

Application of the Rh(II)-Cyclization/Cycloaddition Cascade for the Total Synthesis of (±)-Aspidophytine

José M. Meijia-Oneto and Albert Padwa*

Department of Chemistry, Emory University, Atlanta, Georgia 30322 USA

chemap@emory.edu

Table of Contents for Spectra

Page 2	¹ H-NMR (400 MHz, CDCl ₃) of compound 15
Page 3	¹ H-NMR (400 MHz, CDCl ₃) of Precursor A to compound 16
Page 4	¹³ C-NMR (100 MHz, CDCl ₃) of Precursor B to compound 16
Page 5	¹ H-NMR (400 MHz, CDCl ₃) of compound 16
Page 6	¹ H-NMR (400 MHz, CDCl ₃) of compound 10
Page 7	¹ H-NMR (400 MHz, CDCl ₃) of compound 11
Page 8	¹ H-NMR (400 MHz, CDCl ₃) of Precursor compound 27
Page 9	¹ H-NMR (400 MHz, CDCl ₃) of compound 27
Page 10	¹ H-NMR (400 MHz, CDCl ₃) of Precursor compound 28
Page 11	¹ H-NMR (400 MHz, CDCl ₃) of compound 28
Page 12	¹ H-NMR (400 MHz, CDCl ₃) of compound 29
Page 13	¹ H-NMR (400 MHz, CDCl ₃) of compound 5 (aspidophytine)

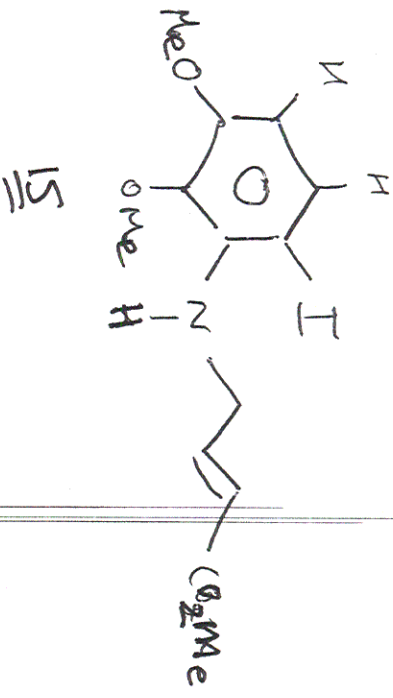
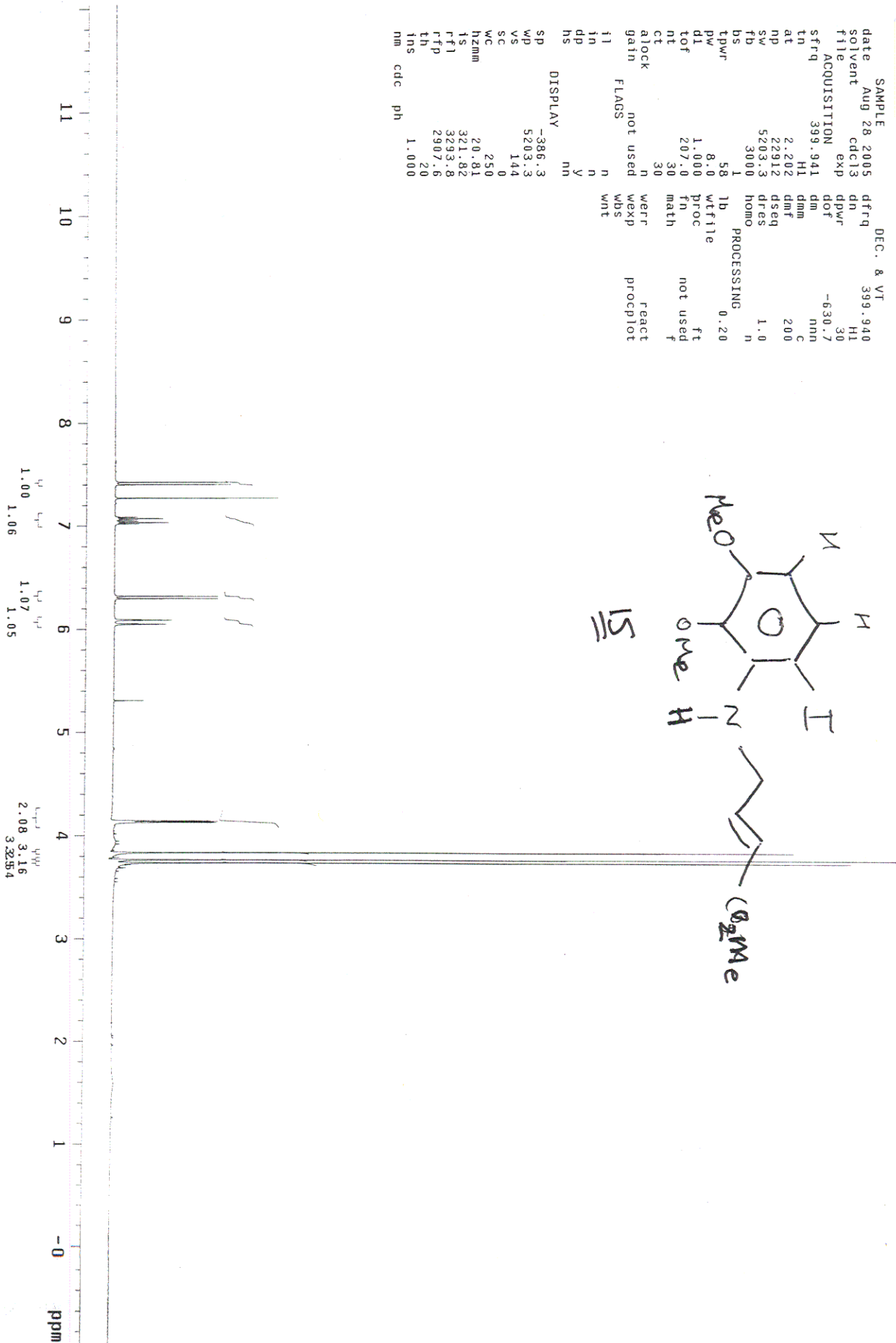
STANDARD 1H OBSERVE

exptl std1h

date	Aug 28 2005	DEC. & VI	399.940
solvent	cdcl3	dn	H1
file	exp	dpwr	30
ACQUISITION	dot	dmf	-630.7
sfrq	399.941	dm	nmn
tn	H1	dmm	C
at	2.202	dmf	200
np	22912	dseq	
sw	5203.3	dres	1.0
fb	3000	homo	n
bs	1	PROCESSING	
tpwr	58	lb	0.20
pw	8.0	wfille	
dl	1.000	proc	fi
tof	207.0	fn	not used
nt	30	math	f
ct	30		
atlock	n	werr	react
gain	not used	wexp	procpilot
flags	n	wbs	
in	n	wnt	
dp	y		
hs	nn		

DISPLAY

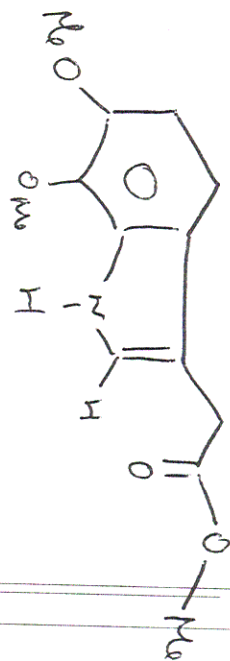
SP -386.3
 WP 5203.3
 VS 144
 SC 0
 WC 250
 hzmm 20.81
 IS 321.82
 rfl 3293.8
 rfp 2907.6
 th 20
 ins 1.000
 nm cdc ph 1.000



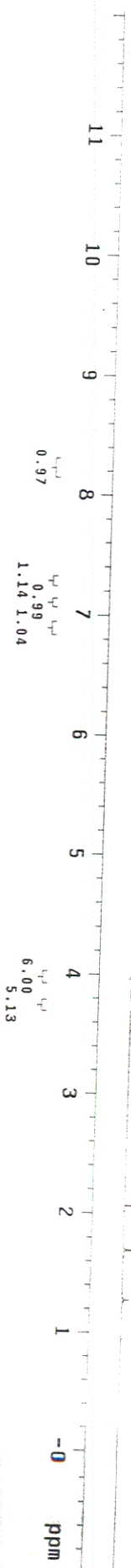
Integration values:
 1.00
 1.06
 1.07
 1.05
 2.08
 3.16
 3.23

expt stidh

SAMPLE DEC. & VI
 date Aug 30 2005 dfrrq 399.940
 solvent cdc13 dn H1
 file exp dpwr H1
 ACQUISITION exp 30
 sffrq 399.941 dm -630.7
 tn H1 dmm nnn
 at 2.202 dmf C
 np 22912 dseq 200
 sw 5203.3 dres 1.0
 fb 3000 homo n
 bs 1 PROCESSING 0.20
 tpwr 58 lb wlfite
 pw 8.0 wlfite
 dl 1.000 pproc ft
 tof 207.0 fn not used
 nt 20 math
 ct 20
 alock n
 gain not used
 flags not used
 in n
 dp n
 hs y mn
 DISPLAY
 sp -386.0
 wp 5203.3
 vs 144
 sc 0
 wc 250
 hzmm 20.81
 ts 288.32
 rfi 3293.5
 rfp 2907.6
 th 20
 ins 6.000
 nm cdc ph

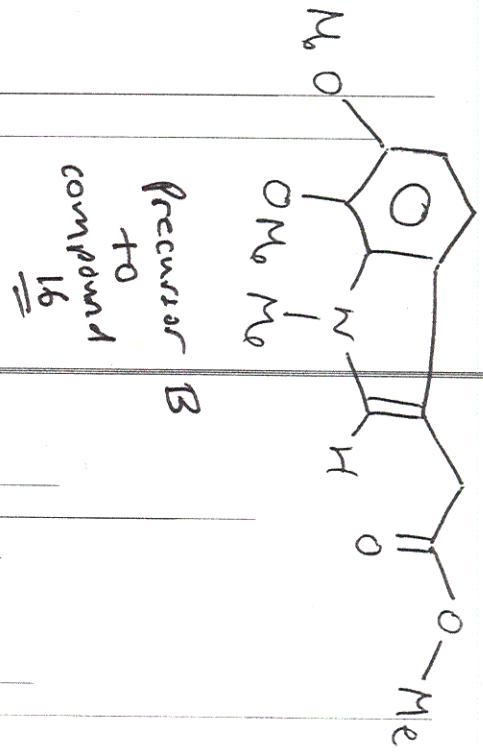
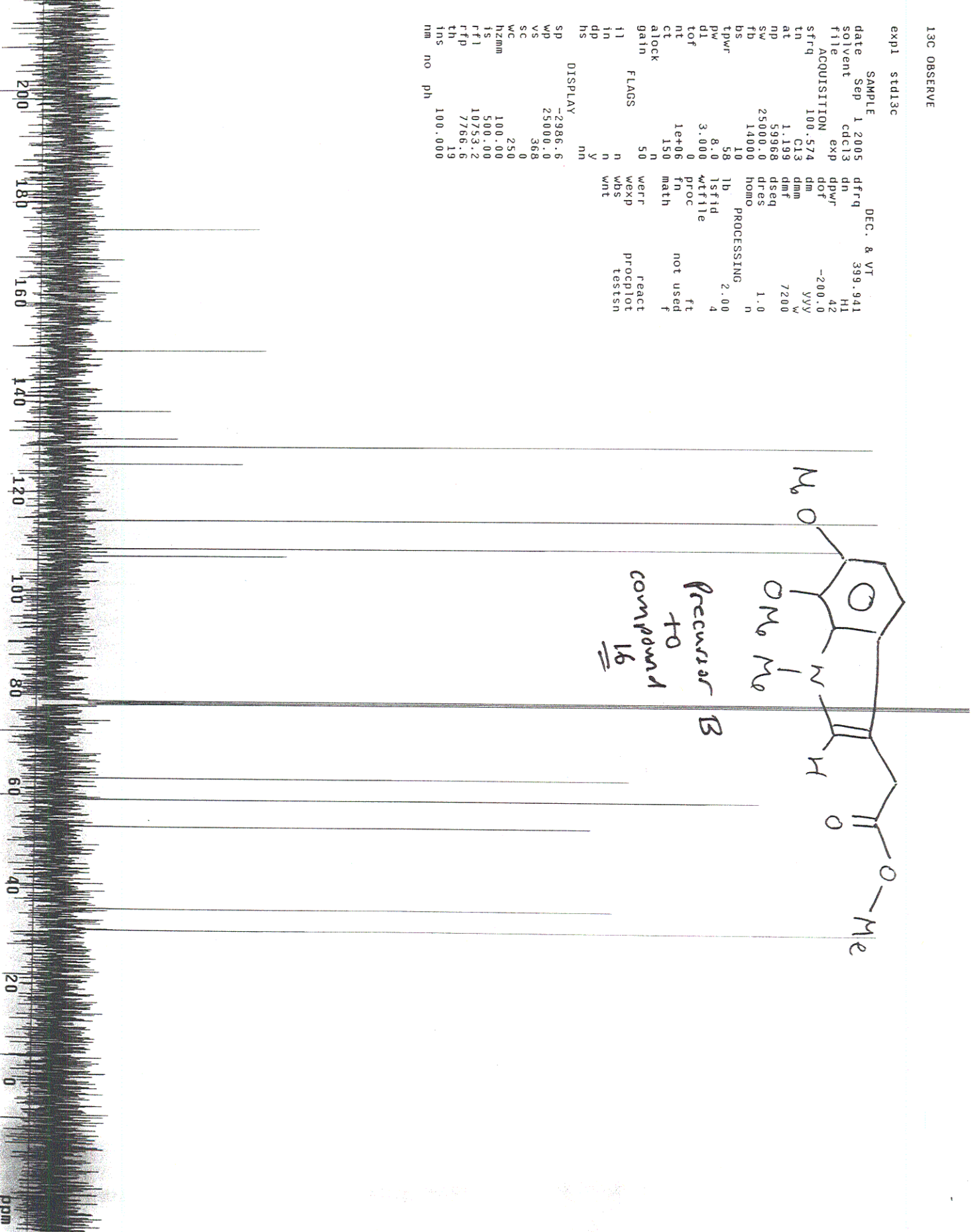


Precursor A to
 compound 16



13C OBSERVE

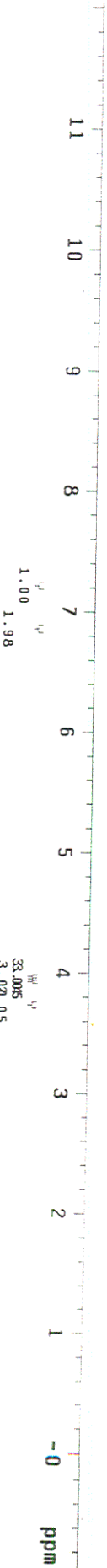
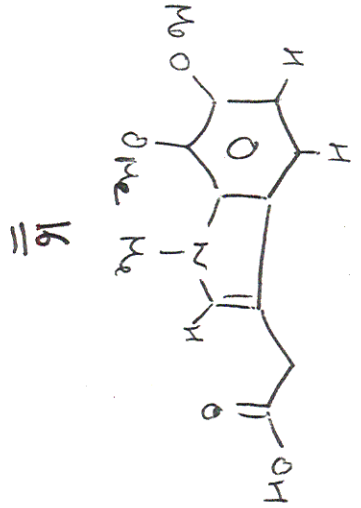
exptl std13c
SAMPLE date Sep 1 2005 dfrq DEC. & VI 399.941
solvent cdc13 dn H1
file exp -200.0
ACQUISITION 100.574 dof 42
sfrq C13 dmm yyy w
tn 1.199 dmf 7200
at 59968 dresq
np 25000.0 dresq 1.0
sw 14000 homo
fb 10 PROCESSING 2.00
bs tpwr 58 lb
pw 8.0 1sfid 4
DI 3.000 wtfille
tof 0 proc ft
nt 1e+06 fn not used f
ct 150 math
alock n
gain 50 werr react
ll 11 flags wexp procpilot
ln n wbs teststn
dp n y
hs mn
DISPLAY
sp -23986.6
wd 25000.0
vs 368
sc 0
wc 250
hzmm 100.00
is 500.00
rfl 10753.2
rfp 7766.6
th 19
ins 100.000
nm no ph



STANDARD 1H OBSERVE

```

expt  std1h
SAMPLE
date Sep 1 2005 dfrq DEC. & VT 399.940
solvent cdc13 dn HI
file ACQUISITION exp dpwr HI
sfrq 399.941 dm -630.7
at 2.202 dmm nnn
np 22912 dseq C
sw 5203.3 dres 200
fb 3000 homo 1.0
bs 1 PROCESSING n
tpwr 58 1b 0.20
pw 8.0 ,wrtfile
d1 1.000 proc ft
tof 207.0 fn not used
nt 30 math f
ct 30
alock gain n warr react
gain not used wexp procpilot
flags not used wds
l1 n wht
l2 n
l3 n
dp y
hs nn
DISPLAY
SP -386.3
WD 5203.3
VS 144
SC 0
WC 250
h2mm 20.81
IS 231.46
rfl 3293.8
th 2907.6
ins 1.12
nm cdc ph 1.000
  
```

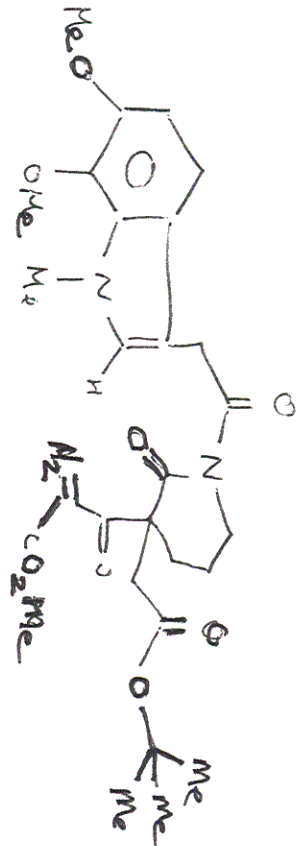


33.0065
3.021.05

STANDARD 1H OBSERVE

expl std1h

date	8 Sep	8 2005	dfreq	DEC. & VT	399.940
solvent	cdcl3	dn	dn		H1
file	ACQUISITION	exp	dpwr		30
sfreq	399.941	dm	dof		-630.7
tn	H1	dmm	dmf		nnn
at	2.202	dseq	dres		C
np	22912	math	hom		200
sw	5203.3	react	procplot		1.0
fb	3000	proc	ft		n
bs	1	math	f		n
tpwr	58	react	ft		0.20
pw	8.0	proc	f		1.000
dl	1.000	math	f		207.0
tof	207.0	react	f		40
nt	40	procplot	f		0
ct	0				0
alock	not used				0
gain	not used				0
fl	n				n
in	n				n
dp	y				y
hs	nn				nn
DISPLAY					
sp	-386.3				
wp	5203.3				
vs	144				
sc	0				
wc	250				
hzmm	20.81				
ts	271.35				
rfl	3293.8				
rflp	2907.6				
th	20				
ins	9.000				
nm	cdc				
ph					



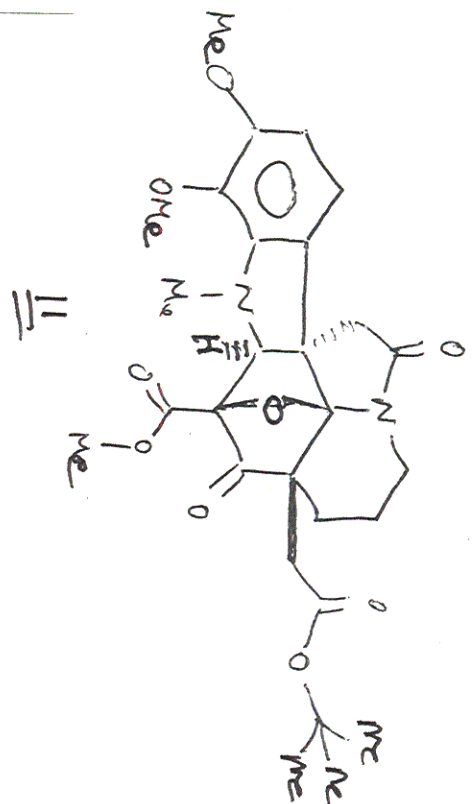
10



STANDARD 1H OBSERVE

exptl std1h

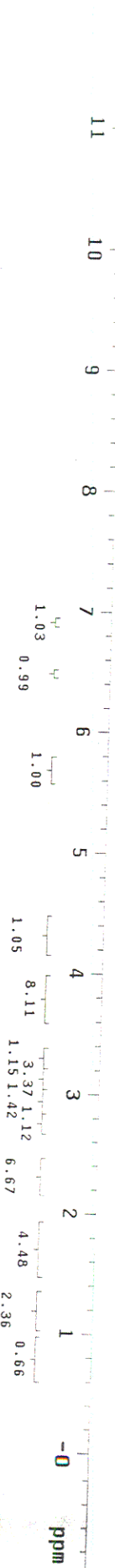
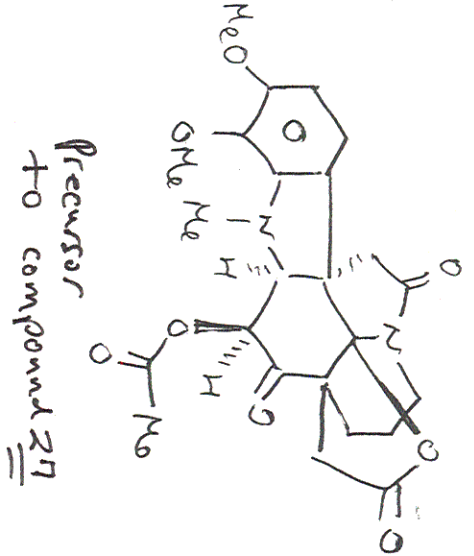
date	Oct 5 2005	DEC. & VT	399.940
solvent	cdcl3	dn	H1
file	exp	dpwr	30
ACQUISITION	dof	dof	-630.7
sfrq	399.941	dm	nmn
tn	H1	dmm	C
at	2.202	dmf	200
np	22912	dseq	
sw	5203.3	dres	1.0
fd	3000	homo	n
bs	1	PROCESSING	0.20
tpwr	58	lb	wf file
pw	8.0	'proc	ft
dl	1.000	fn	not used
tof	207.0	math	f
nt	100	werr	react
ct	0	wexp	procpilot
gain	not used	wps	
flags	not used	wnt	
tl	n		
in	n		
dd	y		
hs	nm		
DISPLAY			
sp	-425.0		
wp	5203.3		
vs	144		
sc	0		
wc	250		
hzm	20.81		
is	236.57		
rfl	3332.6		
rff	2907.6		
th	20		
ins	9.000		
nm	cdc		
ph			



STANDARD 1H OBSERVE

expl std1h

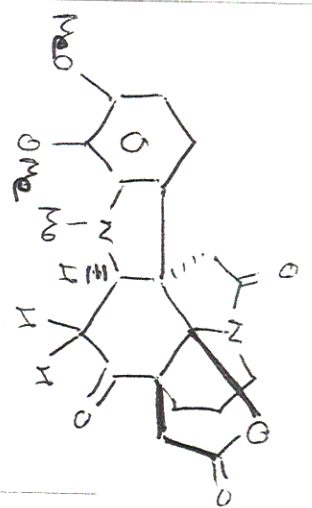
date	Oct 12 2005	DEC. & VT	399.940
solvent	cdcl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	-630.7
sfrq	399.941	dm	nmn
tn	H1	dmm	C
at	2.202	dmt	200
np	2.2912	dseq	
sw	5203.3	dres	1.0
td	3000	homo	n
bs	1	PROCESSING	
tpwr	58	lb	0.20
pw	8.0	wffile	
dl	1.000	proc	ft
tof	207.0	fn	not used
nt	100	math	f
cl	56	werr	react
alock	n	wexp	procpilot
gain	not used	wbs	wht
ll	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-386.0		
wp	5203.3		
vs	144		
sc	0		
wc	250		
hzm	20.81		
is	802.28		
rfl	3293.5		
rtp	2907.6		
th	20		
ins	20		
nm	1.000		



STANDARD 1H OBSERVE

exp1 std1h

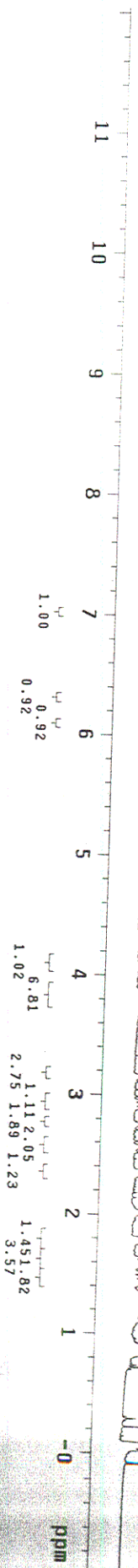
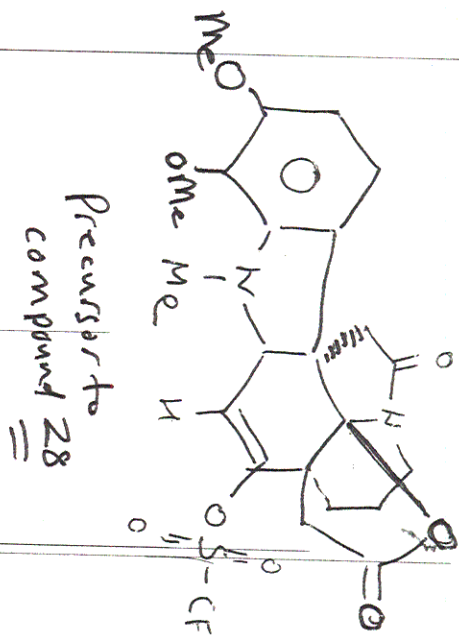
date	Jan 26 2006	dfreq	DEC. & VT	399.940
solvent	cdcl3	dn		H1
file		dpwr		30
ACQUISITION	exp	dof		-630.7
sfrq	399.941	dm		nmn
tn		dmm		C
at	2.202	dmg		200
np	22912	dseq		
sw	5203.3	dres		1.0
fb	3000	homo		n
bs		PROCESSING		
tpwr	58	lb		0.20
pw	8.0	wffile		
dl	1.000	proc		ft
tof	207.0	fn		not used
nt	50	math		f
ct	50			
alock	n	werr	react	
gain	not used	wexp	procpilot	
FLAGS		wps		
fl	n	wt		
in	n			
dp	y			
hs	nn			
DISPLAY				
SP	-386.3			
WP	5203.3			
VS	197			
SC	0			
WC	250			
hzmm	20.81			
ts	2958.92			
rfl	3293.8			
rtp	2907.6			
th	20			
ins	1.000			
nm	cdc	ph		



STANDARD 1H OBSERVE

exp1 std1h

SAMPLE 2 2006 DEC. & VT
 date Feb 2006 dfreq 399.940
 solvent cdcl3 dn
 file exp dpwr
 ACQUISITION exp dof -630.7
 sfreq 399.941 dm
 tn H1 dmm
 at 2.202 dmf
 np 22912 dseq
 sw 5203.3 dres
 fb 3000 homo 1.0
 bs 1
 tpwr 58 1b
 pw 8.0 wfile 0.20
 dl 1.000 proc ft
 tof 207.0 fn not used
 nt 100 math
 ct 94
 alock n
 gain not used
 flags not used
 i1 n
 i2 n
 in y
 dp y
 hs nn
 DISPLAY
 sp -386.3
 wp 5203.3
 vs 921
 sc 0
 wc 250
 hzmm 20.81
 ts 2734.18
 rfl 386.3
 rfp 0
 th 20
 lns 2.000
 nm cdc ph



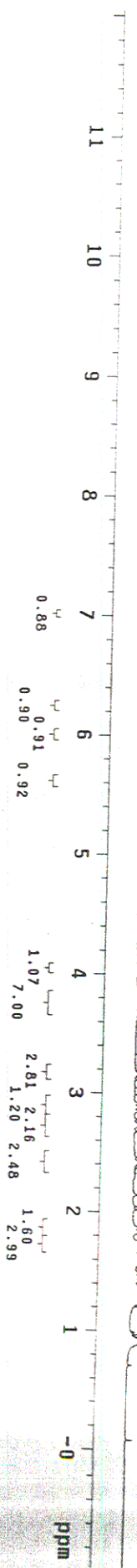
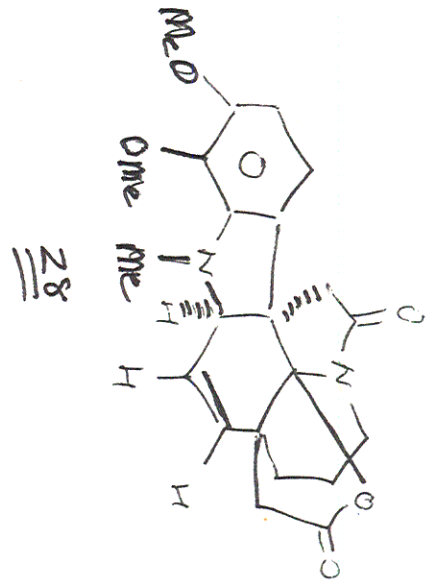
STANDARD 1H OBSERVE

```

expl stidh
SAMPLE
date Feb 4 2006
solvent cdcl3
file exp
ACQUISITION
sfrq 399.941
tn H1
at 2.202
np 22912
sw 5203.3
fb 3000
bs 1
tpwr 58
pw 8.0
dl 1.000
tof 207.0
nt 100
ct 100
alock n
gain not used
flags not used
i1 n
in y
dp n
hs nm
DISPLAY
SP -386.3
WP 5203.3
VS 144
SC 0
WC 250
hzmm 20.81
fs 1435.53
rf1 3293.8
rfp 2907.6
tn 20
nm cdc ph 7.000
    
```

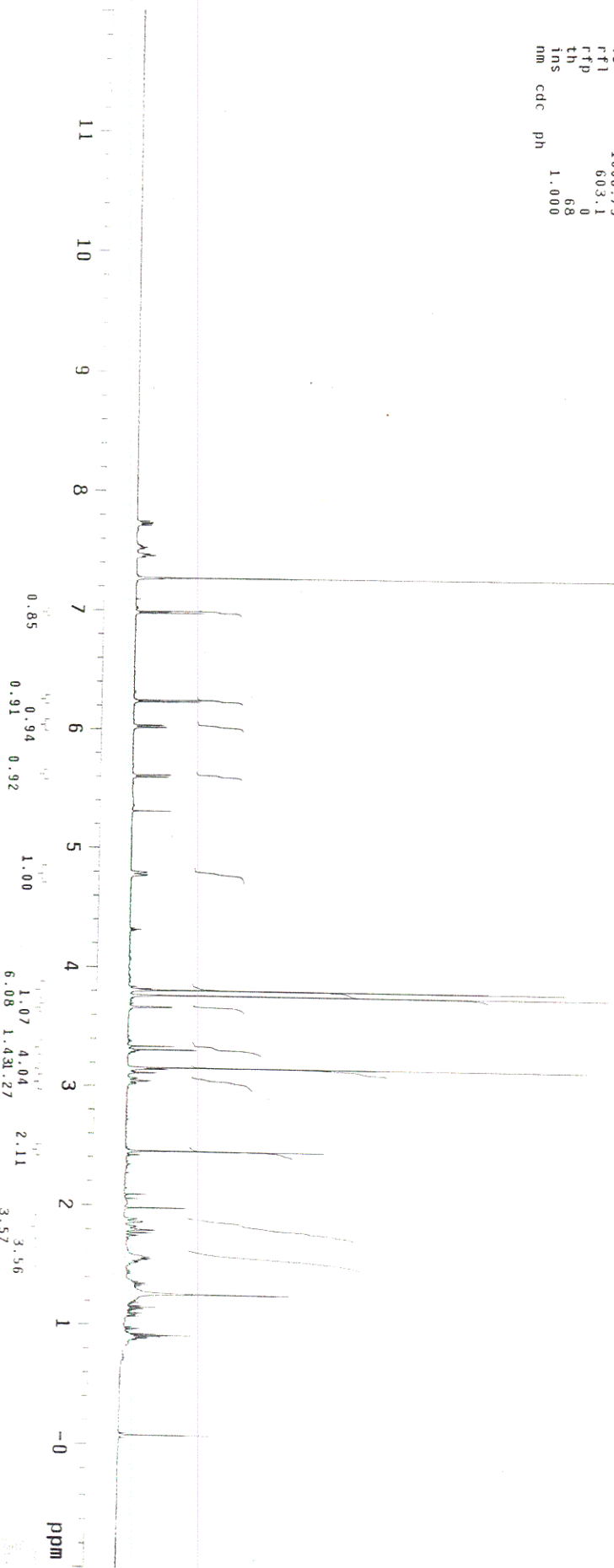
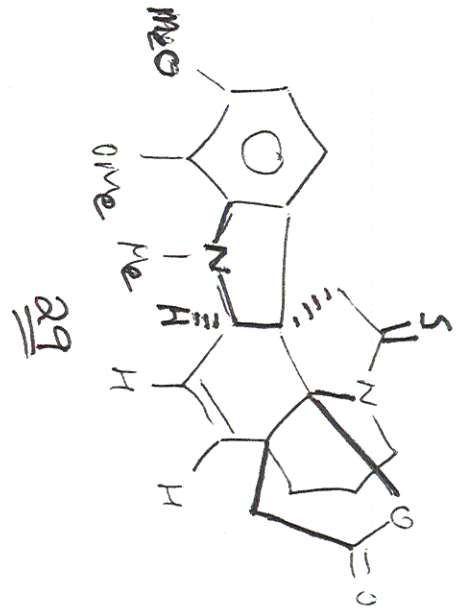
```

DEC. & VT
dfrq 399.940
dn H1
dpwr 30
dot -630.7
dmm nm
dmf 200
dseq 200
dres 1.0
homo n
PROCESSING
lb 0.20
wtfile
proc ft
fn not used
math f
werr react
wexp procpilot
wbs
wnt
    
```



Standard proton parameters
exp3 s2pul

SAMPLE	4.2006	DEC. & VI	599.738
date	Feb	dfreq	H1
solvent	cdcl3	dn	0
title	exp	dpwr	0
ACQUISITION		dof	0
sfrq	599.738	dm	nmn
tn	H1	dmm	w
at	1.598	dmf	200
np	24948	dseq	
sw	7804.1	dres	1.0
fb	4000	homo	n
bs	1	PROCESSING	
tpwr	56	lb	0.20
pw	5.0	wfile	
d1	1.000	proc	ft
tof	285.3	fq	not used
nt	100	math	f
ct	0		
alock	n	werr	react
gain	not used	wexp	procpilot
FLAGS		wbs	testsn
ll	n	wnt	
in	n		
dp	v		
hs	nm		
DISPLAY			
sp	-603.1		
wp	7804.1		
vs	151		
sc	0		
wc	250		
hzmh	31.22		
is	1006.75		
rfl	603.1		
rftp	0		
th	68		
ins	1.000		
nm	cdc	ph	



Standard Proton Parameters

```

exp1 s2pul1
SAMPLE Mar 24 2006 DEC. & VI 599.738
date Mar 24 2006 dfreq 599.738
solvent cdcl3 dn HI 0
file exp13 dnm 0
ACQUISITION dpmr 0
sfrq 599.738 dm 0
tn HI dmm nmn
at 1.598 dmf w
np 24948 dser 200
sw 7804.1 dres 1.0
td 4000 homo n
bs 1 PROCESSING
tpwr 56 lb 0.20
pw 5.0 wfile
dl 1.000 proc ft
tof 285.3 fn not used
nt 10000 math f
ct 0
alock 0
gain not used werr react
flags not used wexp procpilot
hs n Y wbs testis
nm cdc ph 1.000
  
```

