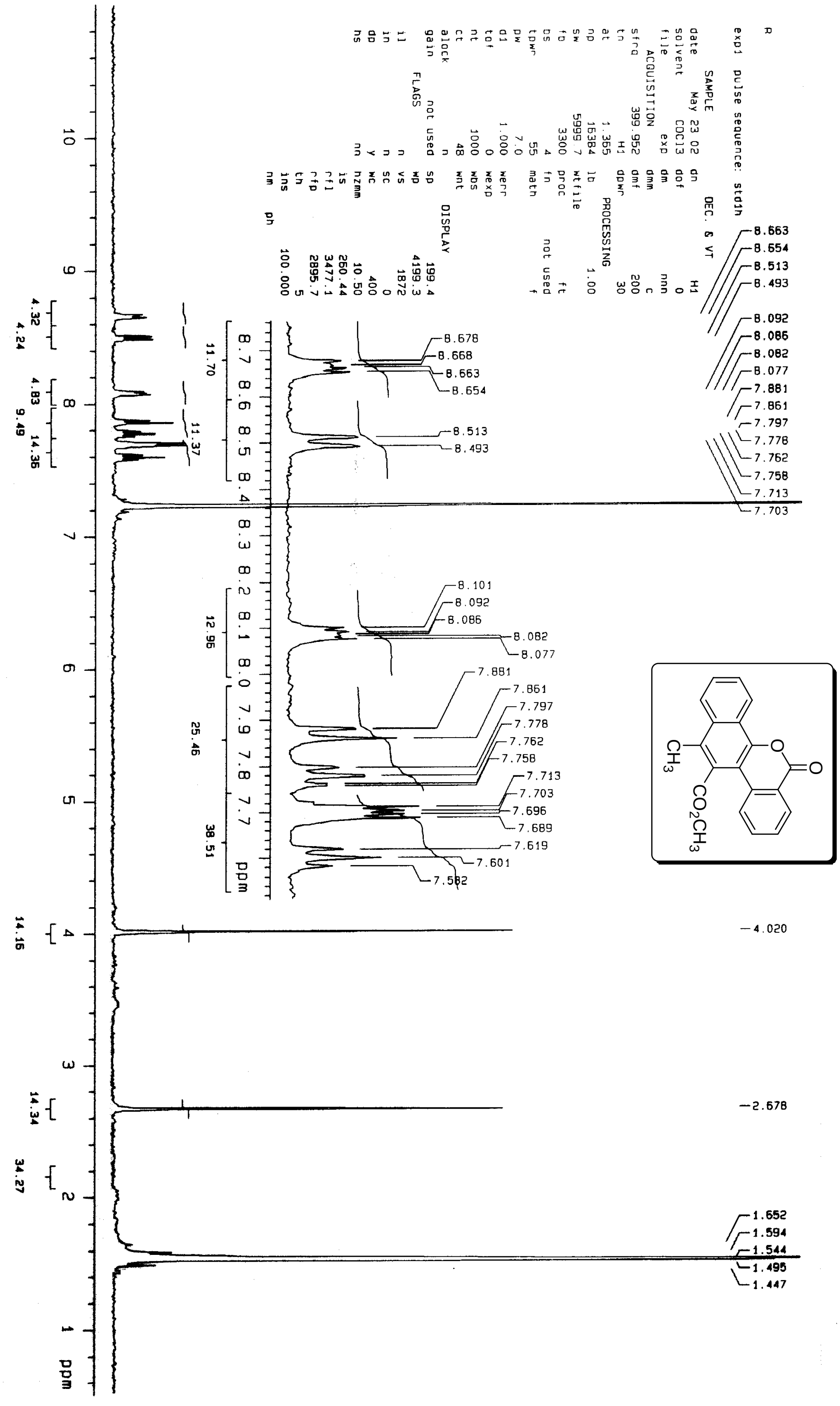

S-96
expl s2pul
8.504
8.489
8.396
8.381
8.097
8.081
7.960
7.942
7.808
7.793
7.781
7.684
7.666
7.587
7.575
7.560
7.557
7.551
7.543
7.536
7.520
7.240
1.658
ppm

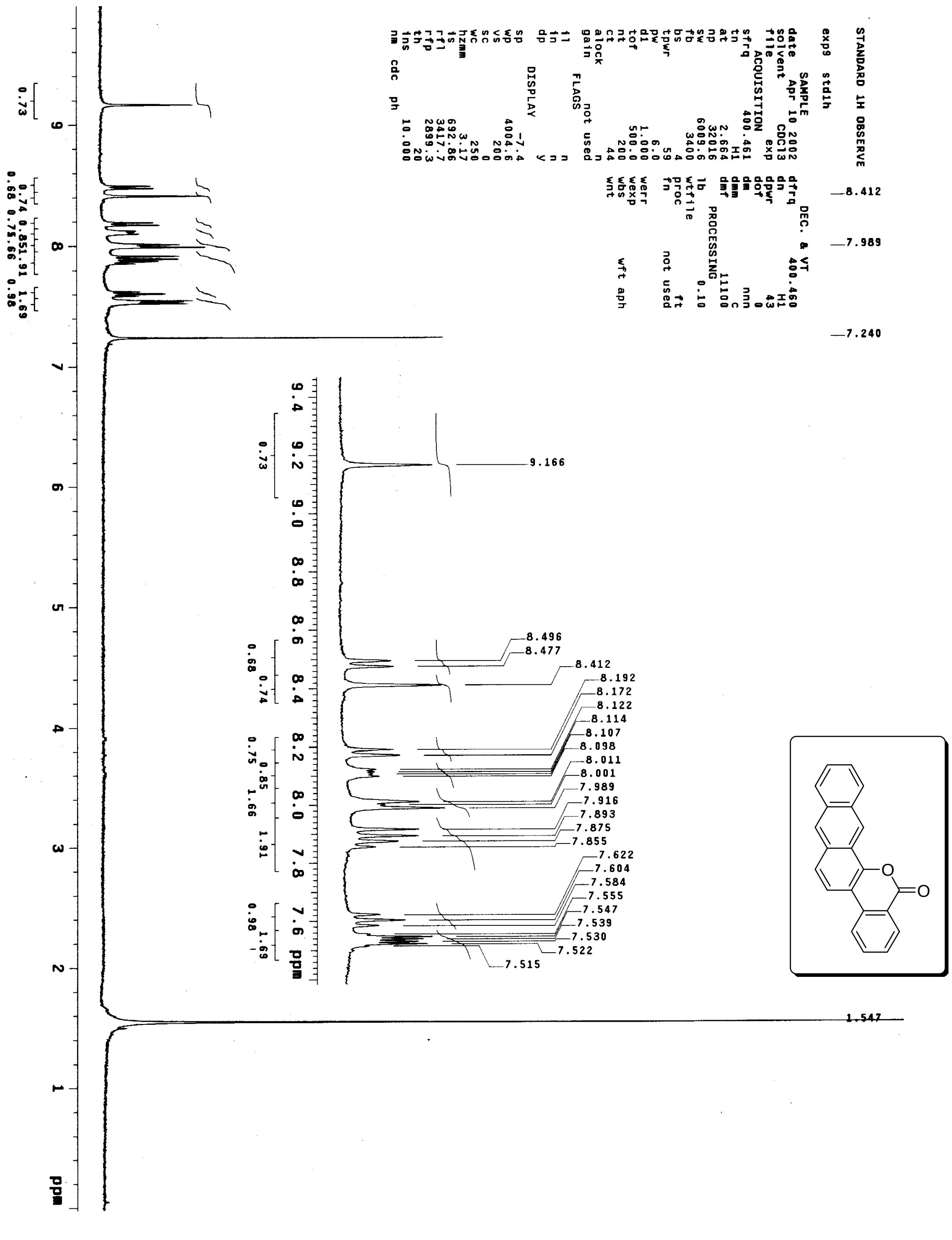

S-96
exp3 DEPT
161.132
147.064
135.231
134.850
134.114
130.486
128.499
127.781
127.559
126.991
124.392
123.718
122.184
121.909
121.013
119.026
112.879
77.257
77.000
76.743
ppm

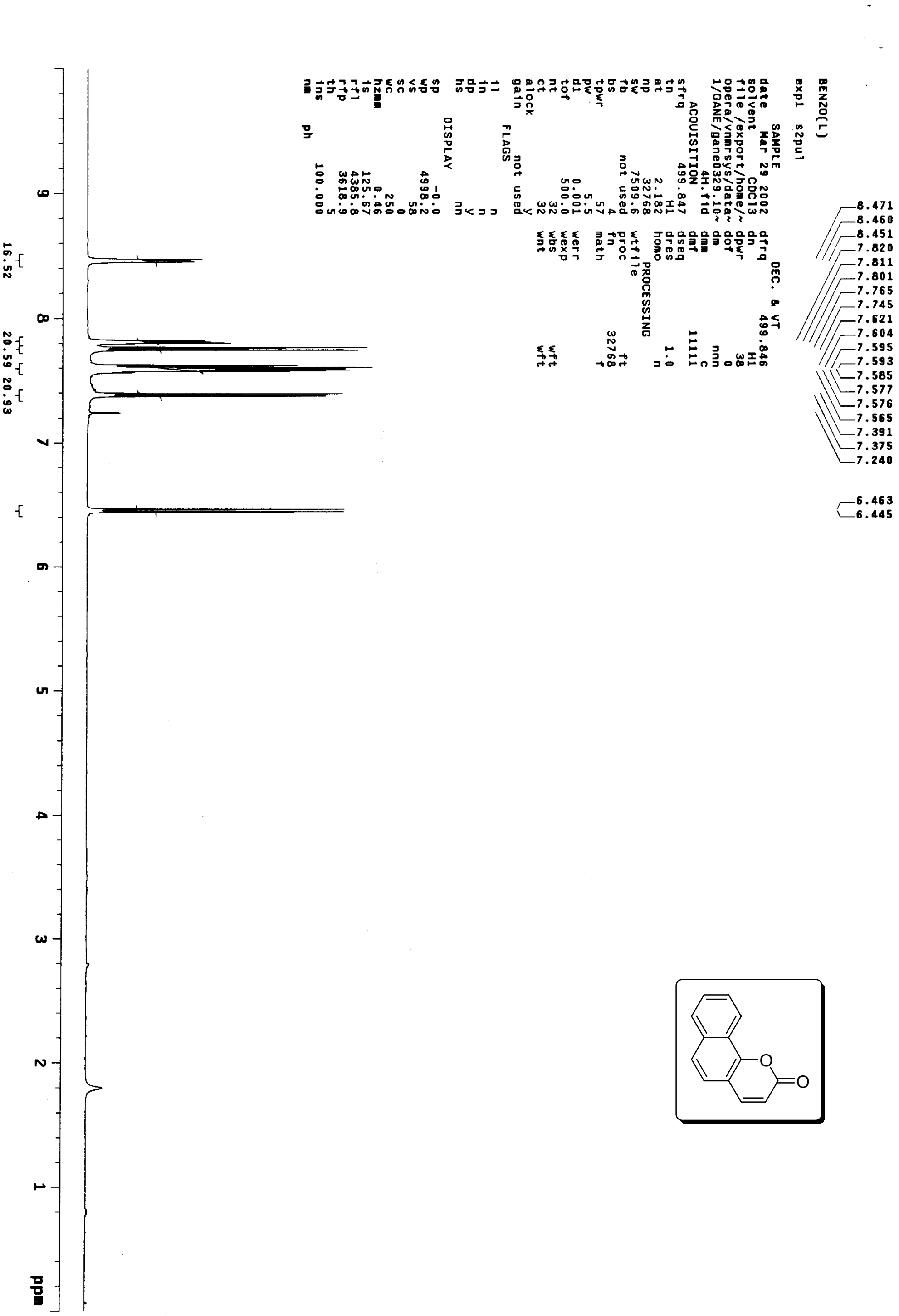

s-75L
exp7 s2pul
SAMPLE
date Mar 29 2002
solvent CDCl3
file /export/home/~
opera/vnmrsys/data~
1/GANE/gane0328.11~
0H
ACQUISITION
sfrq 499.847
tn H1
at 2.182
np 32768
sw 7509.6
fb not used
bs 4
tpwr 57
pw 5.5
d1 0.001
tof 500.0
nt 32
ct 32
alock y
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -0.0
wp 4998.2
vs 115
sc 0
wc 250
hzmm 4.62
is 251.34
rfl 767.8
rfp 0
th 5
ins 100.000
nm ph
DEC. & VT
dfrq 499.846
dn H1
dpwr 38
dof 0
dm nnn
dmm c
dmf 11111
dseq
dres 1.0
homo n
PROCESSING
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs wft
wnt wft
8.436
8.434
8.420
8.417
8.145
8.130
7.915
7.898
7.842
7.840
7.826
7.812
7.809
7.784
7.602
7.585
7.566
7.552
7.537
7.535
7.240
7.134
4.086
4.018
1.562
9
8
7
6
5
4
3
2
1
ppm
5.30
6.34
6.9457
6.0712.05
6.25
19.56
19.66
O
O
O
O

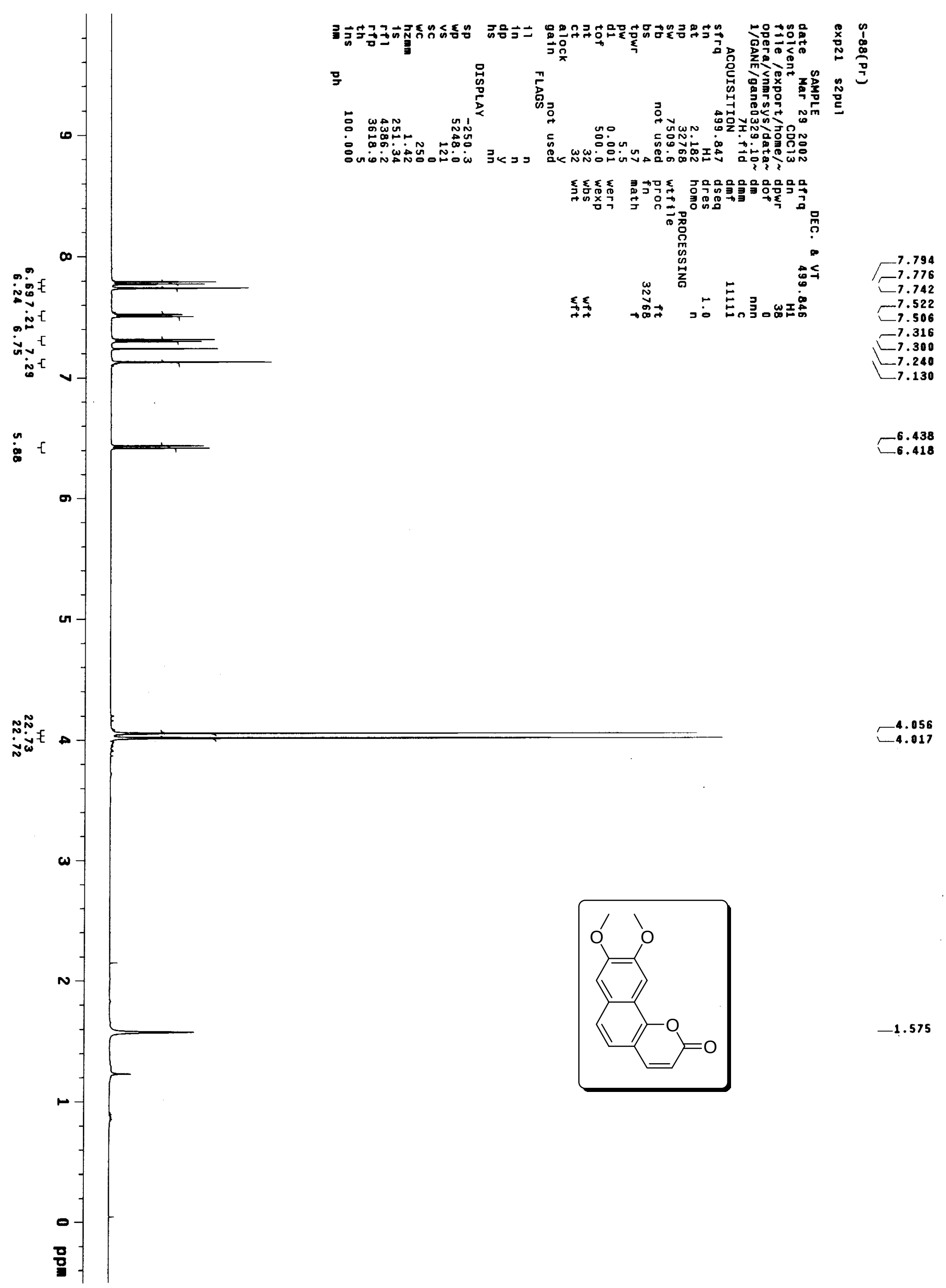

s-75L
exp9 DEPT
SAMPLE
date Mar 29 2002
solvent CDCl3
sample undefined
ACQUISITION
sw 36529.7
at 0.506
np 37004
bs 16
ss -4
d1 1.000
nt 1024
ct 640
TRANSMITTER
tn C13
tof 3769.1
tpwr 54
pw 9.400
DECOUPLER
dn H1
dof 0
dpwr 38
dm nny
dmm ccw
dmf 11111
pplvl 57
DEPT
j1xh 140.0
SPECIAL
temp not used
gain 54
spin not used
PROCESSING
lb 3.00
fn not used
SPECTRUM
wp 27650.0
sp -0.1
rp -6.9
lp 236.9
nm ph
REFERENCE
rfl 2585.4
rfp 0
PLOT
wc 250
vs 18
hzmm 110.60
th 7
161.549
150.905
150.293
146.461
135.790
134.912
130.575
130.433
128.127
122.911
121.767
120.685
119.026
117.527
111.903
106.422
101.055
77.257
76.743
56.368
55.978
29.687
200
180
160
140
120
100
80
60
40
20
ppm

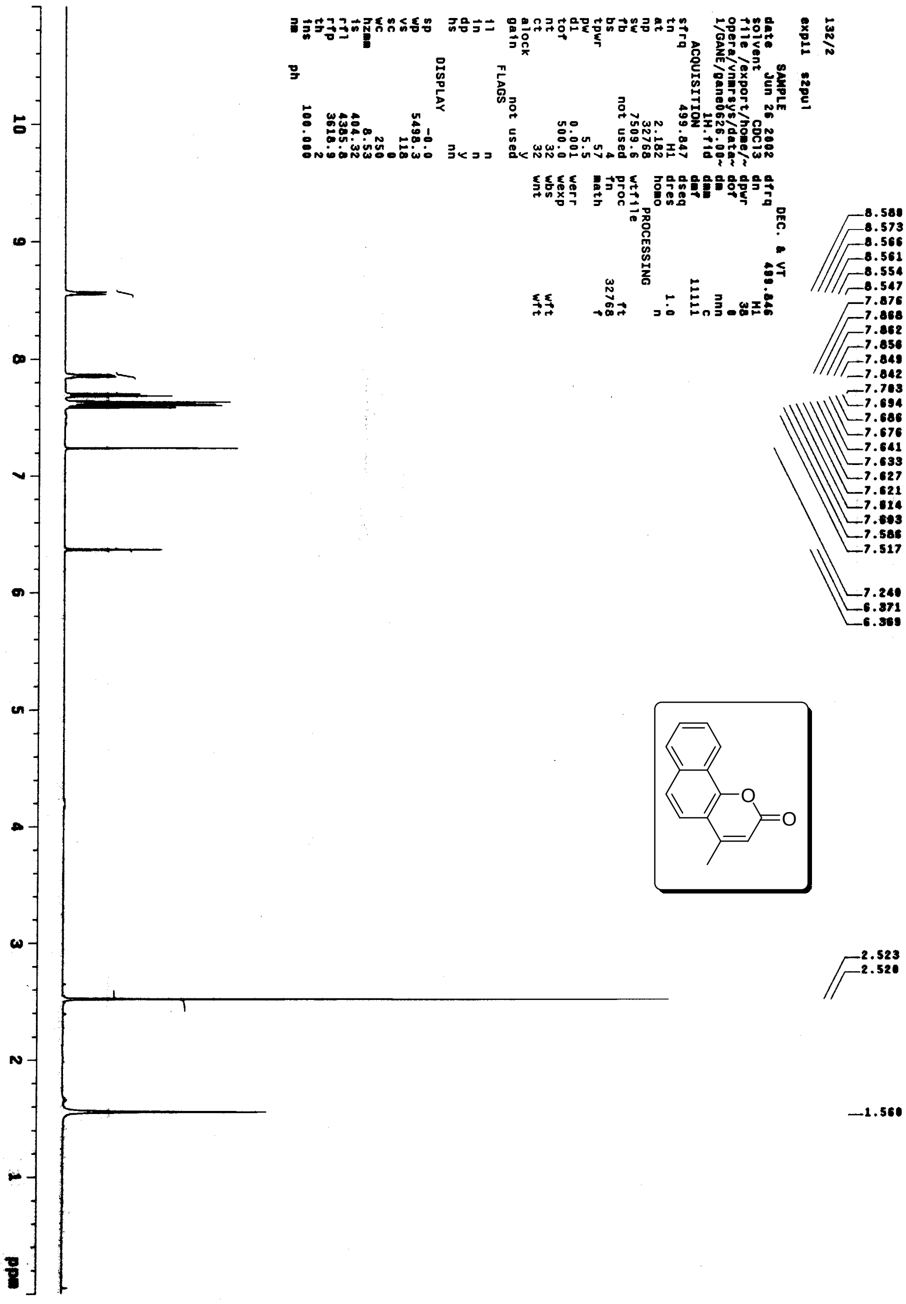


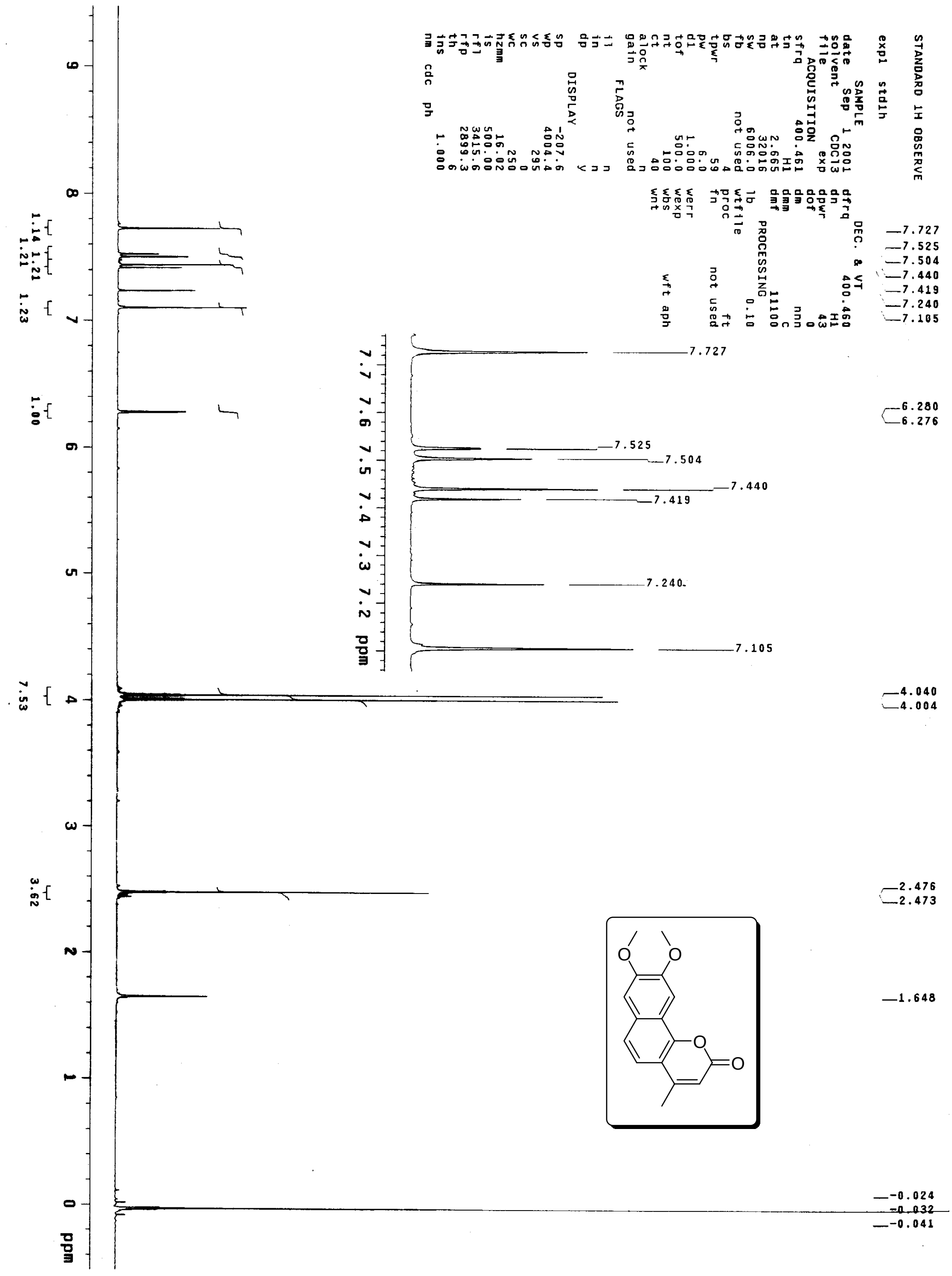

8.663
8.654
8.513
8.493
8.092
8.086
8.082
8.077
7.881
7.861
7.797
7.778
7.762
7.758
7.713
7.703
4.020
2.678
1.652
1.594
1.544
1.495
1.447
CH3
CO2CH3
ppm

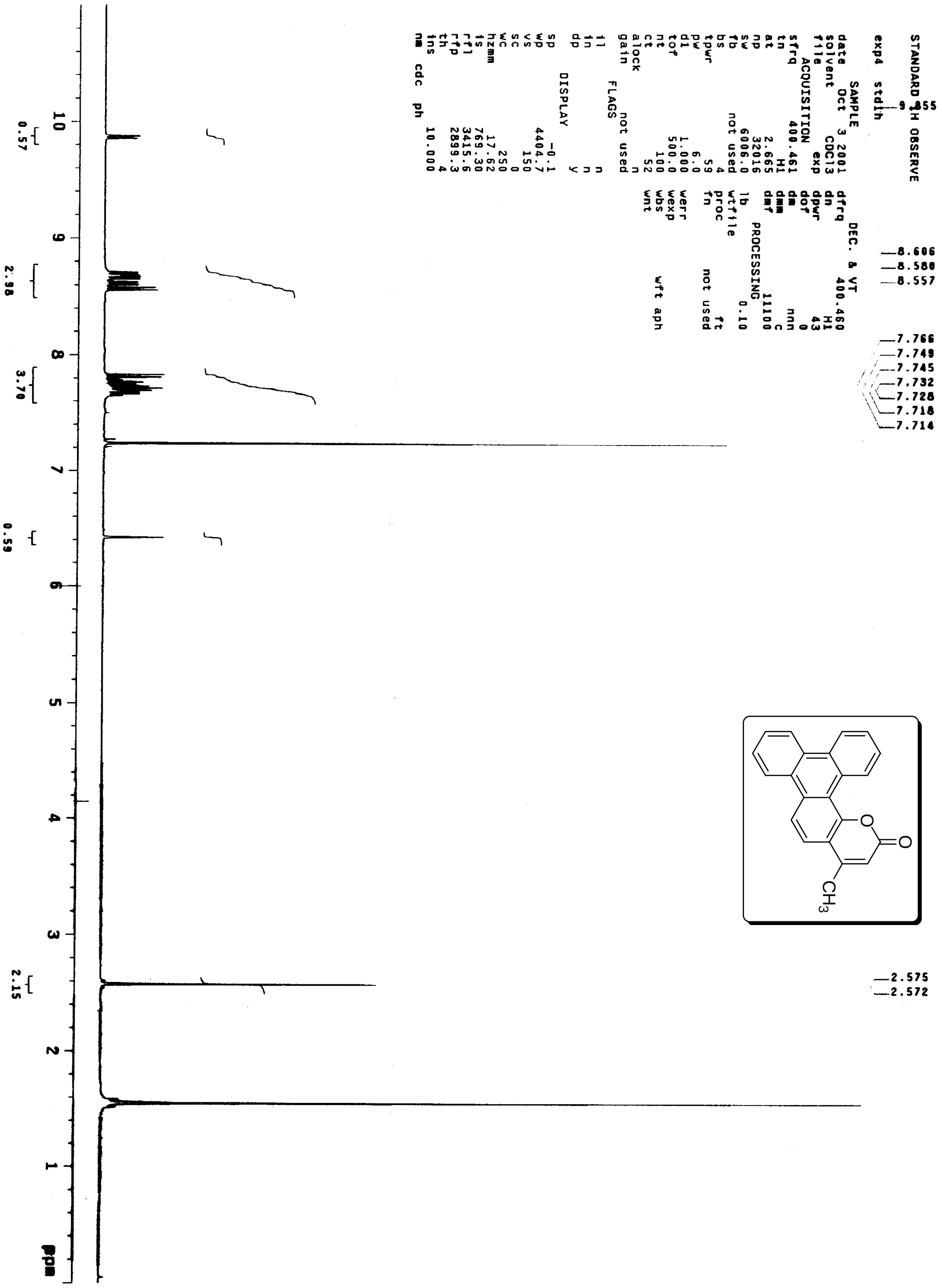

STANDARD 1H OBSERVE
exp9 std1h
SAMPLE
date Apr 10 2002
solvent CDCl3
file exp
ACQUISITION
sfrq 400.461
tn H1
at 2.664
np 32016
sw 6009.6
fb 3400
bs 4
tpwr 59
pw 6.0
d1 1.000
tof 500.0
nt 200
ct 44
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -7.4
wp 4004.6
vs 200
sc 0
wc 250
hzmm 3.17
is 692.86
rfl 3417.7
rfp 2899.3
th 20
ins 10.000
nm cdc ph
DEC. & VT
dfrq 400.460
dn H1
dpwr 43
dof 0
dm nnn
dmm c
dmf 11100
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp wft aph
wbs
wnt
8.412
7.989
7.240
1.547
9.166
8.496
8.477
8.412
8.192
8.172
8.122
8.114
8.107
8.098
8.011
8.001
7.989
7.916
7.893
7.875
7.855
7.622
7.604
7.584
7.555
7.547
7.539
7.530
7.522
7.515
0.73
0.68
0.74
0.75
0.85
1.66
1.91
0.98
1.69
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 ppm
9 8 7 6 5 4 3 2 1 ppm
O
O

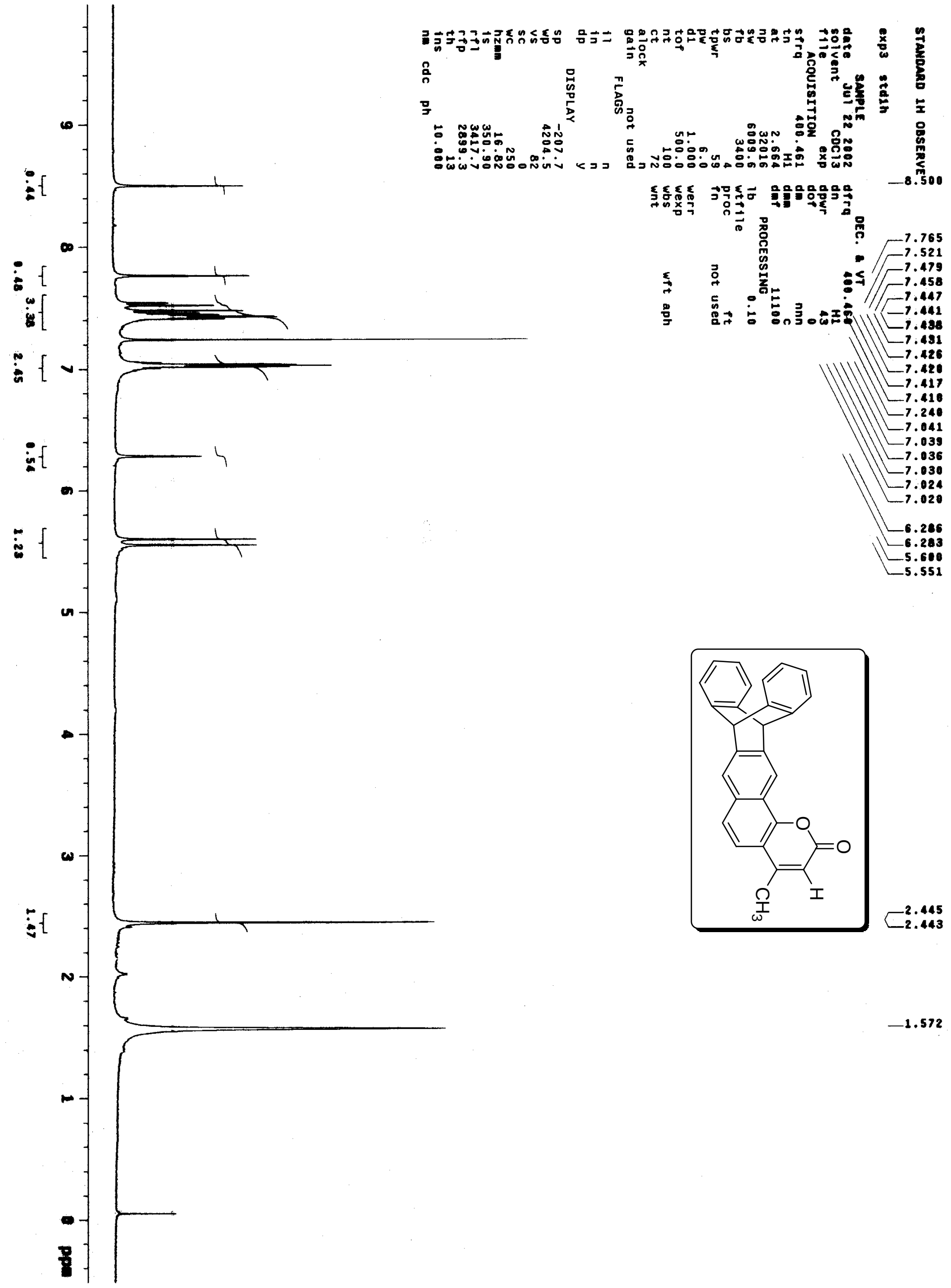

BENZO(L)
exp1 s2pul
8.471
8.460
8.451
7.820
7.811
7.801
7.765
7.745
7.621
7.604
7.595
7.593
7.585
7.577
7.576
7.565
7.391
7.375
7.240
6.463
6.445
16.52
20.59 20.93
16.64
ppm

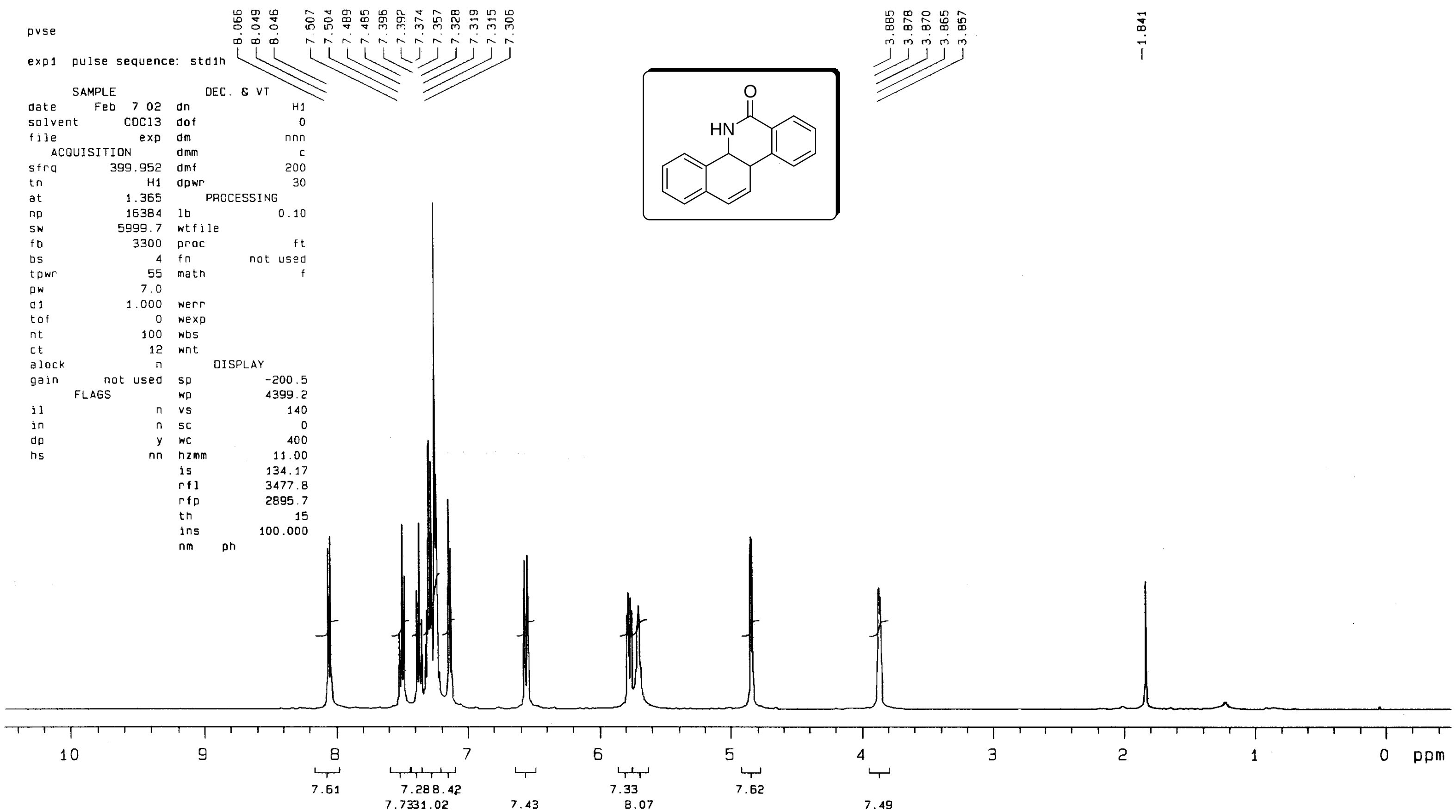


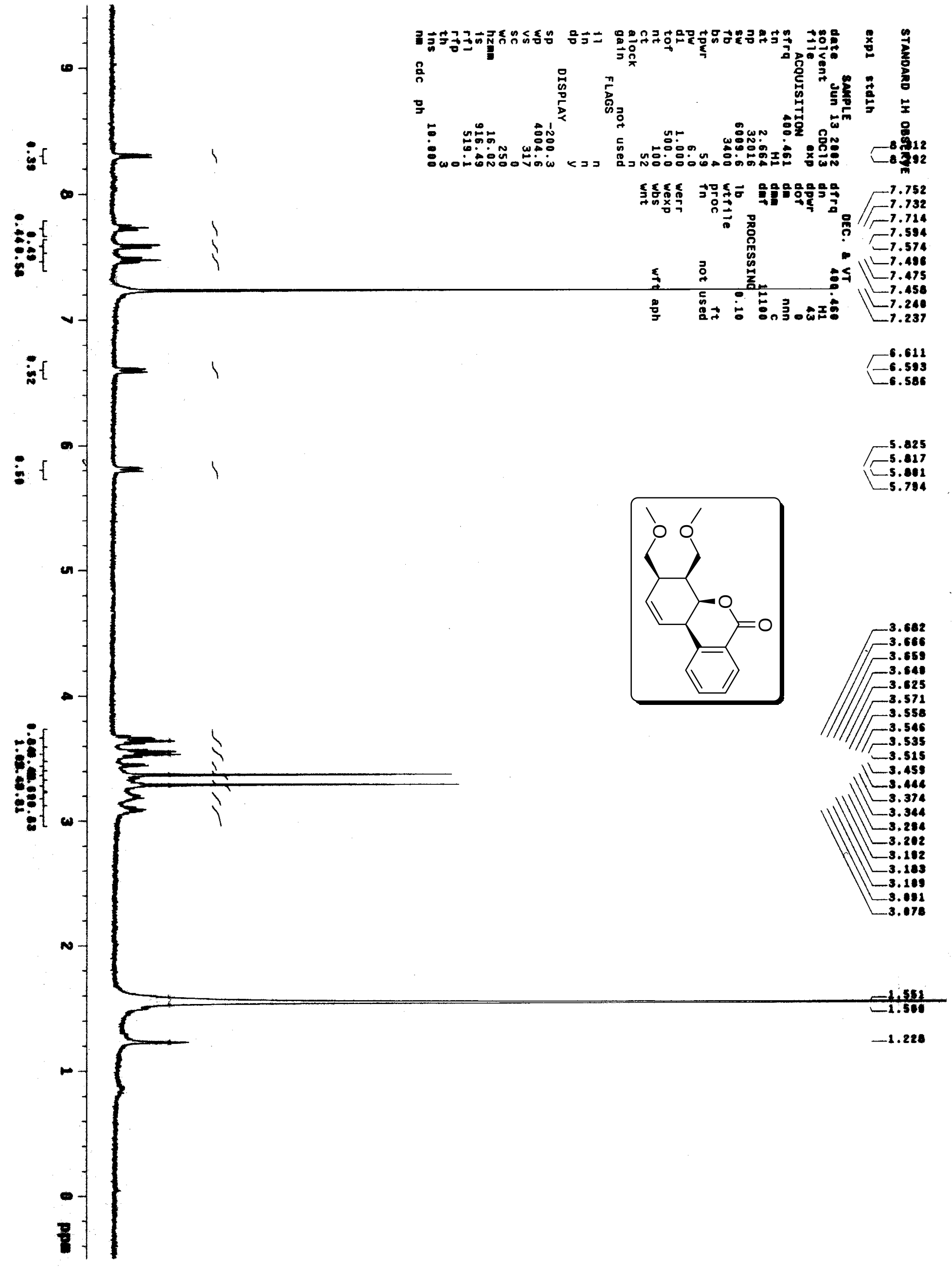



STANDARD 1H OBSERVE
7.727
7.525
7.504
7.440
7.419
7.240
7.105
6.280
6.276
4.040
4.004
2.476
2.473
1.648
-0.024
-0.032
-0.041
ppm


STANDARD 1H OBSERVE
exp4 std1h
SAMPLE
date Oct 3 2001
solvent CDCl3
file exp
ACQUISITION
sfrq 400.461
tn H1
DEC. & VT
dfrq 400.460
dn H1
PROCESSING
DISPLAY
FLAGS
9.855
8.606
8.580
8.557
7.766
7.749
7.745
7.732
7.728
7.718
7.714
2.575
2.572
0.57
2.98
3.70
0.59
2.15
O
O
CH3
ppm


STANDARD 1H OBSERVE
exp3 std1h
SAMPLE
date Jul 22 2002
solvent CDCl3
ACQUISITION
PROCESSING
DEC. & VT
DISPLAY
FLAGS
8.500
7.765
7.521
7.479
7.458
7.447
7.441
7.438
7.431
7.426
7.420
7.417
7.410
7.240
7.041
7.039
7.036
7.030
7.024
7.020
6.286
6.283
5.600
5.551
2.445
2.443
1.572
0.44
0.48
3.38
2.45
0.54
1.23
1.47
ppm
O
H
CH3


pvse
exp1 pulse sequence: std1h
SAMPLE
date Feb 7 02
solvent CDCl3
file exp
ACQUISITION
sfrq 399.952
tn H1
at 1.365
np 16384
sw 5999.7
fb 3300
bs 4
tpwr 55
pw 7.0
d1 1.000
tof 0
nt 100
ct 12
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DEC. & VT
dn H1
dof 0
dm nnn
dmm c
dmf 200
dpwr 30
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
DISPLAY
sp -200.5
wp 4399.2
vs 140
sc 0
wc 400
hzmm 11.00
is 134.17
rfl 3477.8
rfp 2895.7
th 15
ins 100.000
nm ph
8.066
8.049
8.046
7.507
7.504
7.489
7.485
7.396
7.392
7.374
7.357
7.328
7.319
7.315
7.306
3.885
3.878
3.870
3.865
3.857
1.841
HN
O
10
9
8
7
6
5
4
3
2
1
0
ppm
7.61
7.28
8.42
7.73
31.02
7.43
7.33
8.07
7.62
7.49


STANDARD 1H OBSERVE
ppm