

-SI-

Supporting Informations

Hypervalent iodine (III) mediated oxidation of aldoximes to *N*-acetoxy or *N*-hydroxy amides

Harisadhan Ghosh and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati 781 039, Assam, India.

patel@iitg.ernet.in

List of Contents

- | | |
|---|--------|
| 1. General information | S2 |
| 2. Spectra (¹ H NMR, IR and ¹³ C NMR) of compounds | S3-S26 |

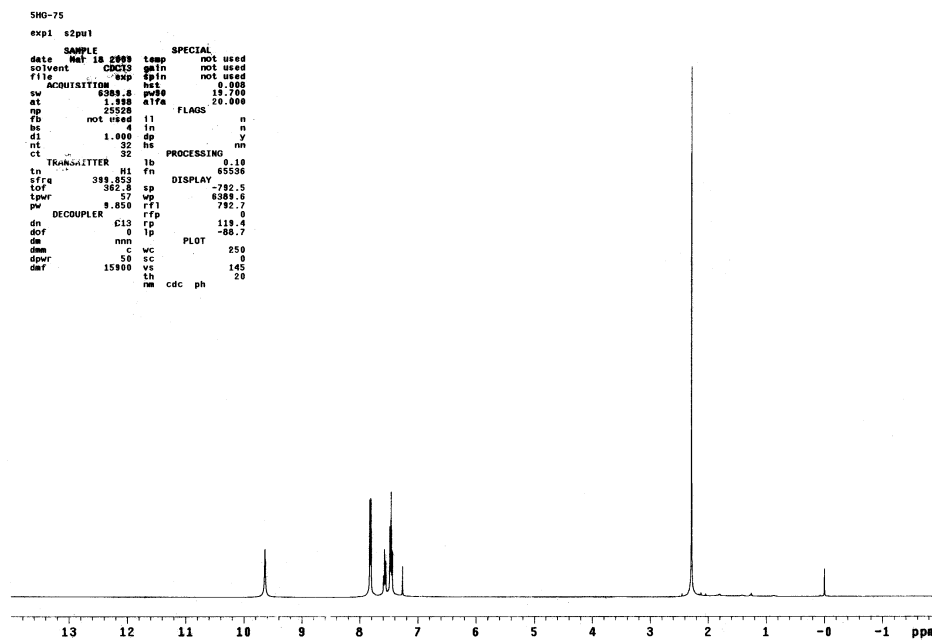
Preparation of starting aldoximes:

All aldoximes were prepared according to the reported procedure [see supporting information of B. A. Mendelsohn, S. Lee, S. Kim, F. Teyssier, V. S. Aulakh, M. A. Ciufolini *Org. Lett.*, **2009**, *11*, 1539–1542 or see E. Hauser in E. Muller, *Methoden der organischen Chemie (Houben-Weyl)* Vol. 2, p. 446. ThiemeVerlag, Stuttgart (1953)] and obtained as a mixture of *syn*- / *anti*- isomers, which were used without further purification.

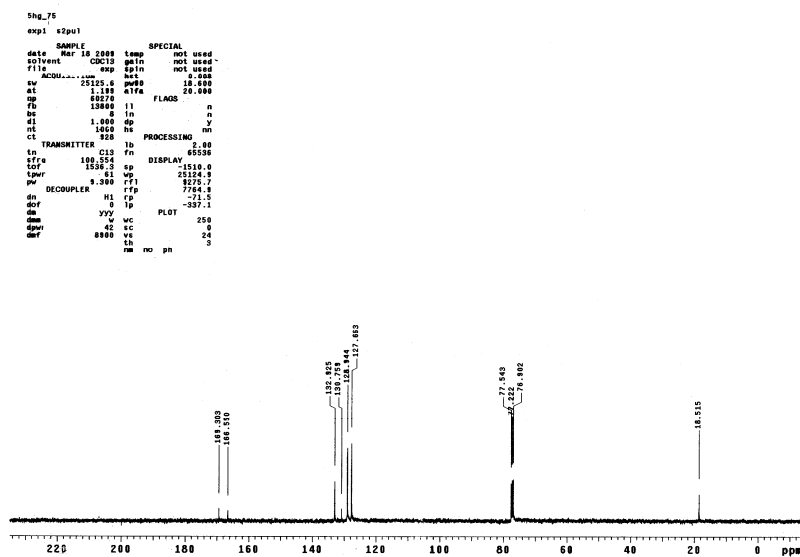
-S3-

Spectra

N-Acetoxy-benzamide (1a): ¹H NMR (400 MHz, CDCl₃):



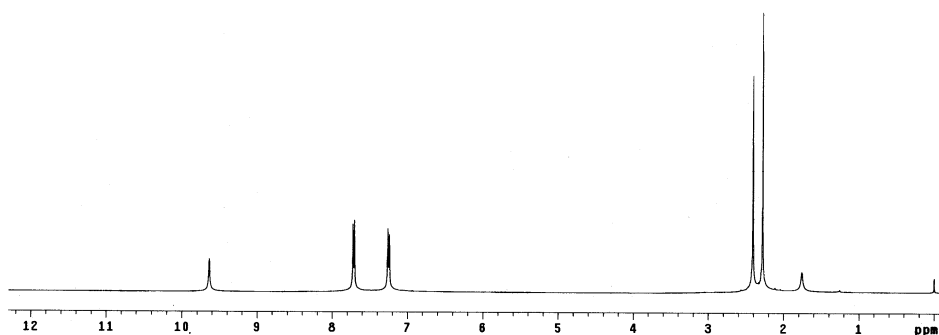
N-Acetoxy-benzamide (1a): ¹³C NMR (100 MHz, CDCl₃):



-S4-

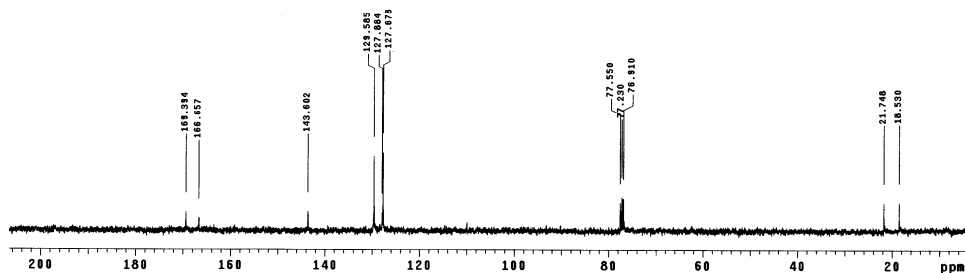
***N*-Acetoxy-4-methyl-benzamide (2a): ¹H NMR (400 MHz, CDCl₃):**

```
5hg_108
exp1 s2pu1
SAMPLE
date Apr 22 2009 temp not used
solvent CDCl3 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 6389.8 hz 19.700
at 1.958 a1fa 20.000
rg 23528
fb not used i1 n
bs 4 in n
d1 1.000 dp y
nt 32 hs y
ct 32 PROCESSING
tn TRANSMITTER lb 0.10
fn 6538
sfrq 399.853
tof 382.0 sp -44.3
tpwr 57 wp 4982.2
pw 8.850 rftl 292.3
DECOUPLER C13 rfp 0
dn 0 lp 121.1
dof 0 lp -93.5
da nnn PLOT
dm C wc 250
dpr 50 sc 0
dfr 15900 vs 78
nm cdc ph 20
```



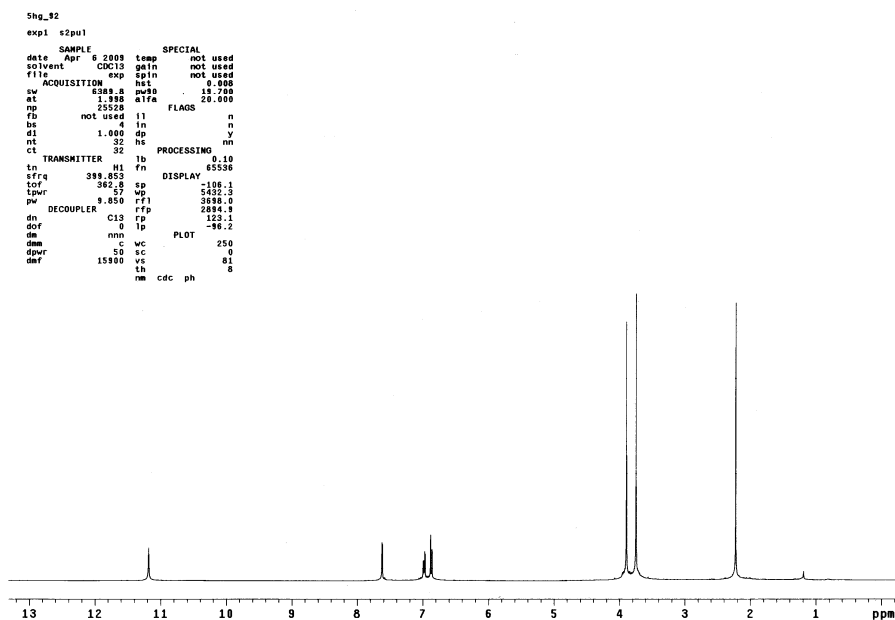
***N*-Acetoxy-4-methyl-benzamide (2a): ¹³C NMR (100 MHz, CDCl₃):**

```
5hg_108
exp1 s2pu1
SAMPLE
date Apr 22 2009 temp not used
solvent CDCl3 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25125.6 hz 18.400
at 1.198 a1fa 20.000
rg 68278
fb 13600 i1 n
bs 16 in n
d1 1.000 dp y
nt 1000 hs y
ct 236 PROCESSING
tn TRANSMITTER lb 2.00
fn 6538
sfrq 100.554
tof 1536.3 sp 372.4
tpwr 61 wp 26483.1
pw 8.300 rftl 3274.3
DECOUPLER C13 rfp 7764.8
dn 0 lp -100.4
dof 0 lp -271.4
da yyy PLOT
dm C wc 250
dpr 42 sc 0
dfr 8900 vs 20
nm no ph 2
```

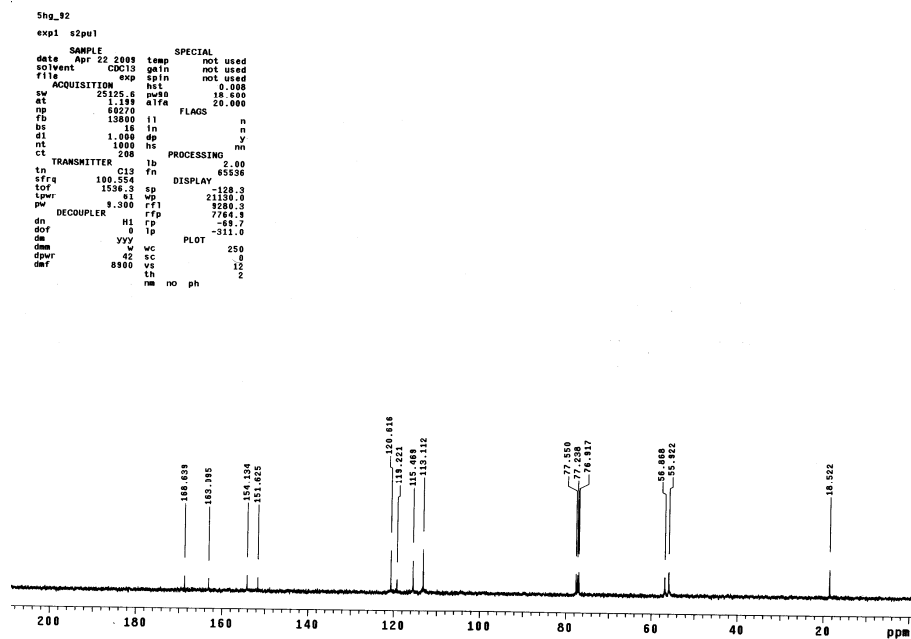


-S5-

***N*-Acetoxy-2,5-dimethoxy-benzamide (3a): ¹H NMR (400 MHz, CDCl₃):**

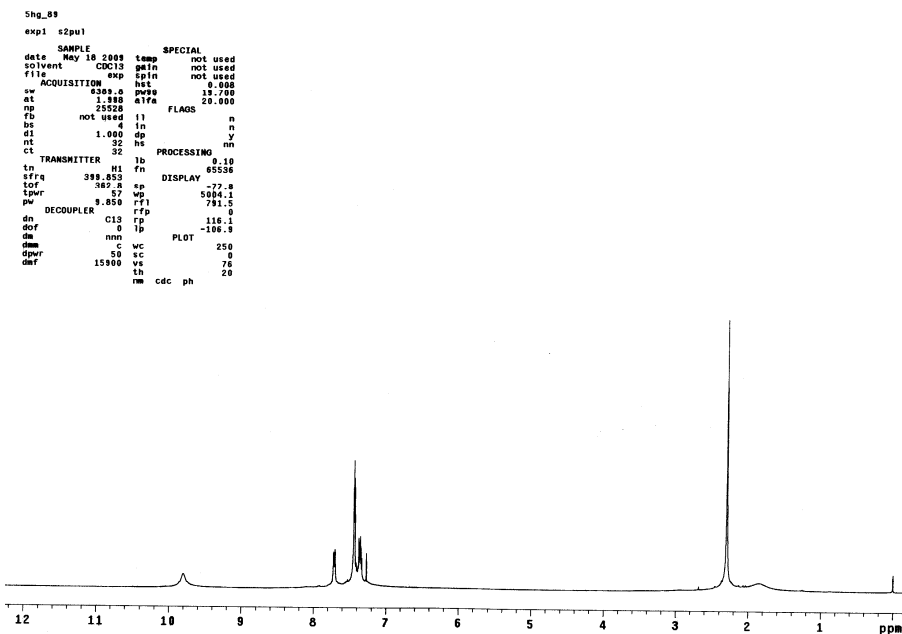


***N*-Acetoxy-2,5-dimethoxy-benzamide (3a): ¹³C NMR (100 MHz, CDCl₃):**

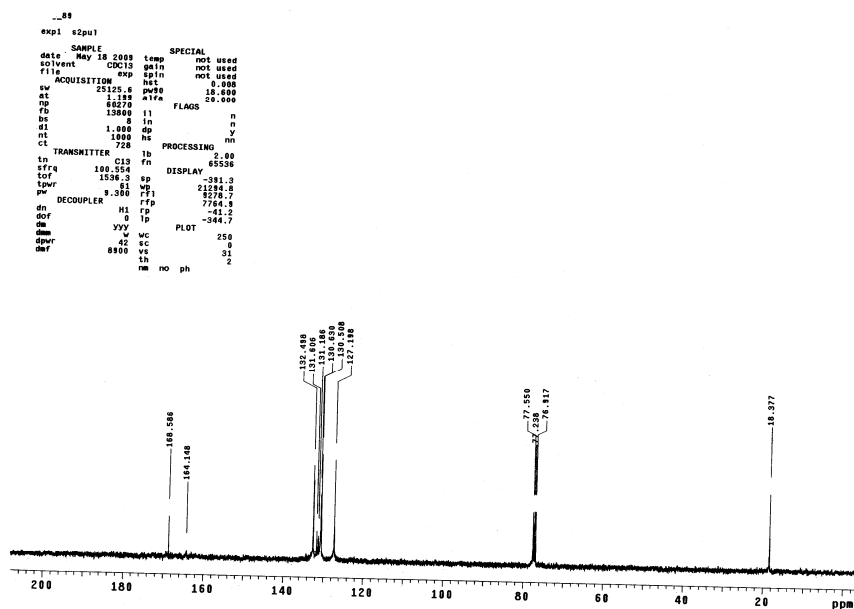


-S6-

***N*-Acetoxy-2-chloro-benzamide (4a): ¹H NMR (400 MHz, CDCl₃):**

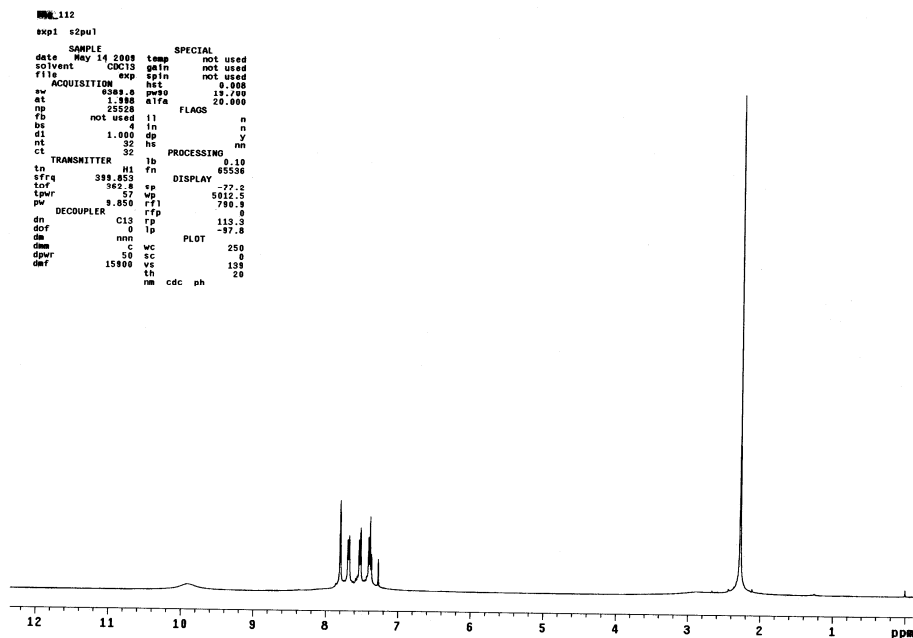


***N*-Acetoxy-2-chloro-benzamide (4a): ¹³C NMR (100 MHz, CDCl₃):**

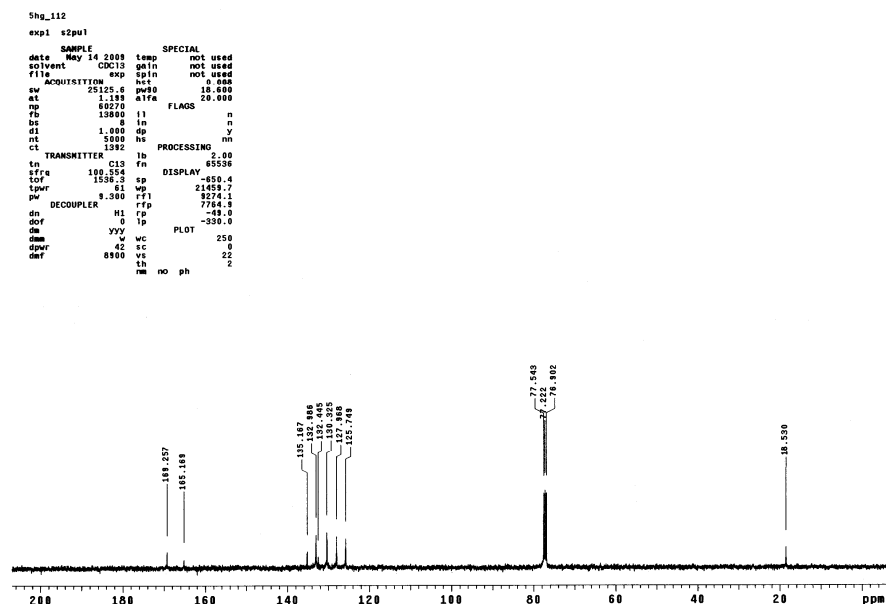


-S7-

***N*-Acetoxy-3-chloro-benzamide (5a): ¹H NMR (400 MHz, CDCl₃):**

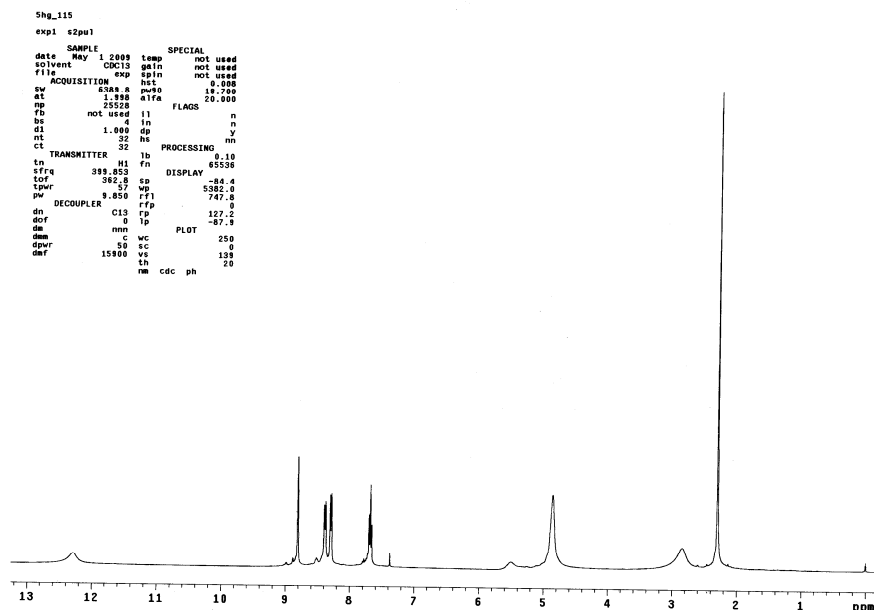


***N*-Acetoxy-3-chloro-benzamide (5a): ¹³C NMR (100 MHz, CDCl₃):**

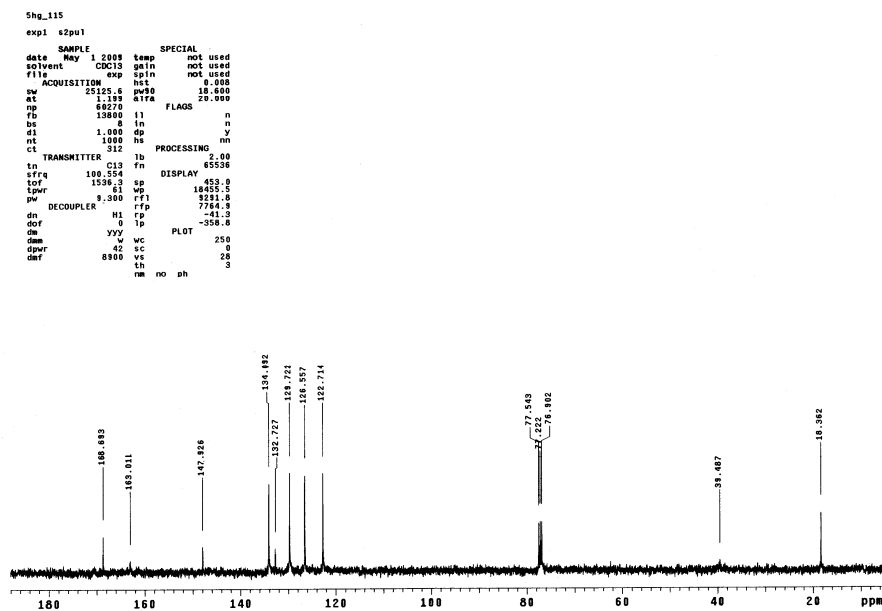


-S8-

***N*-Acetoxy-3-nitro-benzamide (6a): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**

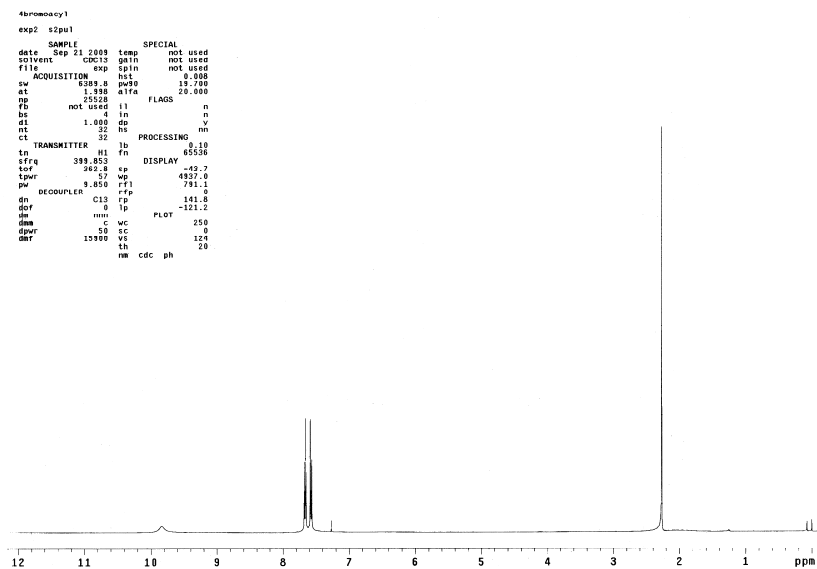


***N*-Acetoxy-3-nitro-benzamide (6a): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**

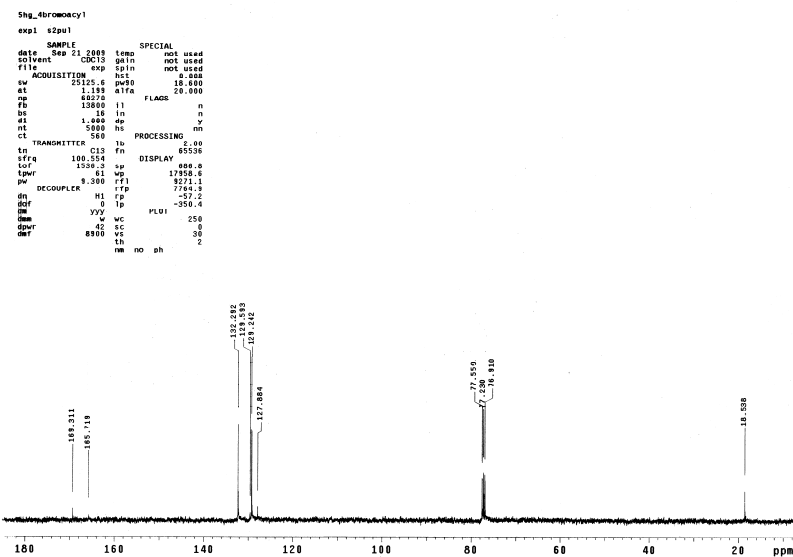


-S9-

***N*-Acetoxy-4-bromo-benzamide (7a): ¹H NMR (400 MHz, CDCl₃):**

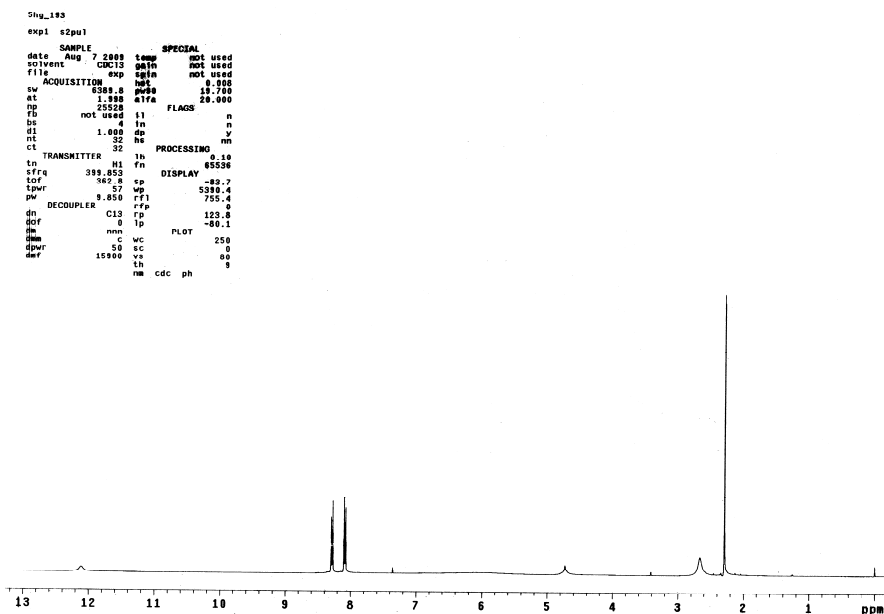


***N*-Acetoxy-4-bromo-benzamide (7a): ¹³C NMR (100 MHz, CDCl₃):**

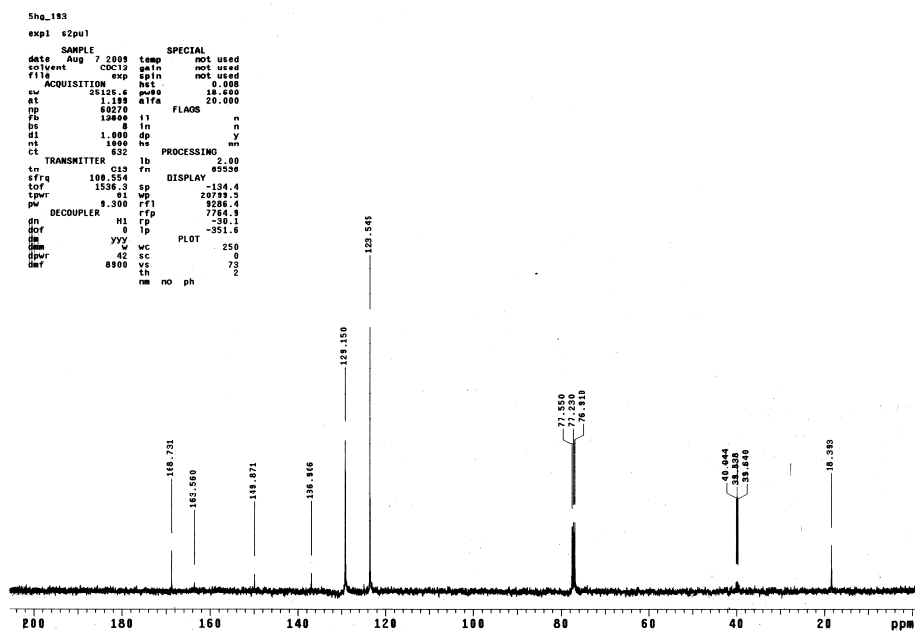


-S10-

***N*-Acetoxy-4-nitro-benzamide (8a): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**

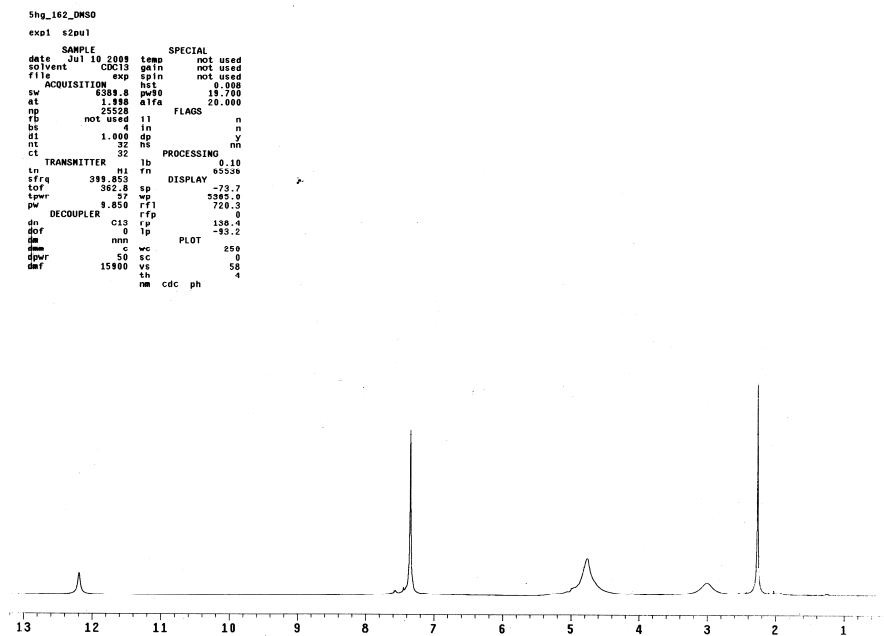


***N*-Acetoxy-4-nitro-benzamide (8a): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**

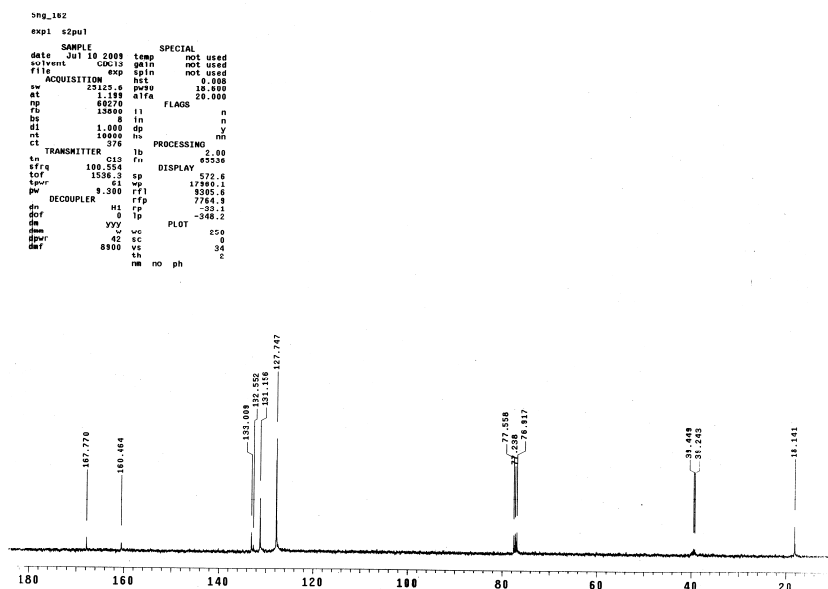


-S11-

***N*-Acetoxy-2,6-dichloro-benzamide (9a): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**

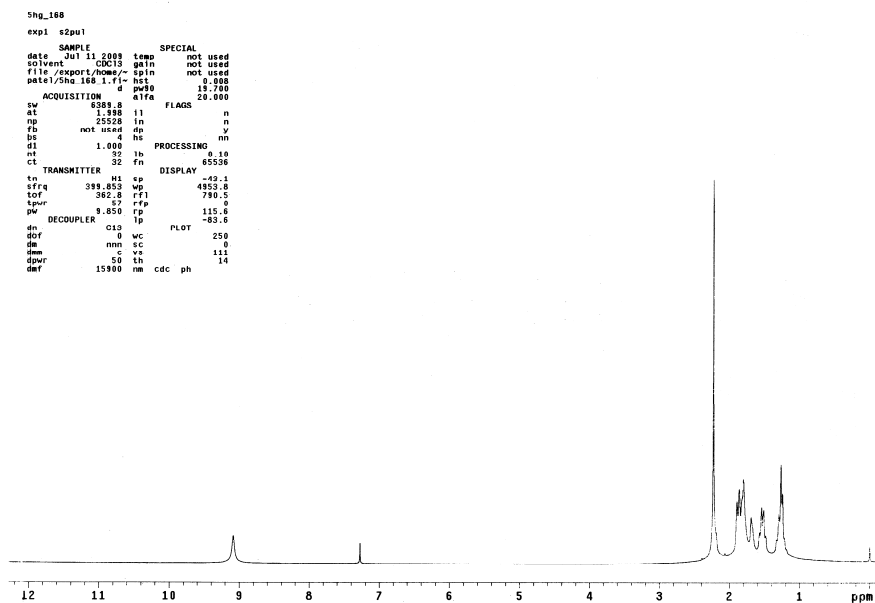


***N*-Acetoxy-2,6-dichloro-benzamide (9a): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**

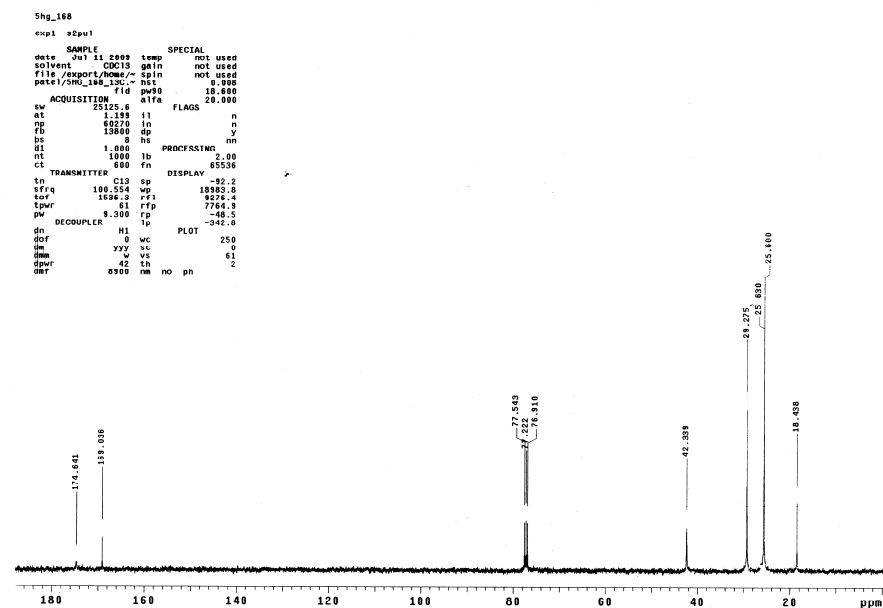


-S12-

Cyclohexanecarboxylic acid acetoxy-amide (10a): ^1H NMR (400 MHz, CDCl_3):

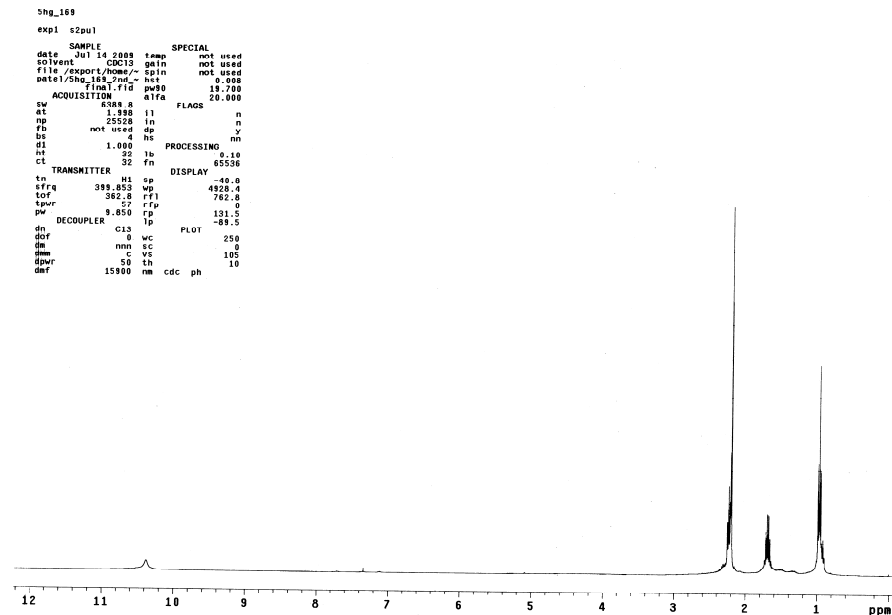


Cyclohexanecarboxylic acid acetoxy-amide (10a): ^{13}C NMR (100 MHz, CDCl_3):

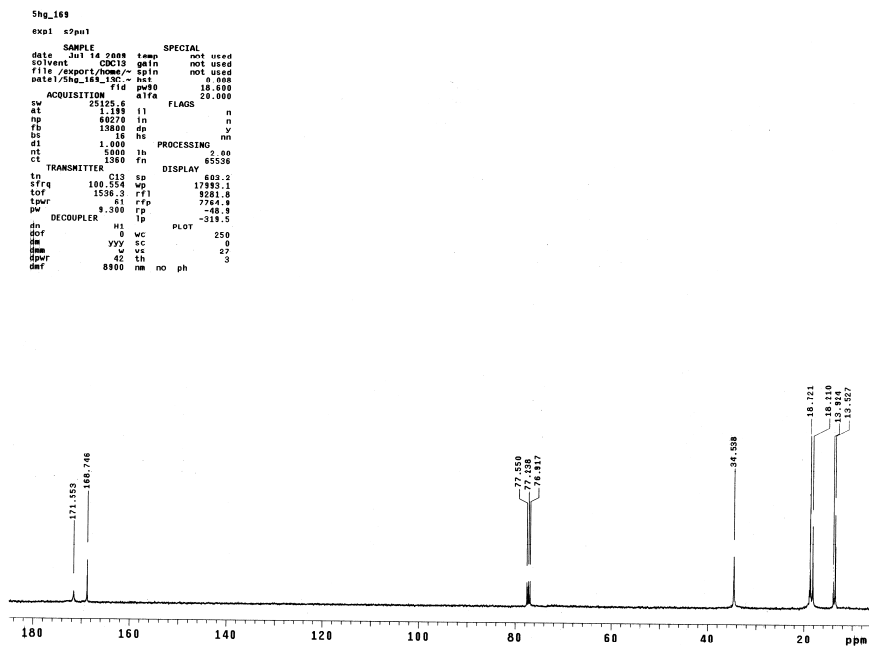


-S13-

***N*-Acetoxy-butylamide (11a): ¹H NMR (400 MHz, CDCl₃):**

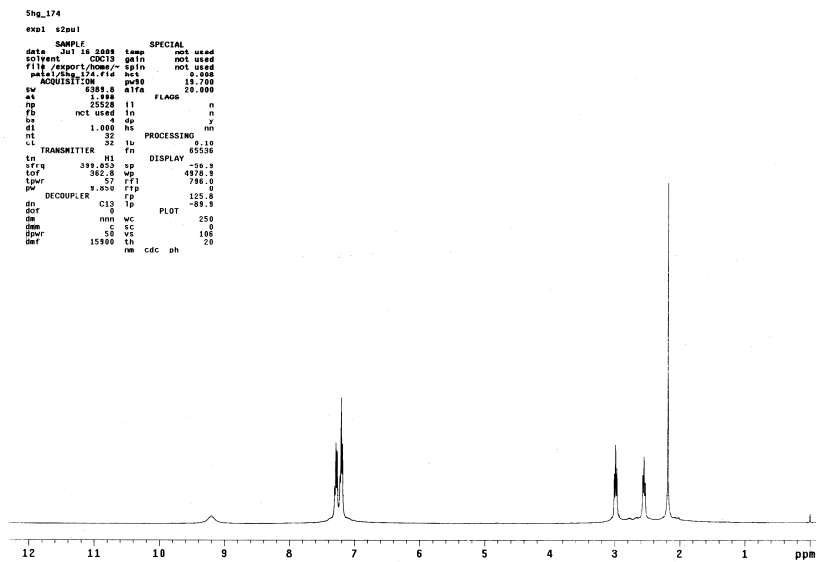


***N*-Acetoxy-butylamide (11a): ¹³C NMR (100 MHz, CDCl₃):**

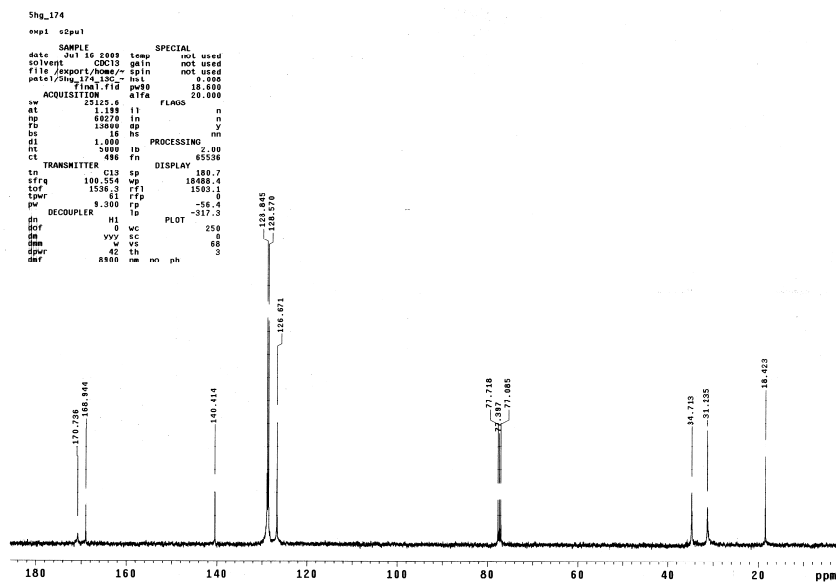


-S15-

***N*-Acetoxy-3-phenyl-propionamide (13a): ¹H NMR (400 MHz, CDCl₃):**



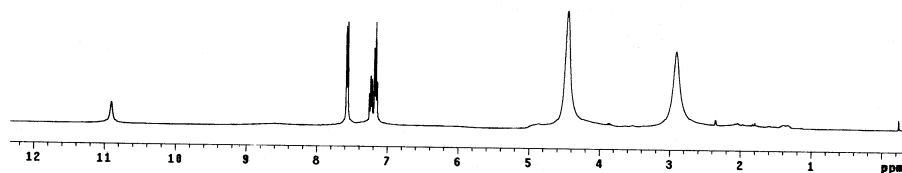
***N*-Acetoxy-3-phenyl-propionamide (13a): ¹³C NMR (100 MHz, CDCl₃):**



-S16-

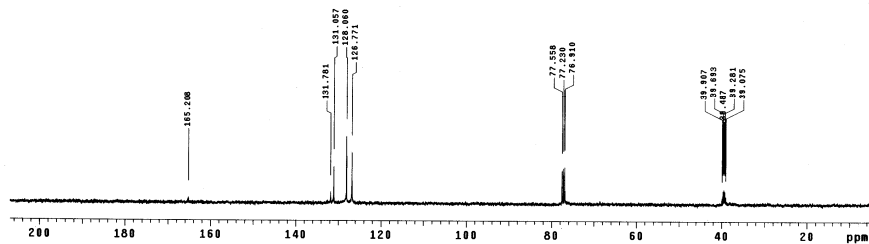
***N*-Hydroxy-benzamide (1b): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**

```
5hg_116
exp1 s2pul
date May 2 2008 temp SPECIAL
solvent CDCl3 gsin not used
file exp spin not used
ACQUISITION exp spin not used
sv 2512.8 pusb 10.000
at 1.198 aTfe 20.000
np 25220
fb not used () FLAGS
bs 4 in n
d1 1.000 dp y
nt ct PROCESSING
TRANSMITTER lb 0.10
tn H1 fn 65536
sfrq 399.855 DISPLAY
tor 282.0 sp -148.2
tpwr 57 wp 5979.6
pw 1.850 rF1 785.8
DECOUPLER C13 rfp 124.0
dr 0 lp -72.7
dof nm PLLOT 250
dm c wc 0
dpr 42 sc 0
def 15900 ve 34
nm cdc ph 8
```



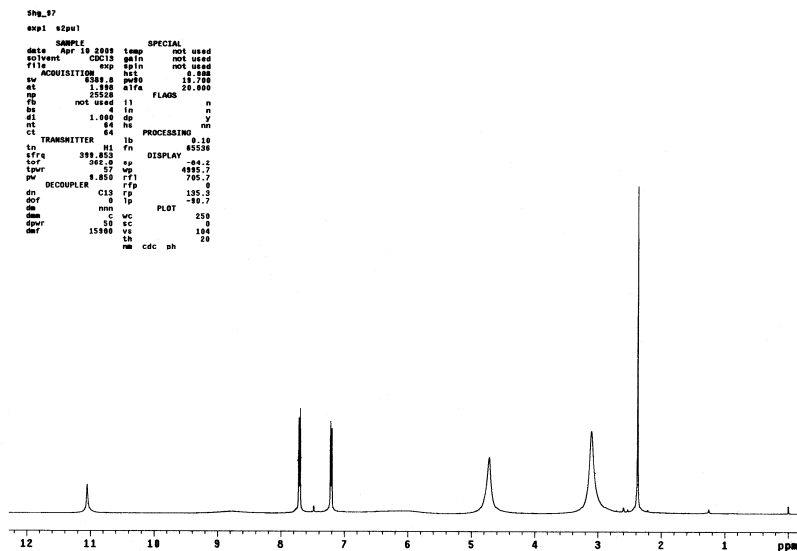
***N*-Hydroxy-benzamide (1b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**

```
5hg_116
exp1 s2pul
date May 2 2008 temp SPECIAL
solvent CDCl3 gsin not used
file exp spin not used
ACQUISITION exp spin not used
sv 25125.8 pusb 10.000
at 1.198 aTfe 20.000
np 88270
fb 13000 i1 FLAGS
bs 8 in n
d1 1.000 dp n
nt 100000 hc nm
TRANSMITTER lb 2.00
tn C13 fn 65536
sfrq 100.554 DISPLAY
tor 1536.2 sp 489.1
tpwr 61 wp 28551.2
pw 3.300 rF1 8310.2
DECOUPLER C13 rfp 7784.3
dr 0 lp -282.1
dof nm PLLOT 250
dm w wc 0
dpr 42 sc 0
def 8900 ve 18
nm no ph 1
```

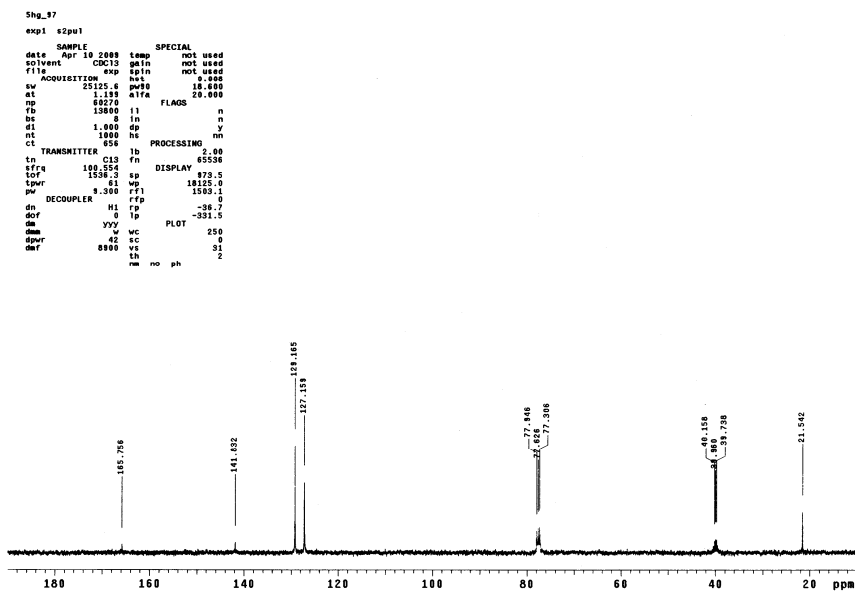


-S17-

***N*-Hydroxy-4-methyl-benzamide (2b): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**

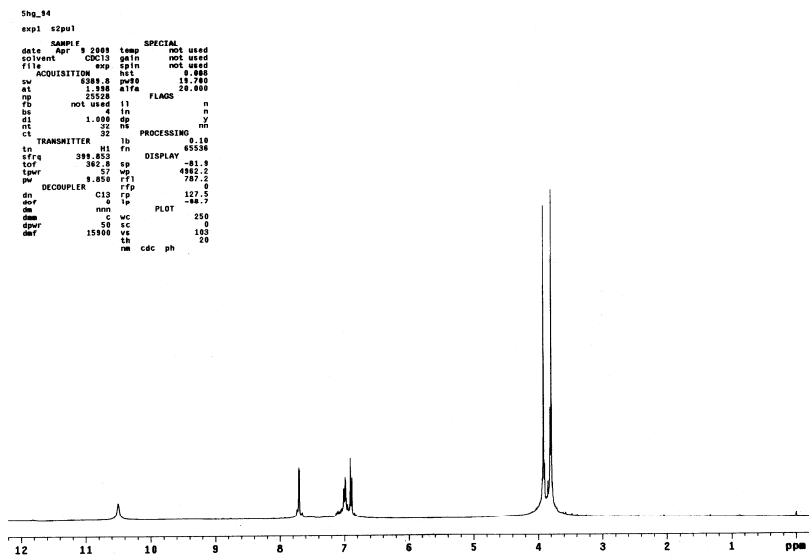


***N*-Hydroxy-4-methyl-benzamide (2b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**

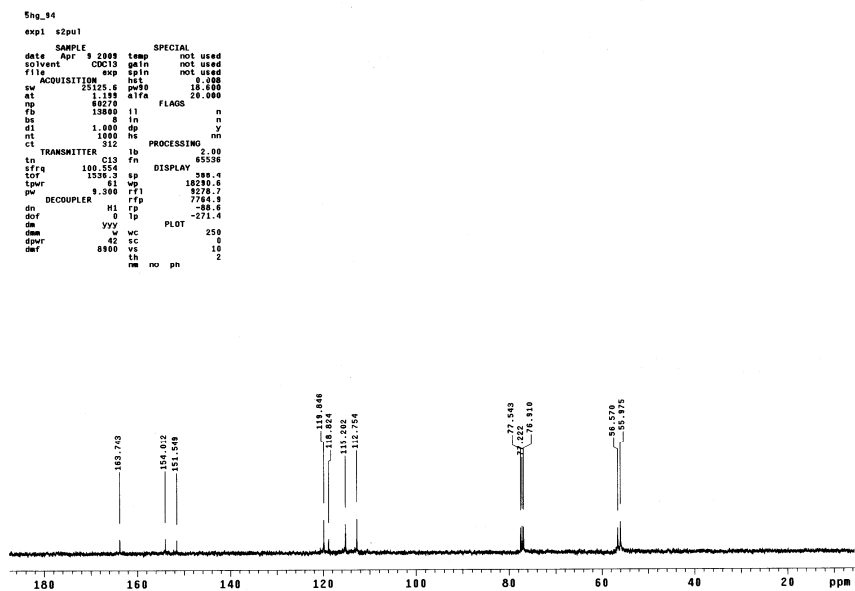


-S18-

***N*-Hydroxy-2,5-dimethoxy-benzamide (3b): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**



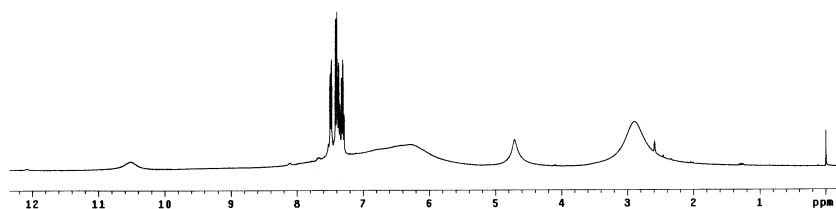
***N*-Hydroxy-2,5-dimethoxy-benzamide (3b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**



-S19-

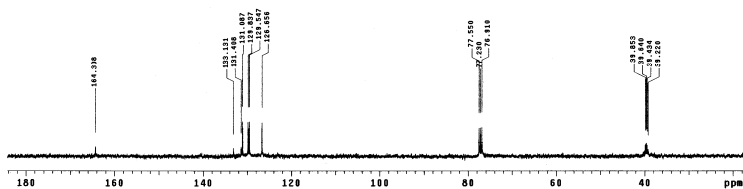
2-Chloro-*N*-hydroxy-benzamide (4b): ^1H NMR (400 MHz, CDCl_3 + DMSO-d_6):

```
5hg_134
exp1 s2pu1
SAMPLE
date May 18 2009 temp SPECIAL
solvent CDCl3 gain not used
file exp1 s2pu1 not used
ACQUISITION exp1 s2pu1 not used
sv 80272.8 prog 16.000
at 1.888 a1fa 20.000
rg 25228 h1 FLAGS
fb not used l1 n
bl 32 in n
dl 1.888 sp y
nl 32 ns PROCESSING
CT TRANSMITTER 32 hb 0.10
tp 853 fn 65536
tfrq 399.853 DISPLAY exp.0
cpf 342.0 sp 5004.1
tpwr 8.859 rfp 732.2
pw 57 wp 5004.1
DECOUPLER c13 rfp 104.6
ds 2 tp -59.2
dof 0 wp PLOT 250
dm 32 uc 0
dwr 15800 vs 49
dwt 15800 vs 49
nm cdc ph 20
```



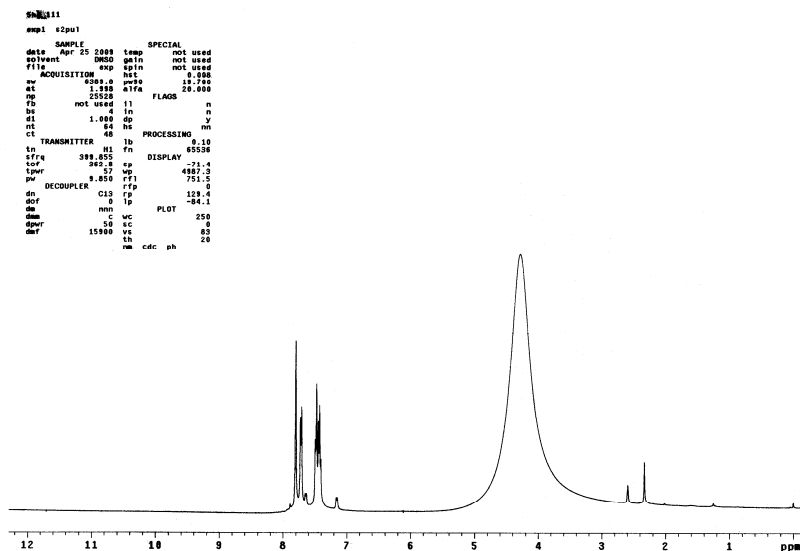
2-Chloro-*N*-hydroxy-benzamide (4b): ^{13}C NMR (100 MHz, CDCl_3 + DMSO-d_6)

```
5hg_134
exp1 s2pu1
SAMPLE
date May 18 2009 temp SPECIAL
solvent CDCl3 gain not used
file exp1 s2pu1 not used
ACQUISITION exp1 s2pu1 not used
sv 80272.8 prog 16.000
at 1.888 a1fa 20.000
rg 25228 h1 FLAGS
fb not used l1 n
bl 32 in n
dl 1.888 sp y
nl 32 ns PROCESSING
CT TRANSMITTER 1b hb 2.00
tp 100.554 fn 65536
tfrq 100.624 DISPLAY exp.0
cpf 1526.2 sp 5111.2
tpwr 8.859 rfp 15800.7
pw 3300 rfp 5286.7
DECOUPLER m1 rfp 764.1
ds 8 tp -232.2
dof 0 wp PLOT 250
dm 32 uc 0
dwr 8800 vs 12
dwt 8800 vs 12
nm no ph 2
```

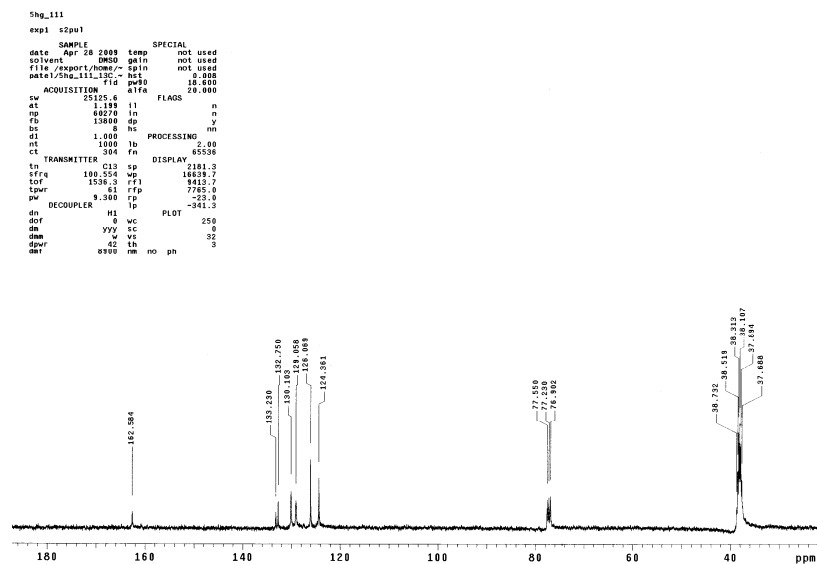


-S20-

3-Chloro-*N*-hydroxy-benzamide (5b): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):



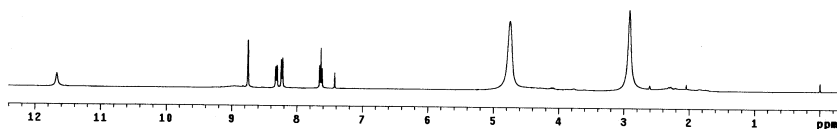
3-Chloro-*N*-hydroxy-benzamide (5b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆)



-S21-

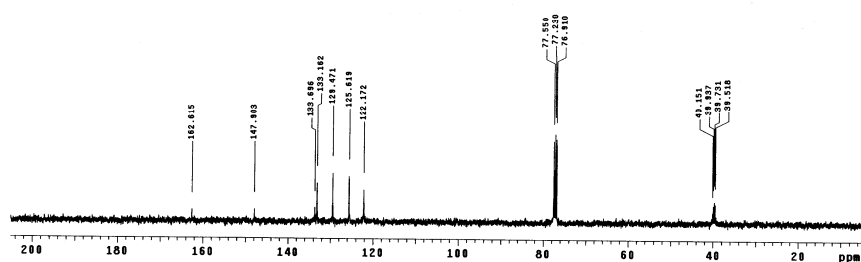
***N*-Hydroxy-3-nitro-benzamide (6b): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):**

```
Shg_114
exp1 s2pu1
SAMPLE SPECIAL
date 08/28/2008 temp not used
solvent CDCl3 gain not used
file /export/home/... spin not used
pate1/Shg_114_c1ae= nit 0.000
p1ae= r1e meta 15.700
ACQUISITION a1fa 20.000
sv 4308.8
at 1.000 f1 n
np 25500 in n
fb not used dp y
bs 4 hc m
d1 1.000 PROCESSING 0.10
nt 04 f1
ct TRANSMITTER 04 fn DISPLAY 65538
tn 05 sp -104.3
effa 389.850 wf 5086.3
tor 362.6 rff1 729.7
tpr 37 rfa 0
pw 8.850 fp 138.6
DECOUPLER fp -34.6
dn C13 PLOT 250
dof 0 wc 0
dm mhm sc 20
dms c vs 25
dprf 50 th 12
dat 15180 nm cdc ph
```



***N*-Hydroxy-3-nitro-benzamide (6b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆):**

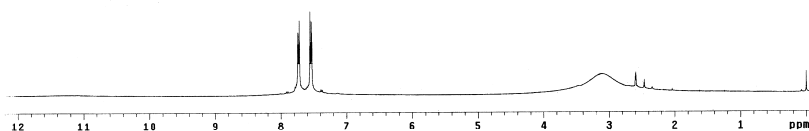
```
Shg_114
exp1 s2pu1
SAMPLE SPECIAL
date 08/28/2008 temp not used
solvent CDCl3 gain not used
file /export/home/... spin not used
pate1/Shg_114_c13c= nit 0.000
p13c= r13c meta 15.000
ACQUISITION a13fa 20.000
sv 15515.5
at 1.199 f1 n
np 08270 in n
fb 13800 dp y
bs 4 hc m
d1 1.000 PROCESSING 2.00
nt 1000 f1
ct TRANSMITTER 438 fn DISPLAY 65538
tn C13 sp 447.6
effa 100.550 wf 20172.3
tor 1536.3 rff1 8236.7
tpr 63 rfa 7784.9
pw 9.380 fp -26.0
DECOUPLER H1 PLOT 250
dof 0 wc 0
dm yyy sc 28
dms 0 vs 26
dprf 42 th 3
dat 0300 nm hvo s"
```



-S22-

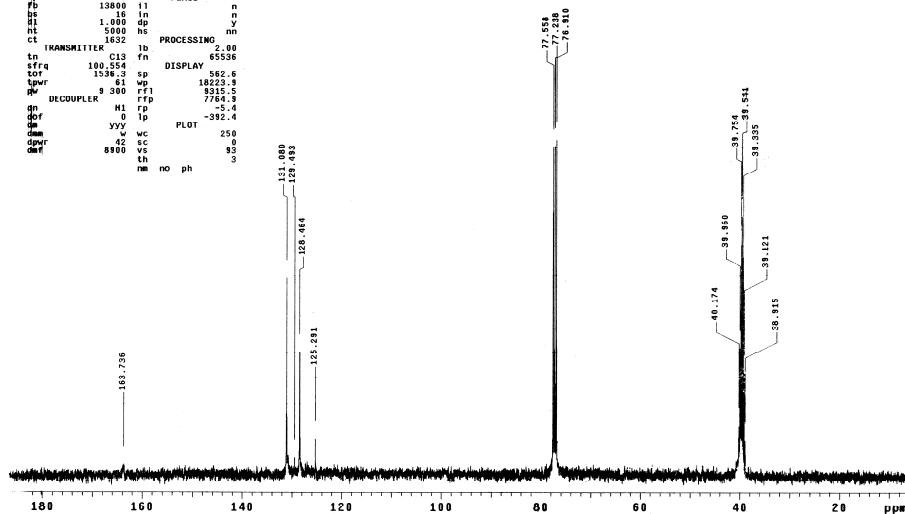
4-Bromo-*N*-hydroxy-benzamide (7b): ¹H NMR (400 MHz, CDCl₃ + DMSO-d₆):

```
Shg_4bromoacid
exp2 42pu1
SAMPLE SPECIAL
date Sep 21 2009 temp not used
solvent CDCl3 gain not used
file ACQUISITION exp sp in not used
sw 6338.8 pw50 18.700
at 1.288 a1fa 20.000
ns 26230
fb not used i1 n
bc 4 in n
d1 1.000 dp y
nt 32 hs n
ct TRANSMITTER 32 lb PROCESSING 0.10
tn H1 fn 65536
sffr 389.853 sp DISPLAY 762.1
tor 362.8 sp 4827.0
tpr 37 mp 688.2
pw 8.850 rfp 189.3
dn C13 fp 81.0
de mlt tp PLOT 250
dm c wc 0
dof 0 tp 83
dpr 8900 vs 0
dnt 15900 lh 26
nm cdc ph 26
```



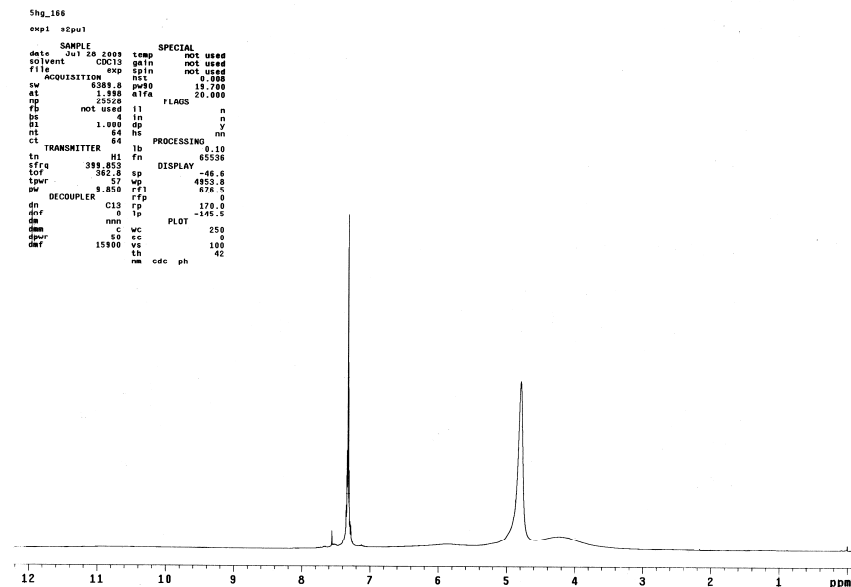
4-Bromo-*N*-hydroxy-benzamide (7b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆)

```
Shg_4bromoacid
exp1 52pu1
SAMPLE SPECIAL
date Sep 21 2009 temp not used
solvent CDCl3 gain not used
file ACQUISITION exp sp in not used
sw 25125.6 pw50 18.400
at 1.199 a1fa 20.000
ns 60270
fb 13800 i1 n
bc 16 in n
d1 1.000 dp y
nt 5000 hs n
ct 1632 lb PROCESSING 2.00
tn TRANSMITTER C13 fn 65536
sffr 100.254 sp DISPLAY 562.6
tor 1536.3 sp 16223.9
tpr 41 mp 5315.5
pw 9.300 rfp 7766.9
dn H1 fp -5.4
dof 0 tp PLOT 250
dm xxy wc 0
dof 0 tp 83
dpr 8900 vs 0
dnt 15900 lh 26
nm no ph 0
```

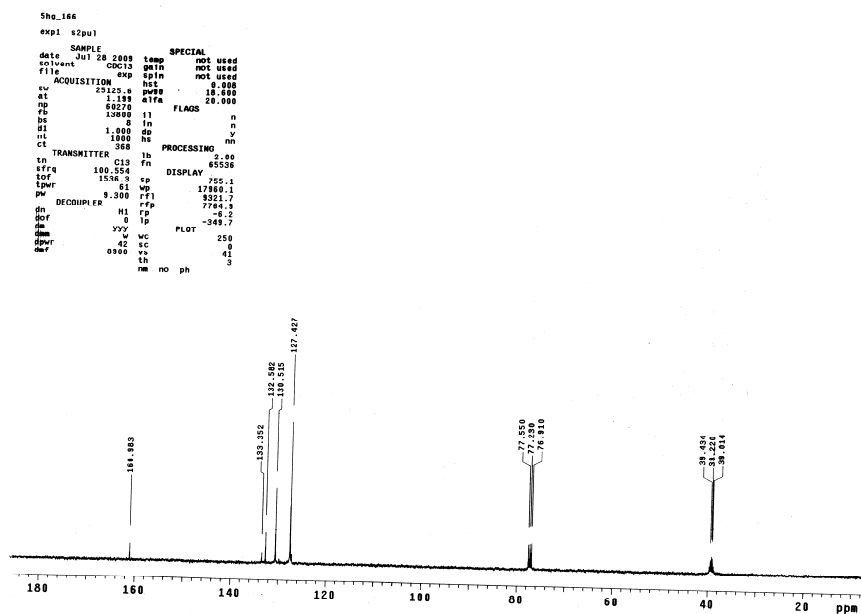


-S23-

2,6-Dichloro-*N*-hydroxybenzamide (9b): ^1H NMR (400 MHz, CDCl_3 + DMSO-d_6):

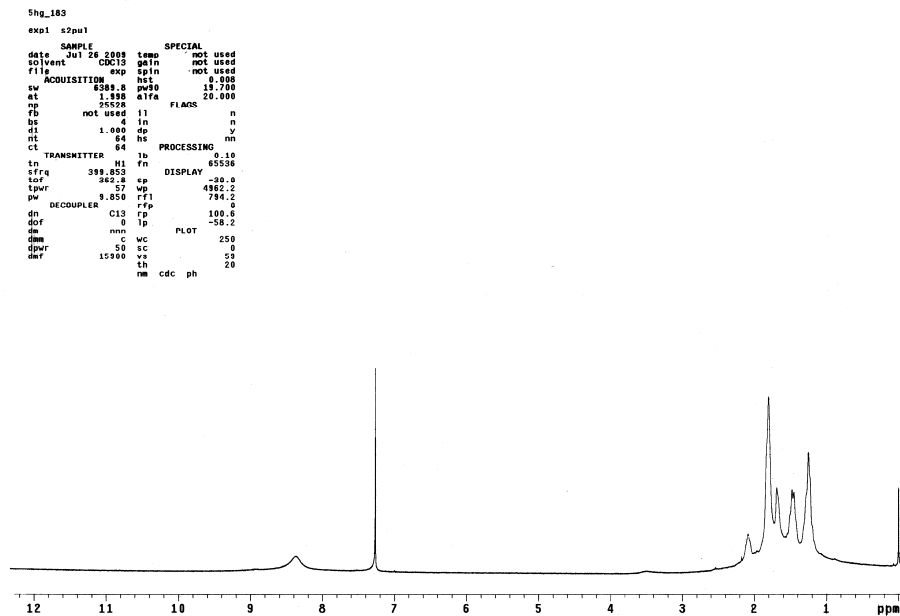


2,6-Dichloro-*N*-hydroxybenzamide (9b): ^{13}C NMR (100 MHz, CDCl_3 + DMSO-d_6)

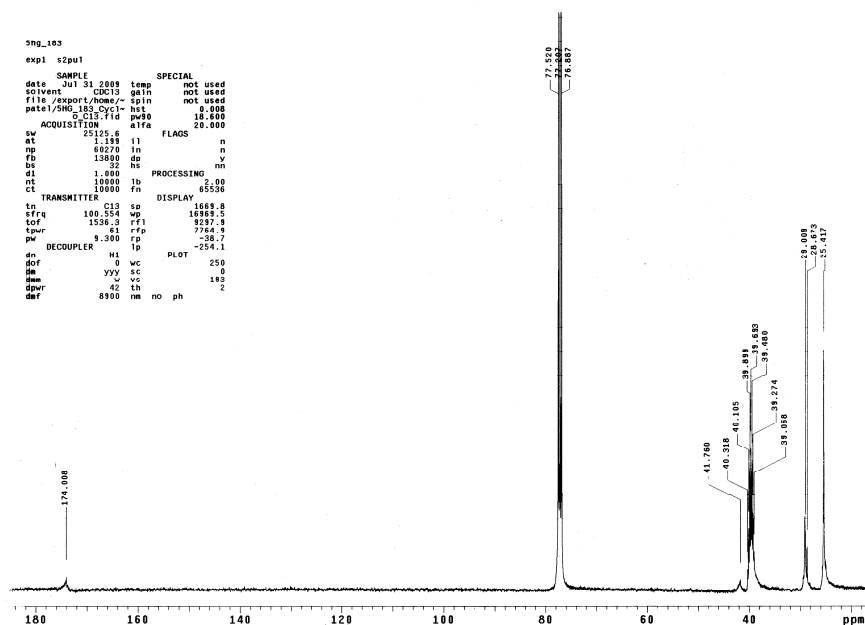


-S24-

***N*-hydroxycyclohexanecarboxamide (10b): ¹H NMR (400 MHz, CDCl₃):**

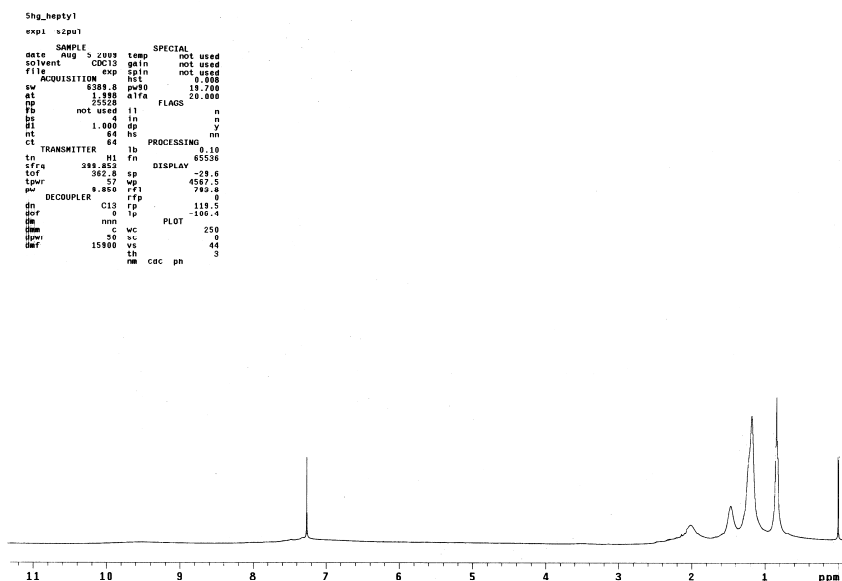


***N*-hydroxycyclohexanecarboxamide (10b): ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆)**

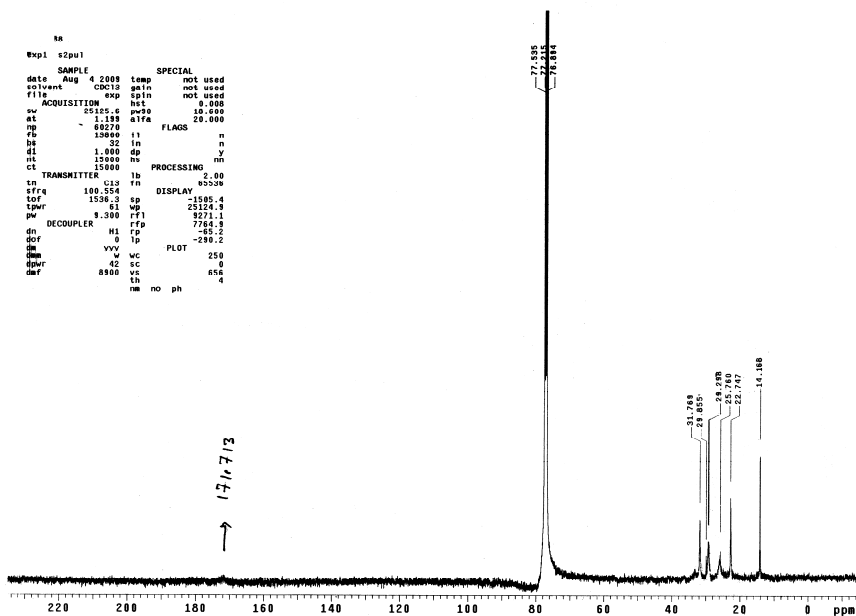


***N*-hydroxyheptanamide (12b): ¹H NMR (400 MHz, CDCl₃):**

-S25-



N-hydroxyheptanamide (12b): ¹³C NMR (100 MHz, CDCl₃)



-S26-

***N*-Acetoxy-benzamide (1a) + *N*-Propionyloxy-benzamide (1c): ¹H NMR (400 MHz, CDCl₃): (59:41)**

```
5hg_128
exp1 s2pu1
data SAMPLE SPECIAL
  date May 18 2009 temp not used
  solvent CDCl3 gelin not used
  file exp1 not used
ACQUISITION
  av 4289.8 pps 13.760
  at 1.258 n1FA 20.000
  rs 25528
  fb not used i1 FLAGS n
  bs 4 in n
  st 1.040 dp y
  nt 84 hs nm
  ct PROCESSING
  tn H1 fb 0.10
  sfrq 398.953 DISPLAY 85536
  tof 362.8 sp -78.0
  tpar 1.857 wp 5920.3
  pw 1.850 rfg 782.7
  dn C13 fp 122.1
  dof 0 fp -84.2
  de mm PLOT 250
  dm c WC 0
  dpar 50 VC 0
  def 15800 VE 85
  nm ch 20
  nm cdc ph
```

