Supporting Information

Highly Diastereoselective Mannich-Type Reactions of Chiral *N*-Acylhydrazones

*Mikkel F. Jacobsen, Liviu Ionita and Troels Skrydstrup**

Department of Chemistry, University of Aarhus, Langelandsgade 140, 8000 Aarhus C, Denmark

ts@chem.au.dk

Contents:

General Experimental Methods and spectroscopic data for **3a-c**	S2-S3
Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **2a-i** and **6**	S4-S23
Spherical-atom plot of X-ray structure of compound **2a**	S24
Single crystal X-ray crystallographic data for compound **2a**	S25-S32

General Experimental Methods. Unless otherwise stated, all reactions were carried out under nitrogen. Acetonitrile and dichloromethane were freshly distilled from CaH_2. Methanol was freshly distilled from $CaCl_2$. Tetrahydrofuran was freshly distilled from Na/benzophenone ketyl. Reactions were monitored by thin-layer chromatography (TLC) analysis. Compounds **3a-c** were prepared using the standard procedure published.[1] Compounds **5a-c** were prepared according to a literature procedure.[2] NMR spectra were recorded at 400 MHz (^{1}H NMR). Samarium diiodide was prepared according to a literature procedure.[3] All Lewis acids used for the Mannich-type reactions were obtained commercially and used without further purifications.

(*S*)-Ethyl 2-(4-benzyl-2-oxooxazolidin-3-ylimino)acetate (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, *J* = 7.0 Hz, 3H), 2.90 (dd, *J* = 9.4, 13.3 Hz, 1H), 3.33 (dd, *J* = 3.9, 13.3 Hz, 1H), 4.20 (dd, *J* = 4.7, 9.4 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 4.47–4.53 (m, 1H), 7.16–7.36 (m, 5H), 8.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 37.7, 58.0, 61.8, 66.1, 127.6, 129.2 (2C), 129.5 (2C), 134.6, 139.6, 152.6, 163.4; MS (electrospray) *m/z* 299.1 (M + Na); HRMS *m/e* calcd for $C_{13}H_{16}N_2NaO_4$ (M + Na) 299.1008, found 299.1002.

(*S*)-Ethyl 2-(4-isopropyl-2-oxooxazolidin-3-ylimino)acetate (3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, *J* = 7.2 Hz, 3H), 0.94 (d, *J* =7.2 Hz, 3H), 2.30–2.41 (m, 1H), 4.17–4.25 (m, 2H), 4.31 (q, *J* = 8.0 Hz, 2H), 4.40 (t, *J* = 8.4 Hz, 1H), 8.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 14.6, 17.6, 28.5, 61.2, 61.7, 63.1, 139.1, 152.9, 163.4; MS (electrospray) *m/z* 251.1 (M + Na); HRMS *m/e* calcd for $C_{10}H_{16}N_2NaO_4$ (M + Na) 251.1008, found 251.0999.

(*S*)-Ethyl 2-(2-oxo-4-phenyloxazolidin-3-ylimino)acetate (3c). Mp 121-122ºC (CH_2Cl_2/pentanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 6.8 Hz, 3H), 4.23–4.29 (m, 3H), 4.84 (t, *J* = 8.8 Hz, 1H), 5.20 (dd, *J* = 5.2, 8.8 Hz, 1H), 7.25–7.27 (m, 3H), 7.38–7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 58.5, 61.7, 70.2, 125.8, 129.4 (2C), 129.9 (2C), 135.5, 135.6, 153.4, 162.6; MS (electrospray) *m/z* 285.1 (M + Na); HRMS *m/e* calcd for $C_{13}H_{14}N_2NaO_4$ (M + Na) 285.0851, found 285.0859.

References

(1) Shen, Y.; Friestad, G. K. *J. Org. Chem.* **2002**, *67*, 6236.

(2) Wu, Y.; Shen, X. *Tetrahedron: Asymmetry* **2000**, *11*, 4359.

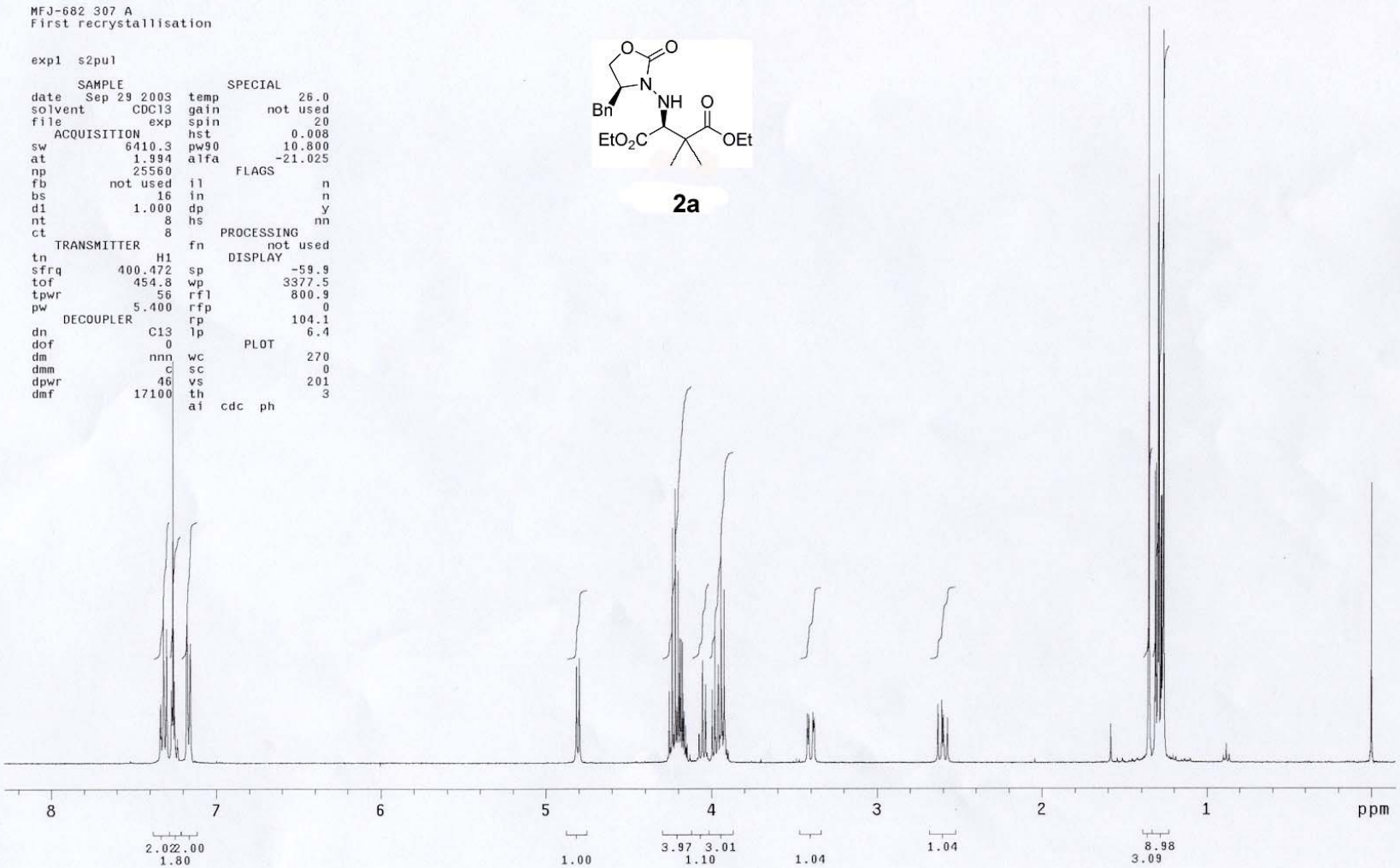
(3) Namy, J. L.; Girard, P.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

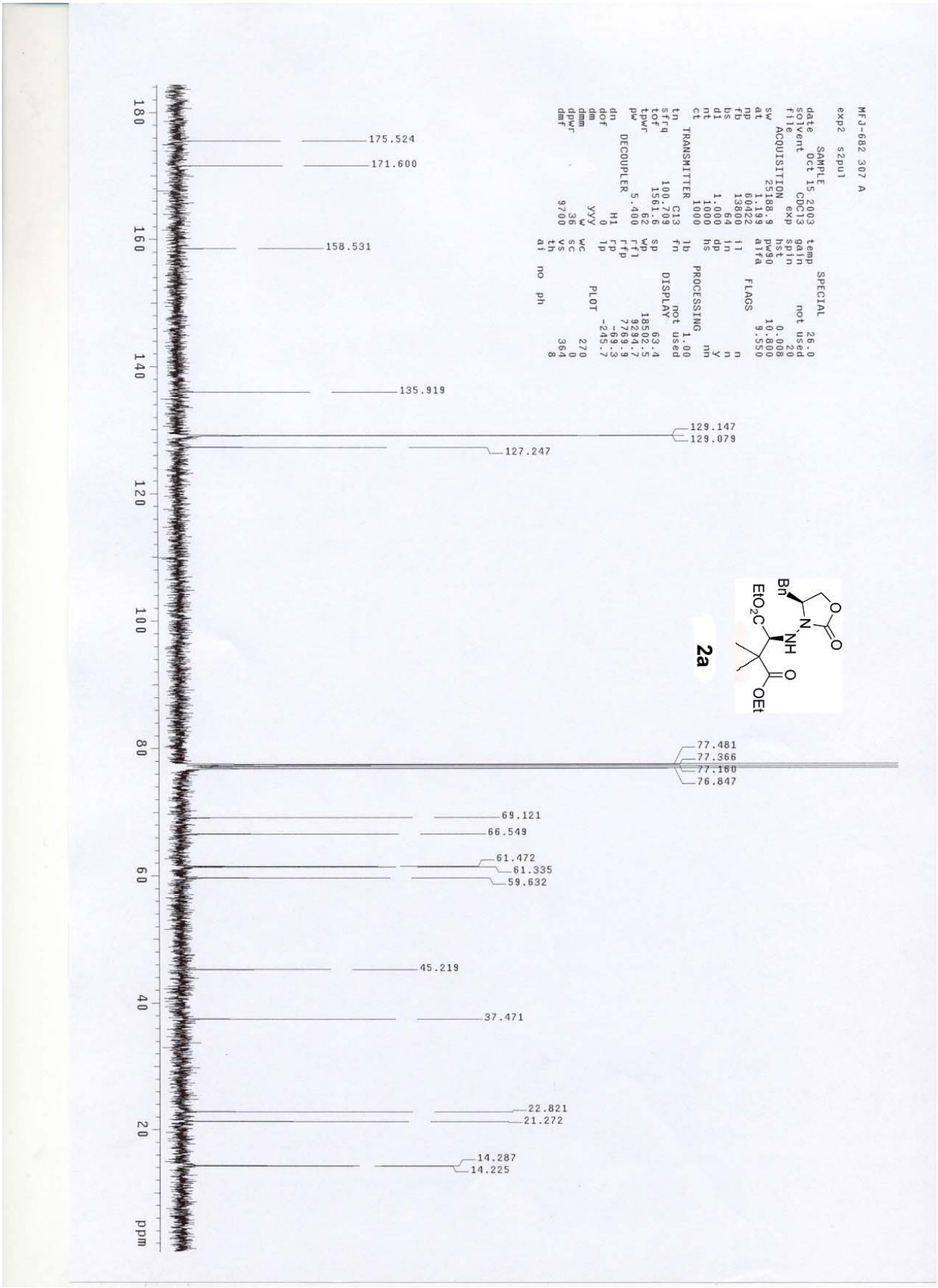
MFJ-682 307 A
First recrystallisation

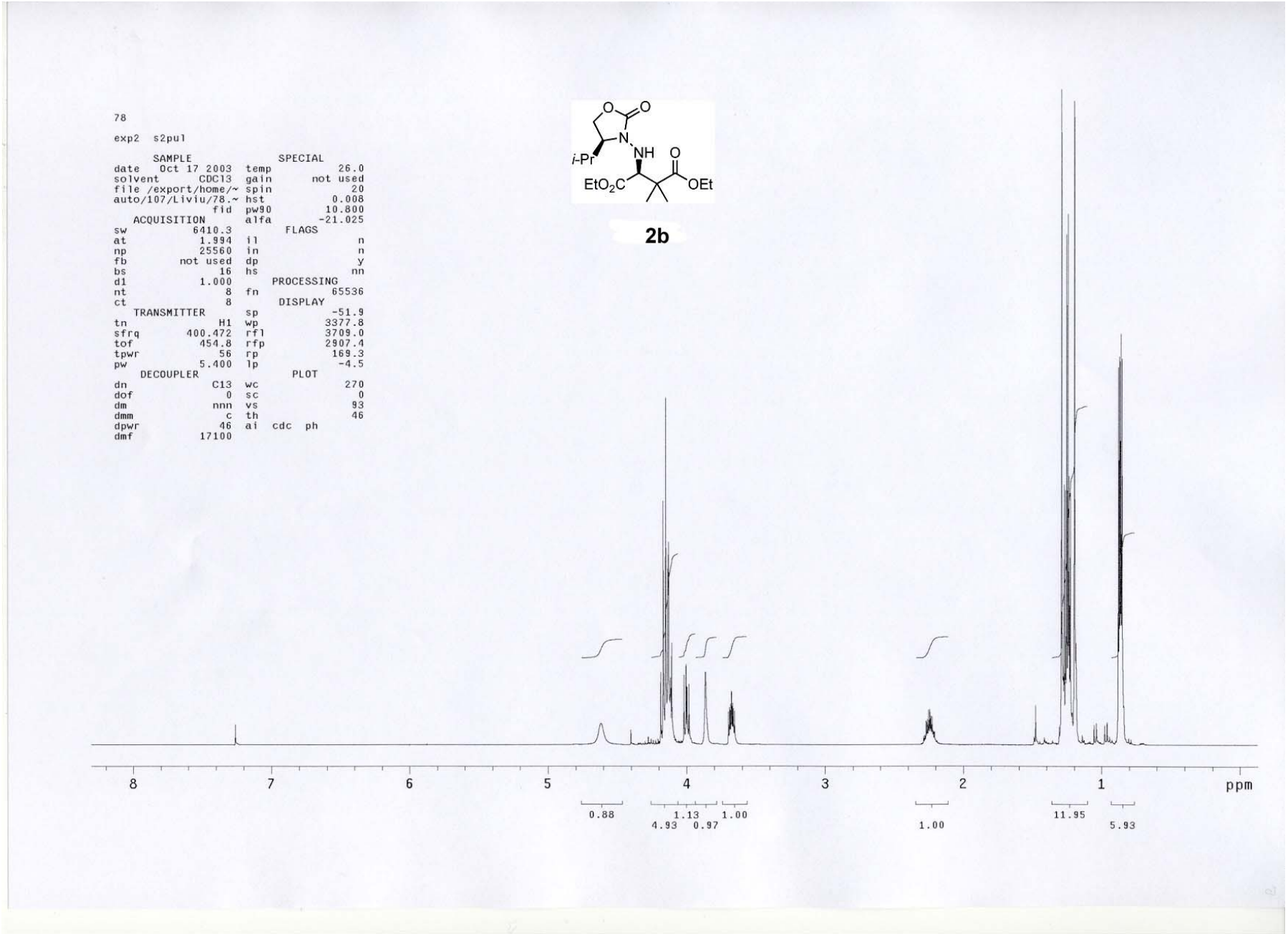
exp1 s2pul

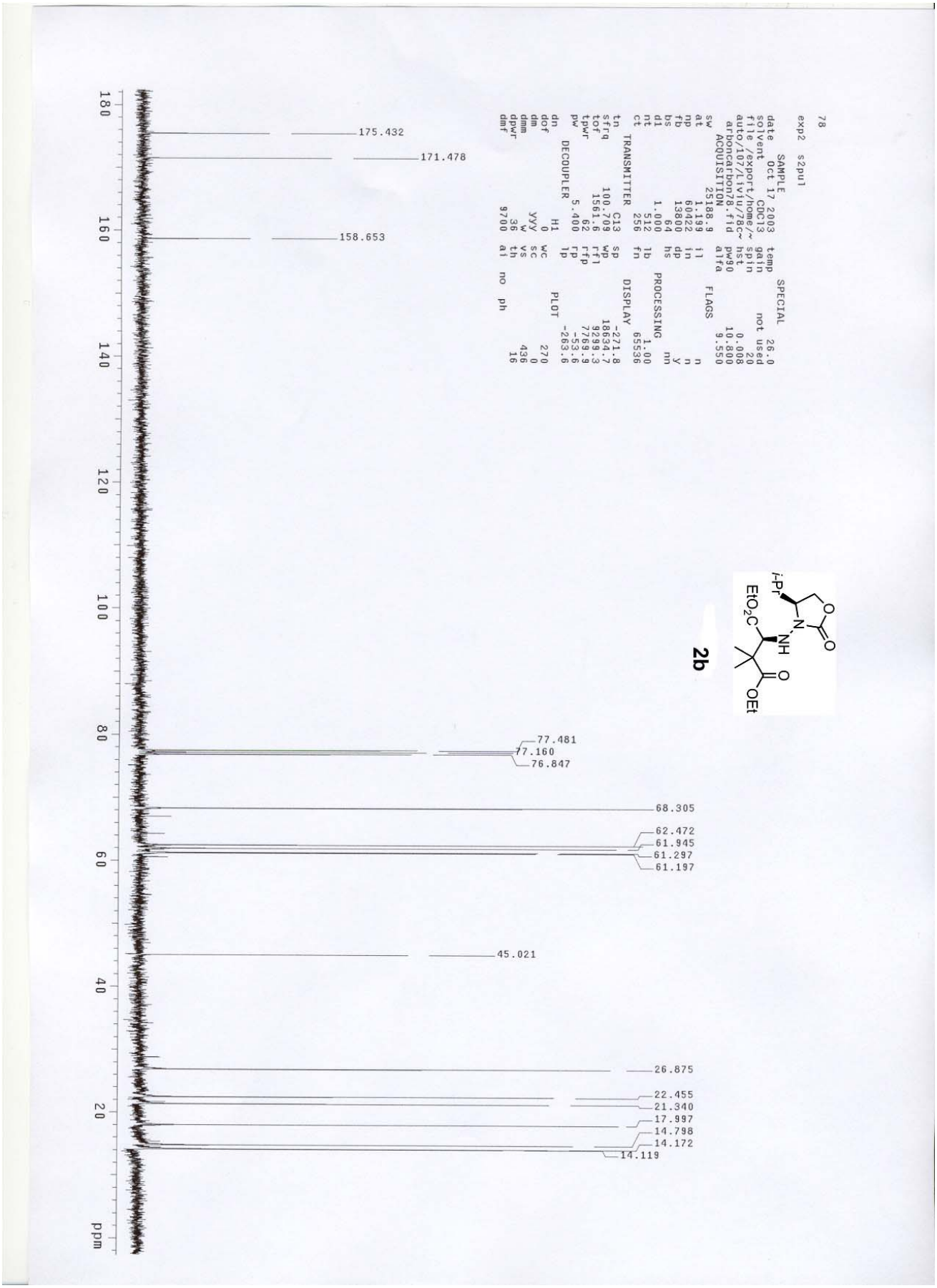
SAMPLE		SPECIAL	
date	Sep 29 2003	temp	26.0
solvent	CDCl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	6410.3	pw90	10.800
at	1.994	alfa	-21.025
np	25560	FLAGS	
fb	not used	il	n
bs	16	in	n
d1	1.000	dp	y
nt	8	hs	nn
ct	8	PROCESSING	
TRANSMITTER		fn	not used
tn	H1	DISPLAY	
sfrq	400.472	sp	-59.9
tof	454.8	wp	3377.5
tpwr	56	rfl	800.9
pw	5.400	rfp	0
DECOUPLER		rp	104.1
dn	C13	lp	6.4
dof	0	PLOT	
dm	nnn	wc	270
dmm	c	sc	0
dpwr	46	vs	201
dmf	17100	th	3
		ai cdc ph	

2a




MFJ-682 307 A
exp2 s2pul
SAMPLE
date Oct 15 2003
solvent CDCl3
file exp
ACQUISITION
sw 25188.9
at 1.199
np 60422
fb 13800
bs 64
d1 1.000
nt 1000
ct 1000
TRANSMITTER
tn C13
sfrq 100.709
tof 1561.6
tpwr 62
pw 5.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dmf 36
dpwr 9700
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa 9.550
FLAGS
il n
in y
dp nn
hs n
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 63.4
wp 18502.5
rf1 8294.7
rfp 7769.9
rp -69.3
lp -245.7
PLOT
wc 270
sc 0
vs 364
th 8
al
no
ph
SPECIAL
175.524
171.600
158.531
135.919
129.147
129.079
127.247
77.481
77.366
77.160
76.847
69.121
66.549
61.472
61.335
59.632
45.219
37.471
22.821
21.272
14.287
14.225
2a
Bn
EtO2C
NH
OEt
ppm

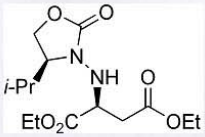

78
exp2 s2pul
SAMPLE
date Oct 17 2003
solvent CDCl3
file /export/home/~
auto/107/Liviu/78.~
fid
ACQUISITION
sw 6410.3
at 1.994
np 25560
fb not used
bs 16
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 400.472
tof 454.8
tpwr 56
pw 5.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 46
dmf 17100
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa -21.025
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -51.9
wp 3377.8
rf1 3709.0
rfp 2907.4
rp 169.3
lp -4.5
PLOT
wc 270
sc 0
vs 93
th 46
ai cdc ph
i-Pr
NH
O
EtO2C
OEt
2b
8
7
6
5
4
3
2
1
ppm
0.88
4.93
1.13
0.97
1.00
1.00
11.95
5.93


78
exp2 s2pul
SAMPLE
date Oct 17 2003 temp 26.0
solvent CDCl3 gain not used
file /export/home/~ spin 20
auto/107/Liviu/78c~ hst 0.008
arboncarbon78.fid pw90 10.800
ACQUISITION alfa 9.550
sw 25188.9 FLAGS
at 1.199 il n
np 60422 in n
fb 13800 dp y
bs 64 hs nn
d1 1.000 PROCESSING
nt 512 lb 1.00
ct 256 fn 65536
TRANSMITTER DISPLAY
tn C13 sp -271.8
sfrq 100.709 wp 18634.7
tof 1561.6 rfl 9299.3
tpwr 62 rfp 7769.9
pw 5.400 rp -53.6
DECOUPLER lp -263.6
dn H1 PLOT
dof 0 wc 270
dm yyy sc 0
dmm w vs 436
dpwr 36 th 16
dmf 9700 al no ph
2b
175.432
171.478
158.653
77.481
77.160
76.847
68.305
62.472
61.945
61.297
61.197
45.021
26.875
22.455
21.340
17.997
14.798
14.172
14.119
180
160
140
120
100
80
60
40
20
ppm

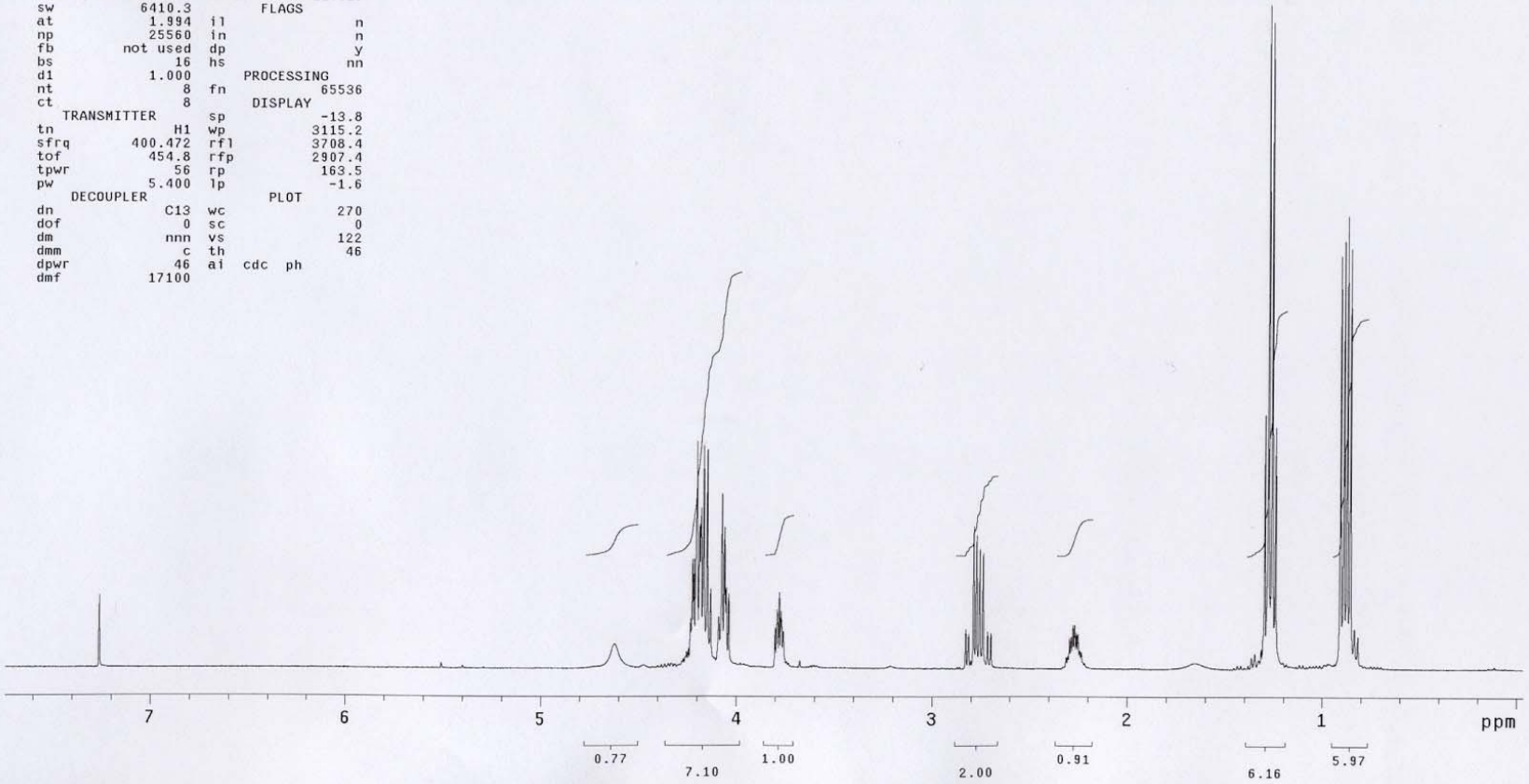
Liviu94-3

exp2 s2pul

SAMPLE		SPECIAL	
date	Oct 15 2003	temp	26.0
solvent	CDCl3	gain	not used
file	/export/home/~	spin	20
auto/107/Liviu/Liv~		hst	0.008
	iu94-3.fid	pw90	10.800
ACQUISITION		alfa	-21.025
sw	6410.3	FLAGS	
at	1.994	il	n
np	25560	in	n
fb	not used	dp	y
bs	16	hs	nn
d1	1.000	PROCESSING	
nt	8	fn	65536
ct	8	DISPLAY	
TRANSMITTER		sp	-13.8
tn	H1	wp	3115.2
sfrq	400.472	rfl	3708.4
tof	454.8	rfp	2907.4
tpwr	56	rp	163.5
pw	5.400	lp	-1.6
DECOUPLER		PLOT	
dn	C13	wc	270
dof	0	sc	0
dm	nnn	vs	122
dmm	c	th	46
dpwr	46	ai cdc ph	
dmf	17100		



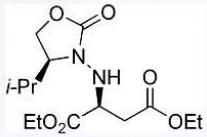
2c



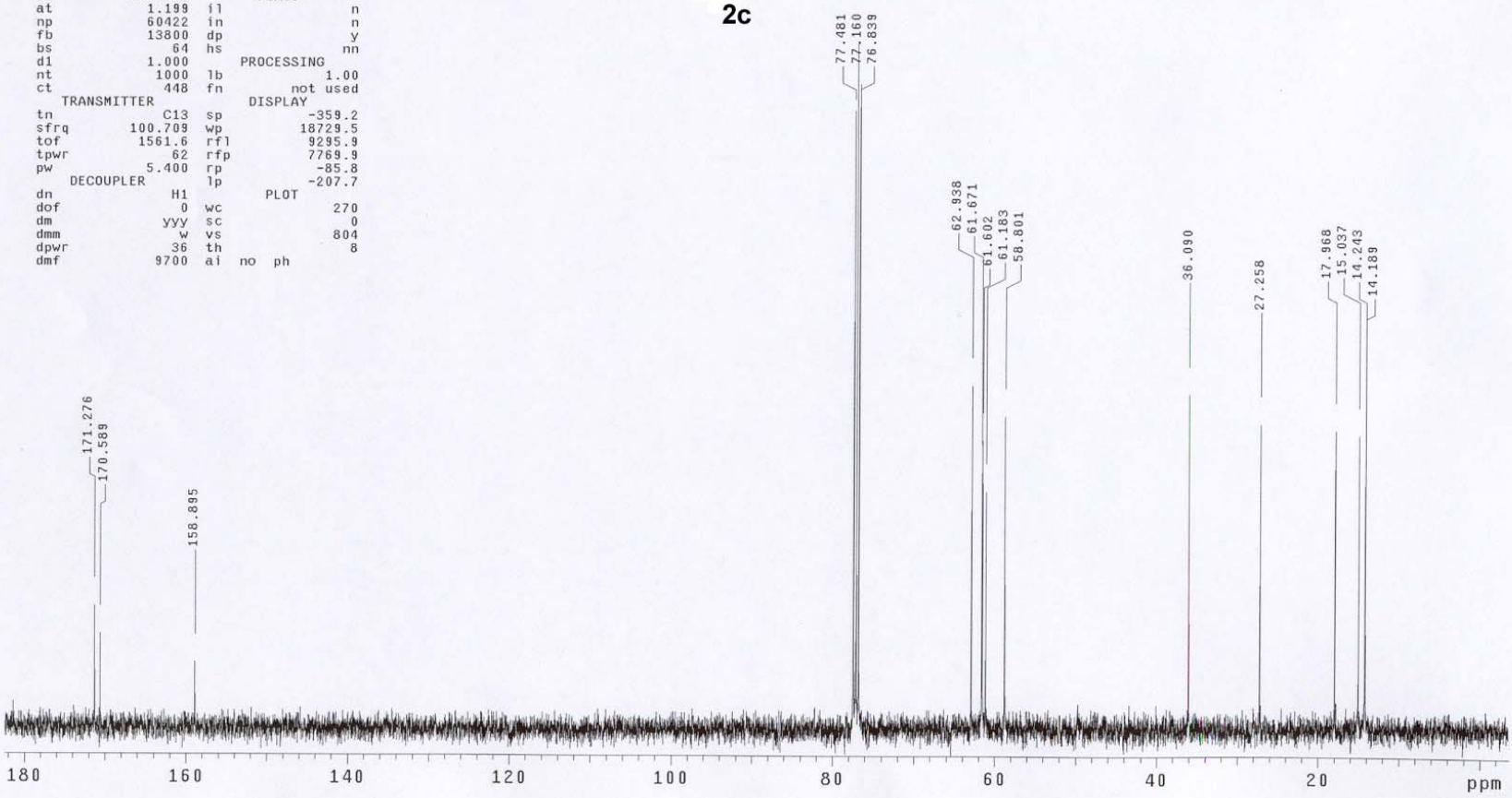
94-1

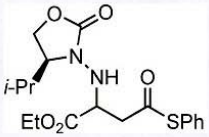
exp1 s2pul

SAMPLE		SPECIAL	
date	Nov 17 2003	temp	26.0
solvent	CDCl3	gain	not used
file	/export/home/~	spin	20
auto/107/Liviu/94-~		hst	0.008
	1carbon.fid	pw90	10.800
ACQUISITION		alfa	9.550
sw	25188.9	FLAGS	
at	1.199	il	n
np	60422	in	n
fb	13800	dp	y
bs	64	hs	nn
d1	1.000	PROCESSING	
nt	1000	lb	1.00
ct	448	fn	not used
TRANSMITTER		DISPLAY	
tn	C13	sp	-359.2
sfrq	100.709	wp	18729.5
tof	1561.6	rfl	9295.9
tpwr	62	rfp	7769.9
pw	5.400	rp	-85.8
DECOUPLER		lp	-207.7
dn	H1	PLOT	
dof	0	wc	270
dm	yyy	sc	0
dmm	w	vs	804
dpwr	36	th	8
dmf	9700	al no ph	



2c

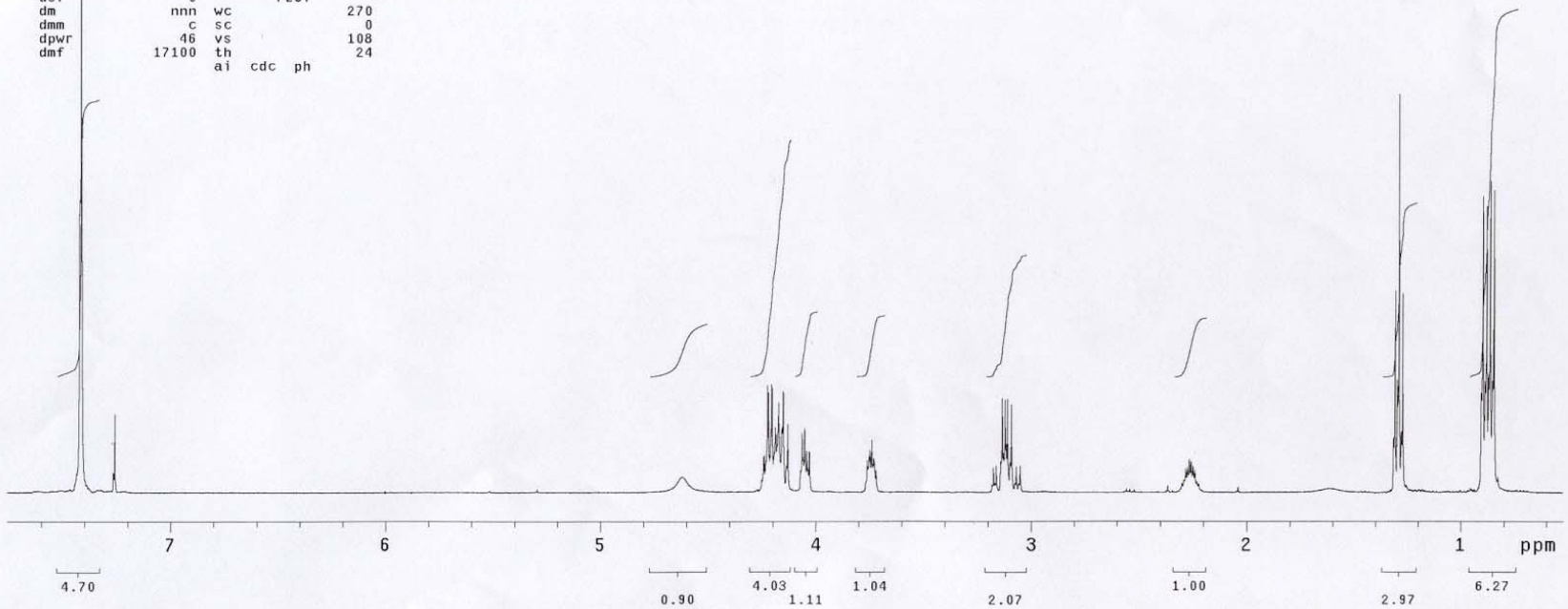


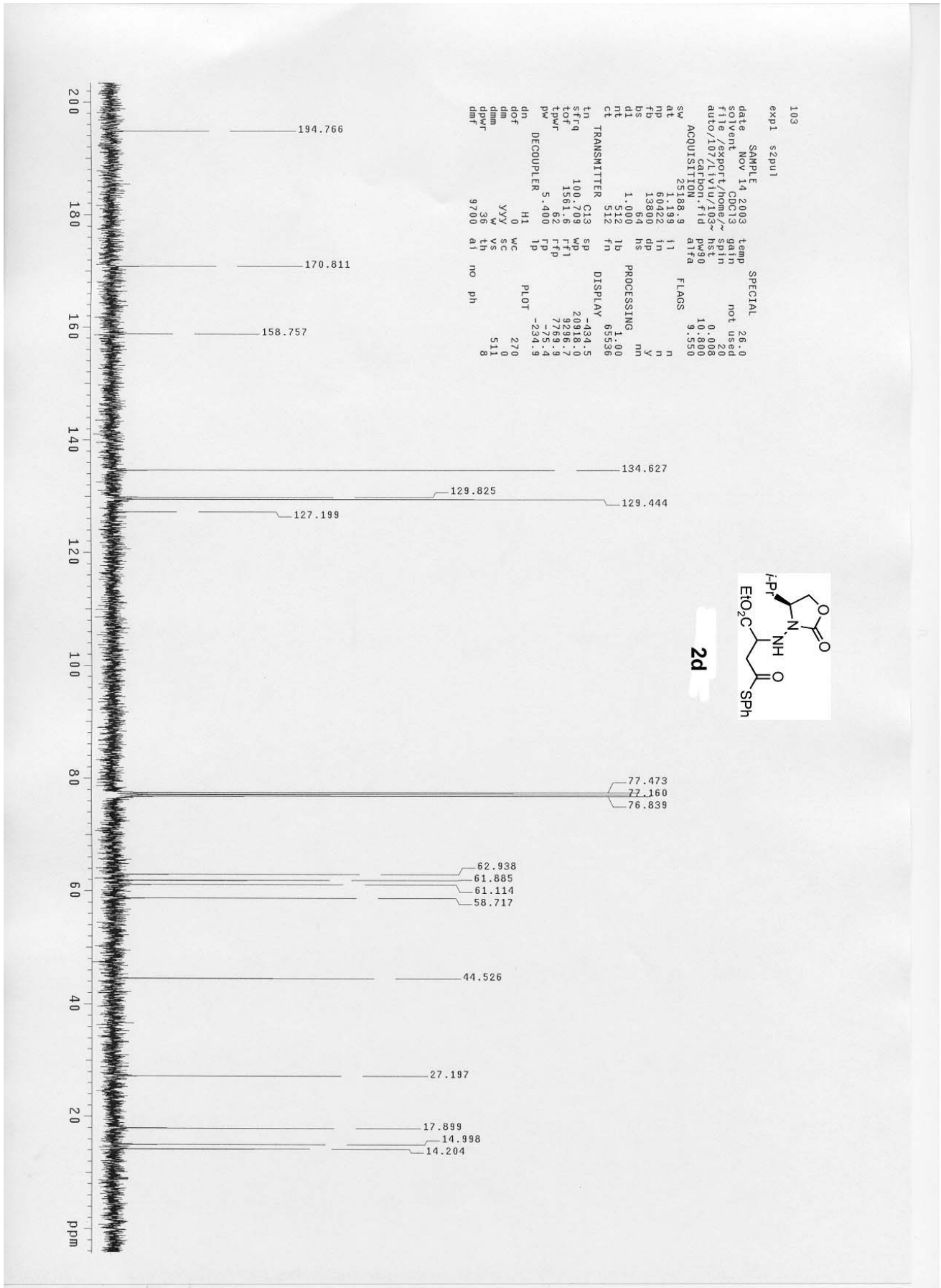


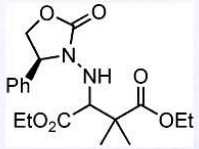
2d

```
103
exp1  s2pul

        SAMPLE                SPECIAL
date   Nov 14 2003  temp            26.0
solvent       CDCl3  gain       not used
file            exp  spin             20
   ACQUISITION       hst            0.008
sw           6410.3  pw90          10.800
at            1.994  alfa        -21.025
np            25560          FLAGS
fb        not used  il                 n
bs              16  in                 n
d1           1.000  dp                 y
nt               8  hs                nn
ct               8          PROCESSING
   TRANSMITTER      fn             65536
tn               H1          DISPLAY
sfrq        400.472  sp            209.3
tof           454.8  wp           2897.5
tpwr             56  rfl          3708.8
pw            5.400  rfp          2907.4
    DECOUPLER        rp            155.7
dn               C13  lp            13.7
dof               0           PLOT
dm              nnn  wc              270
dmm               c  sc                0
dpwr             46  vs              108
dmf           17100  th               24
                     ai  cdc  ph
```




103
expl s2pul
SAMPLE
date Nov 14 2003
solvent CDCl3
file /export/home/~
auto/107/Liviu/103~
carbon.fid
ACQUISITION
sw 25188.9
at 1.199
np 60422
fb 13800
bs 64
d1 1.000
nt 512
ct 512
TRANSMITTER
tn C13
sfrq 100.709
tof 1561.6
tpwr 62
pw 5.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 36
dmf 9700
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa 9.550
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn 65536
DISPLAY
sp -434.5
wp 20918.0
rf1 9296.7
rfp 7769.9
rp -75.4
lp -234.9
PLOT
wc 270
sc 0
vs 511
th 8
al
no
ph
194.766
170.811
158.757
134.627
129.825
129.444
127.199
77.473
77.160
76.839
62.938
61.885
61.114
58.717
44.526
27.197
17.899
14.998
14.204
200
180
160
140
120
100
80
60
40
20
ppm
i-Pr
EtO2C
NH
SPh
2d

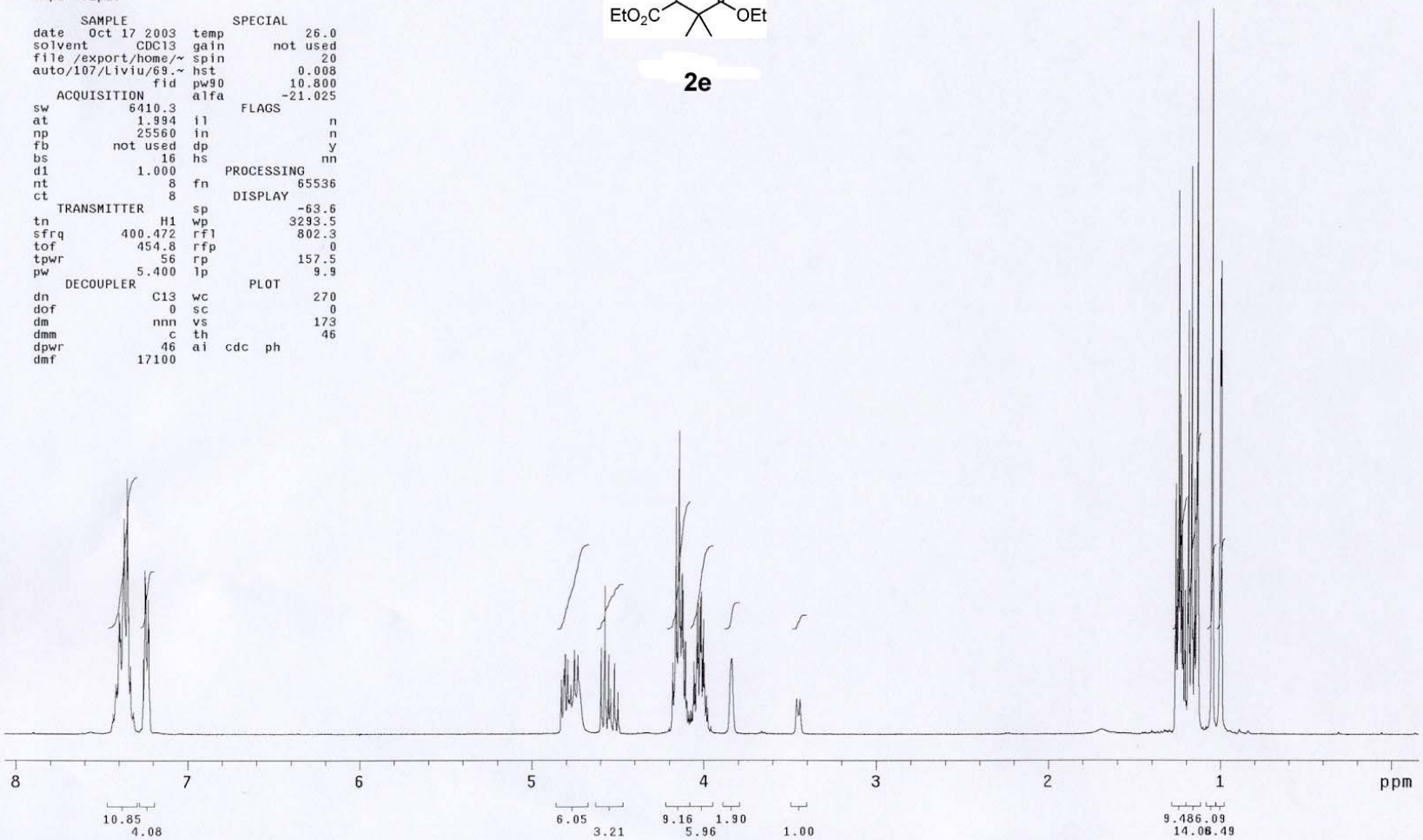


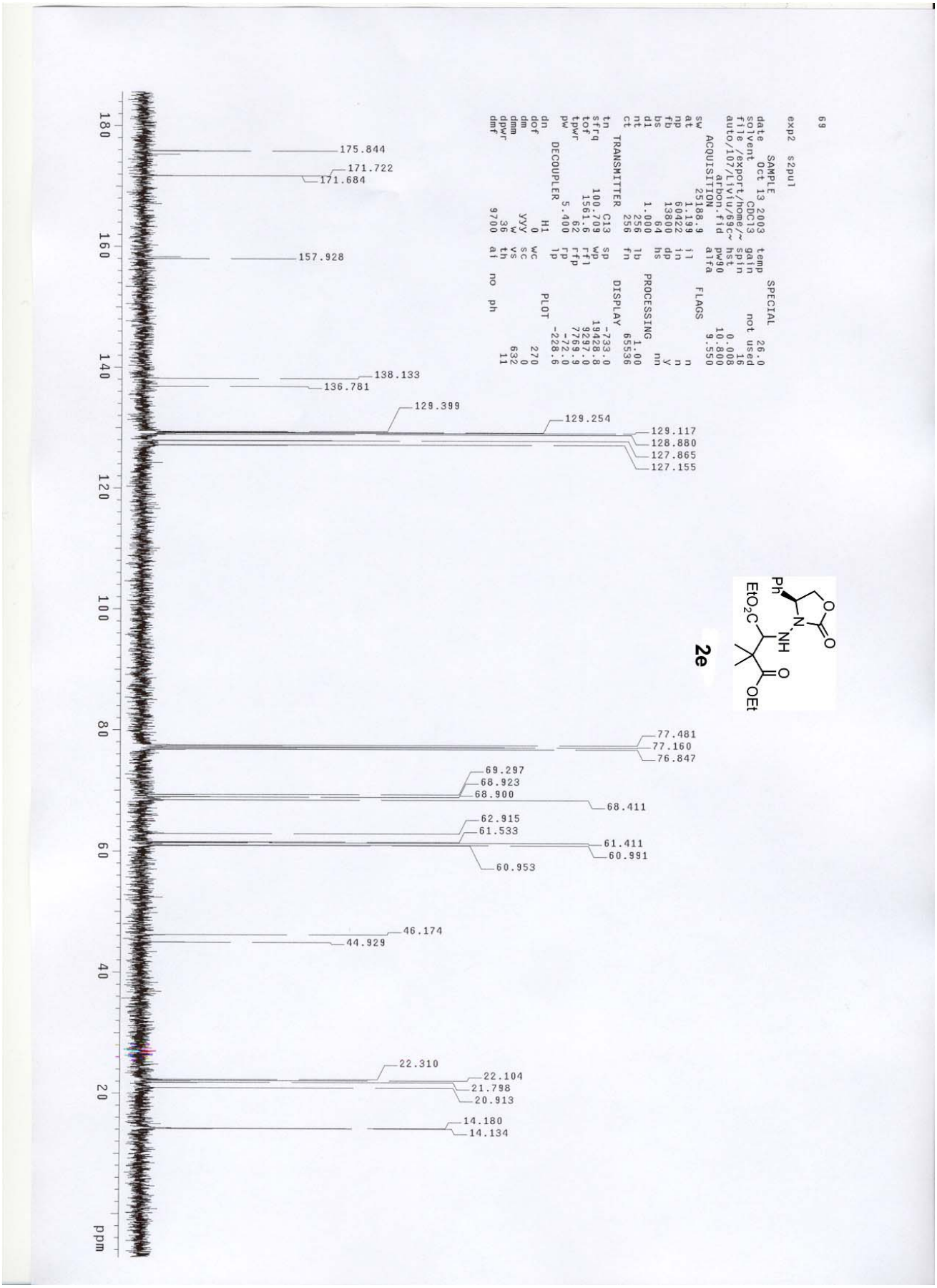
2e

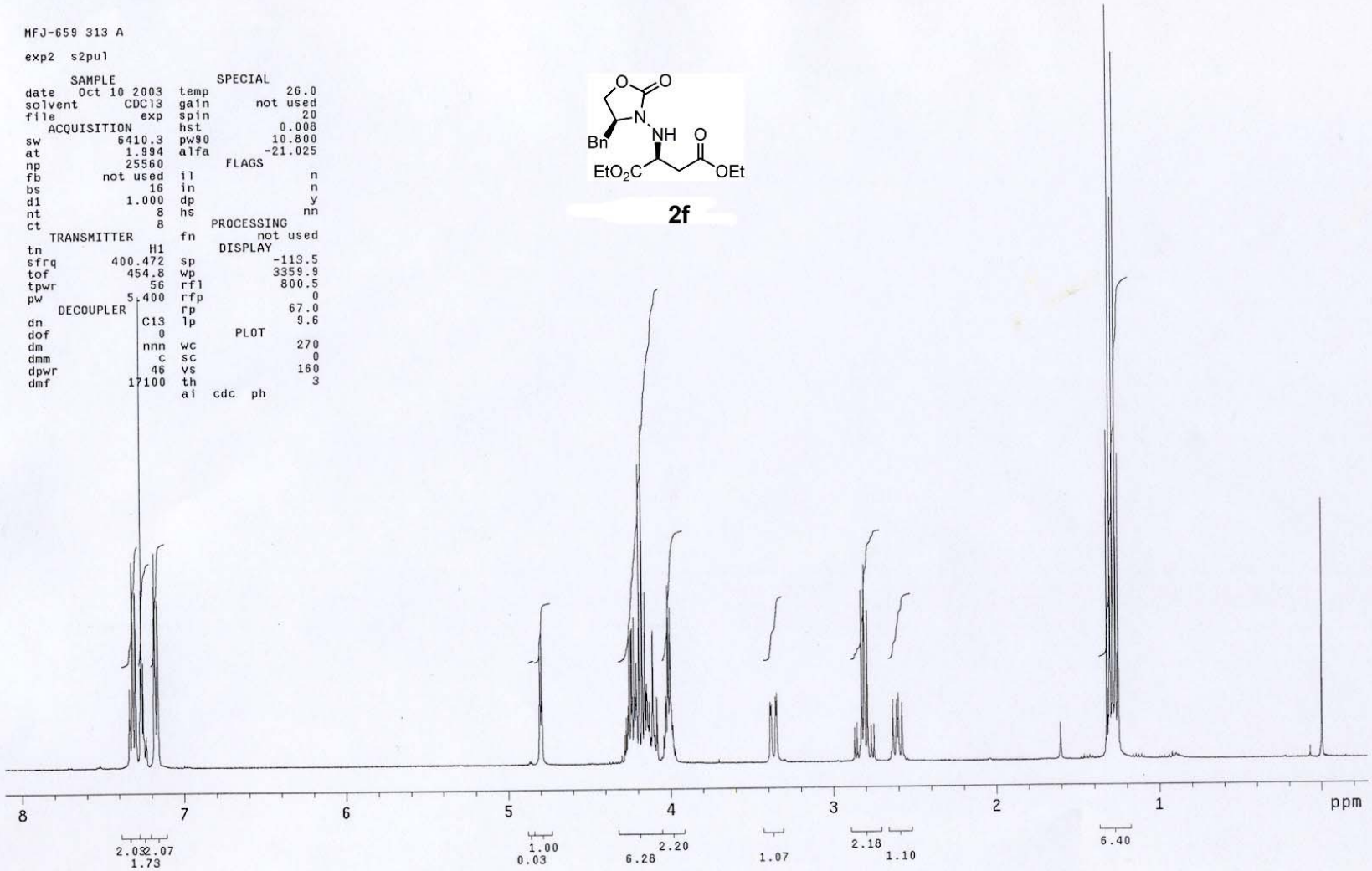
```
69

exp2  s2pul

      SAMPLE                SPECIAL
date   Oct 17 2003  temp            26.0
solvent       CDCl3  gain        not used
file /export/home/~  spin            20
auto/107/Liviu/69.~  hst           0.008
                fid  pw90         10.800
   ACQUISITION       alfa        -21.025
sw           6410.3         FLAGS
at            1.994  il                n
np            25560  in                n
fb         not used  dp                y
bs               16  hs               nn
d1            1.000      PROCESSING
nt                8  fn            65536
ct                8       DISPLAY
   TRANSMITTER       sp            -63.6
tn               H1  wp           3293.5
sfrq        400.472  rfl           802.3
tof           454.8  rfp               0
tpwr             56  rp            157.5
pw            5.400  lp              9.9
    DECOUPLER                PLOT
dn               C13  wc              270
dof                0  sc                0
dm               nnn  vs              173
dmm                c  th               46
dpwr              46  ai  cdc  ph
dmf           17100
```




69
exp2 s2pul
SAMPLE
date Oct 13 2003
solvent CDCl3
file /export/home/~
auto/107/Liu/69c~
ACQUISITION
sw 25188.9
at 1.199
np 60422
fb 13800
bs 64
d1 1.000
nt 256
ct 256
TRANSMITTER
tn C13
sfrq 100.709
tof 1561.6
tpwr 62
pw 5.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 36
dmf 9700
temp
gain
spin
hst
pw90
alfa
FLAGS
n
n
y
nn
PROCESSING
lb 1.00
fn 65536
DISPLAY
sp -733.0
wp 19428.8
rf1 9297.0
rfp 7769.9
rp -72.0
lp -228.6
PLOT
wc 270
sc 0
vs 632
th 11
SPECIAL
temp 26.0
gain not used
spin 16
hst 0.008
pw90 10.800
alfa 9.550
al no ph
175.844
171.722
171.684
157.928
138.133
136.781
129.399
129.254
129.117
128.880
127.865
127.155
77.481
77.160
76.847
69.297
68.923
68.900
68.411
62.915
61.533
61.411
60.991
60.953
46.174
44.929
22.310
22.104
21.798
20.913
14.180
14.134
ppm
2e

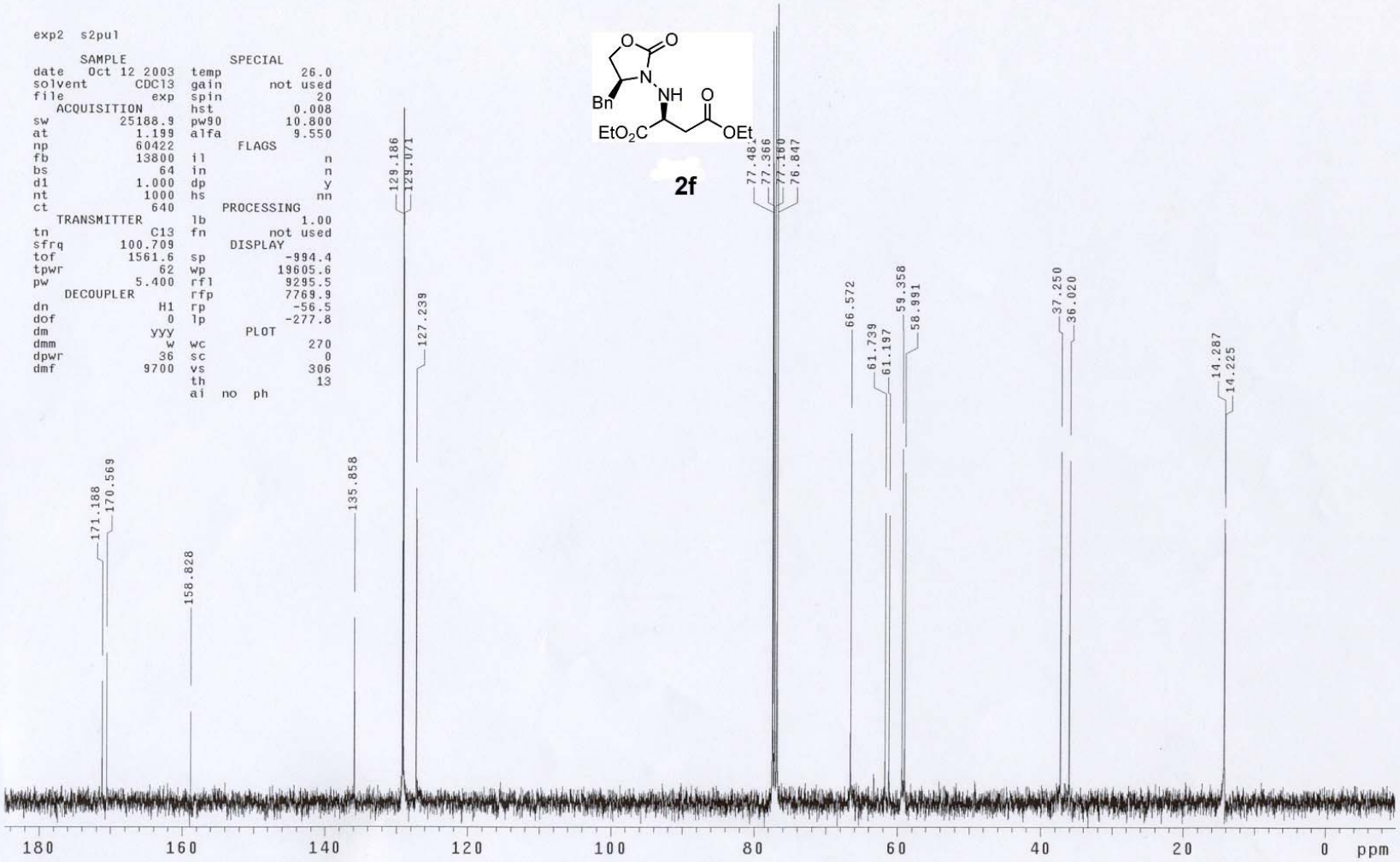

MFJ-659 313 A
exp2 s2pul
SAMPLE
date Oct 10 2003
solvent CDCl3
file exp
ACQUISITION
sw 6410.3
at 1.994
np 25560
fb not used
bs 16
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 400.472
tof 454.8
tpwr 56
pw 5.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 46
dmf 17100
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa -21.025
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -113.5
wp 3359.9
rfl 800.5
rfp 0
rp 67.0
lp 9.6
PLOT
wc 270
sc 0
vs 160
th 3
ai cdc ph
Bn
NH
O
EtO2C
OEt
2f
8
7
6
5
4
3
2
1
ppm
2.03
2.07
1.73
1.00
0.03
6.28
2.20
1.07
2.18
1.10
6.40

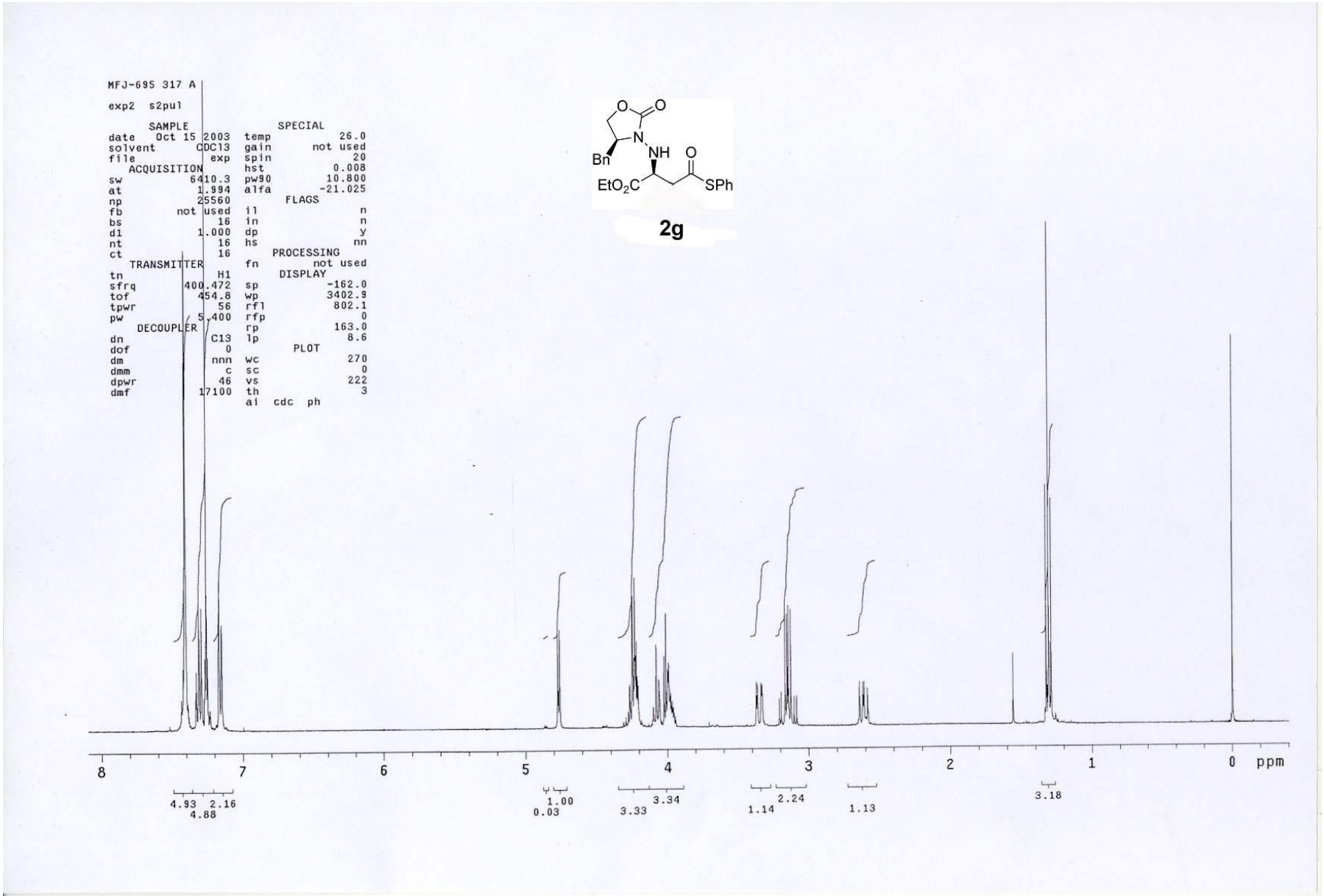
MFJ-659 313 A

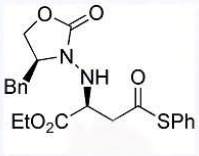
exp2 s2pul

SAMPLE		SPECIAL	
date	Oct 12 2003	temp	26.0
solvent	CDCl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	25188.9	pw90	10.800
at	1.199	alfa	9.550
np	60422	FLAGS	
fb	13800	il	n
bs	64	in	n
d1	1.000	dp	y
nt	1000	hs	nn
ct	640	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	100.709	DISPLAY	
tof	1561.6	sp	-994.4
tpwr	62	wp	19605.6
pw	5.400	rf1	9295.5
DECOUPLER		rfp	7769.9
dn	H1	rp	-56.5
dof	0	lp	-277.8
dm	yyy	PLOT	
dmm	w	wc	270
dpwr	36	sc	0
dmf	9700	vs	306
		th	13
		ai no ph	

2f




MFJ-695 317 A
exp2 s2pul
SAMPLE
date Oct 15 2003
solvent CDCl3
file exp
ACQUISITION
sw 6410.3
at 1.994
np 25560
fb not used
bs 16
d1 1.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 400.472
tof 454.8
tpwr 56
pw 5.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 46
dmf 17100
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa -21.025
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -162.0
wp 3402.9
rfl 802.1
rfp 0
rp 163.0
lp 8.6
PLOT
wc 270
sc 0
vs 222
th 3
ai cdc ph
Bn
NH
O
EtO2C
SPh
2g
8
7
6
5
4
3
2
1
0
ppm
4.93 2.16
4.88
1.00
0.03
3.33
3.34
1.14
2.24
1.13
3.18

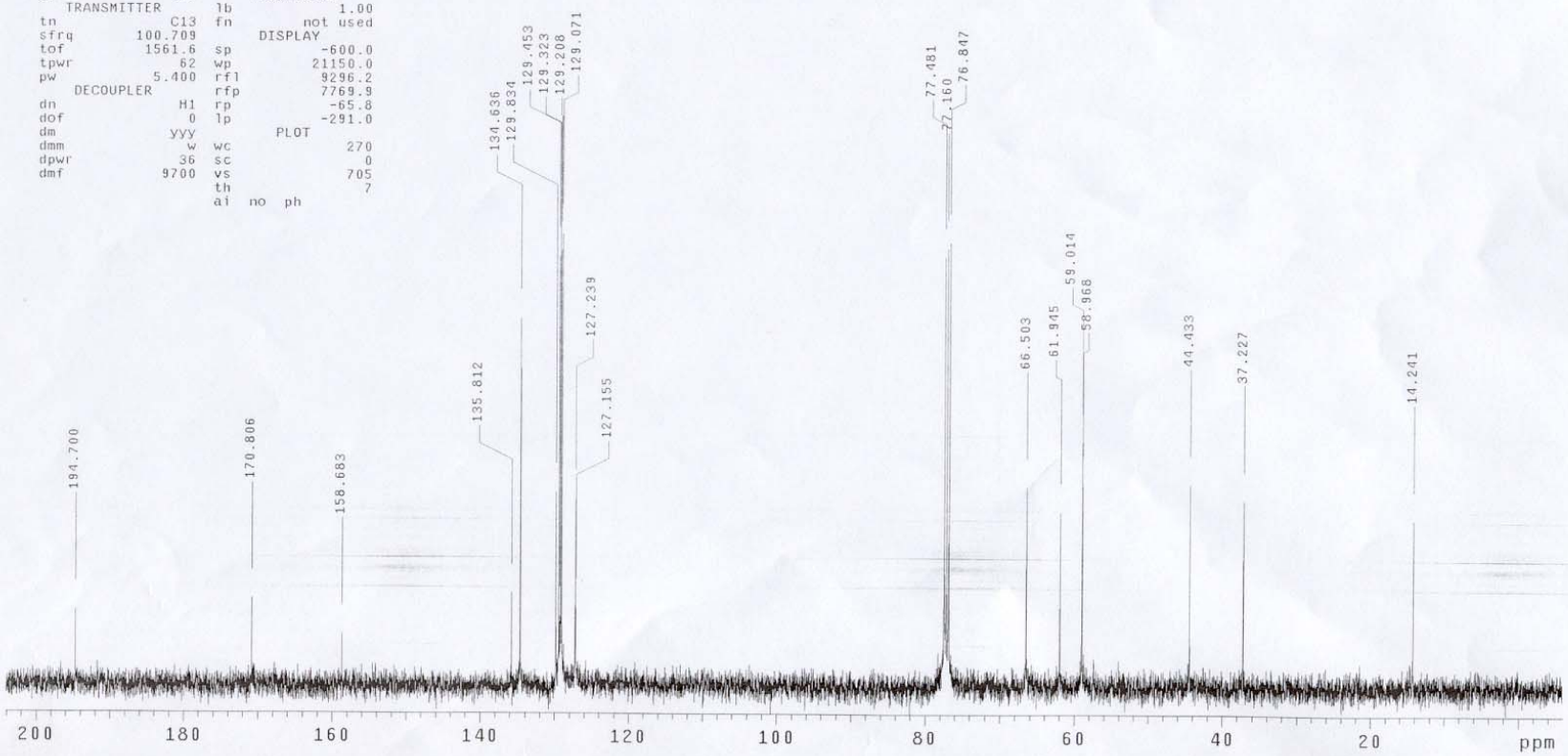


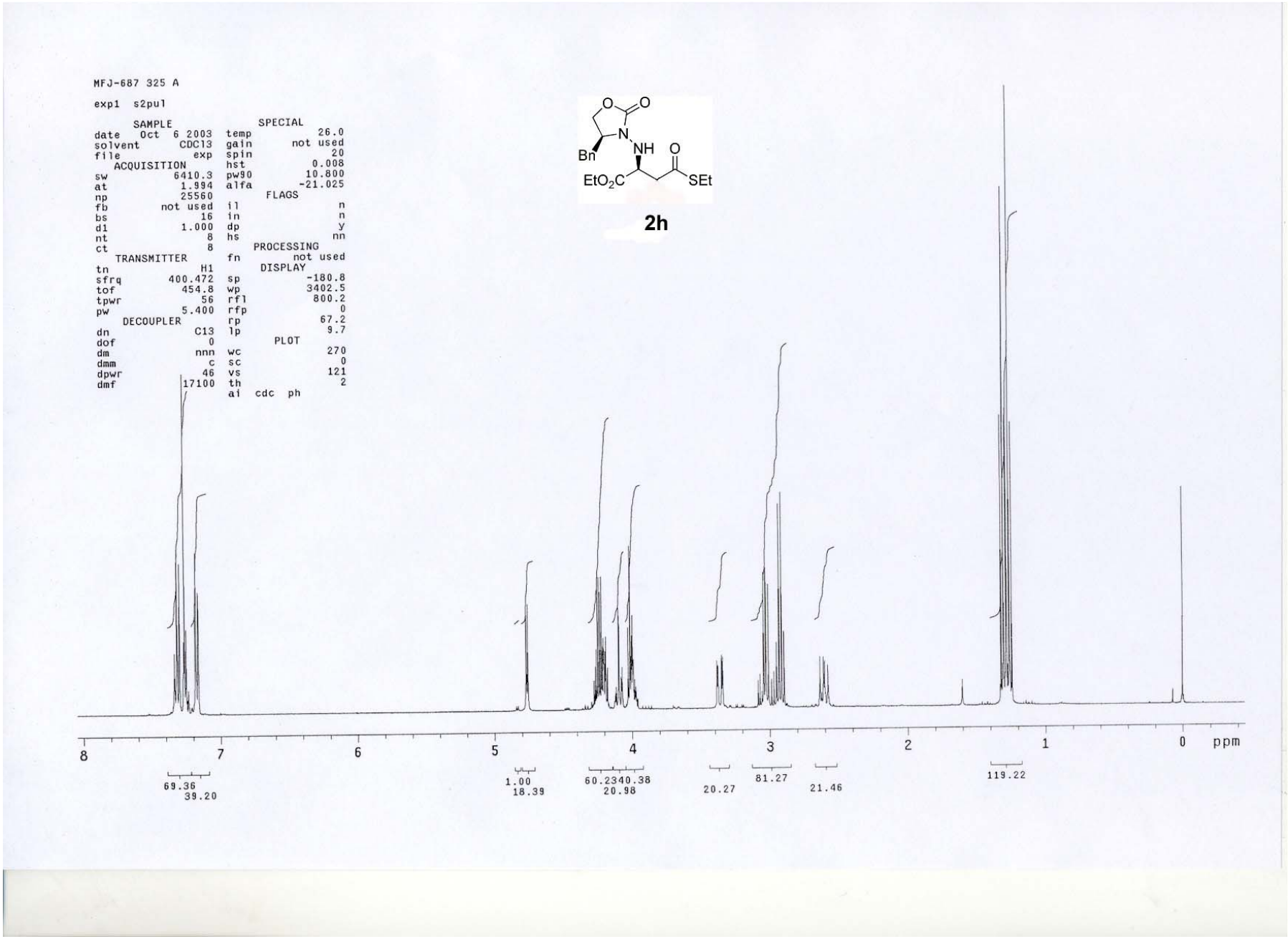
2g

MFJ-671 317 A

exp1 s2pul

SAMPLE		SPECIAL	
date	Sep 15 2003	temp	25.0
solvent	CDCl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	25188.9	pw90	10.800
at	1.199	alfa	9.550
np	60422	FLAGS	
fb	13800	il	n
bs	64	in	n
dl	1.000	dp	y
nt	512	hs	nn
ct	512	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	100.709	DISPLAY	
tof	1561.6	sp	-600.0
tpwr	62	wp	21150.0
pw	5.400	rfl	9296.2
DECOUPLER		rfp	7769.9
dn	H1	rp	-65.8
dof	0	lp	-291.0
dm	yyy	PLOT	
dmm	w	wc	270
dpwr	36	sc	0
dmf	9700	vs	705
		th	7
		ai no ph	



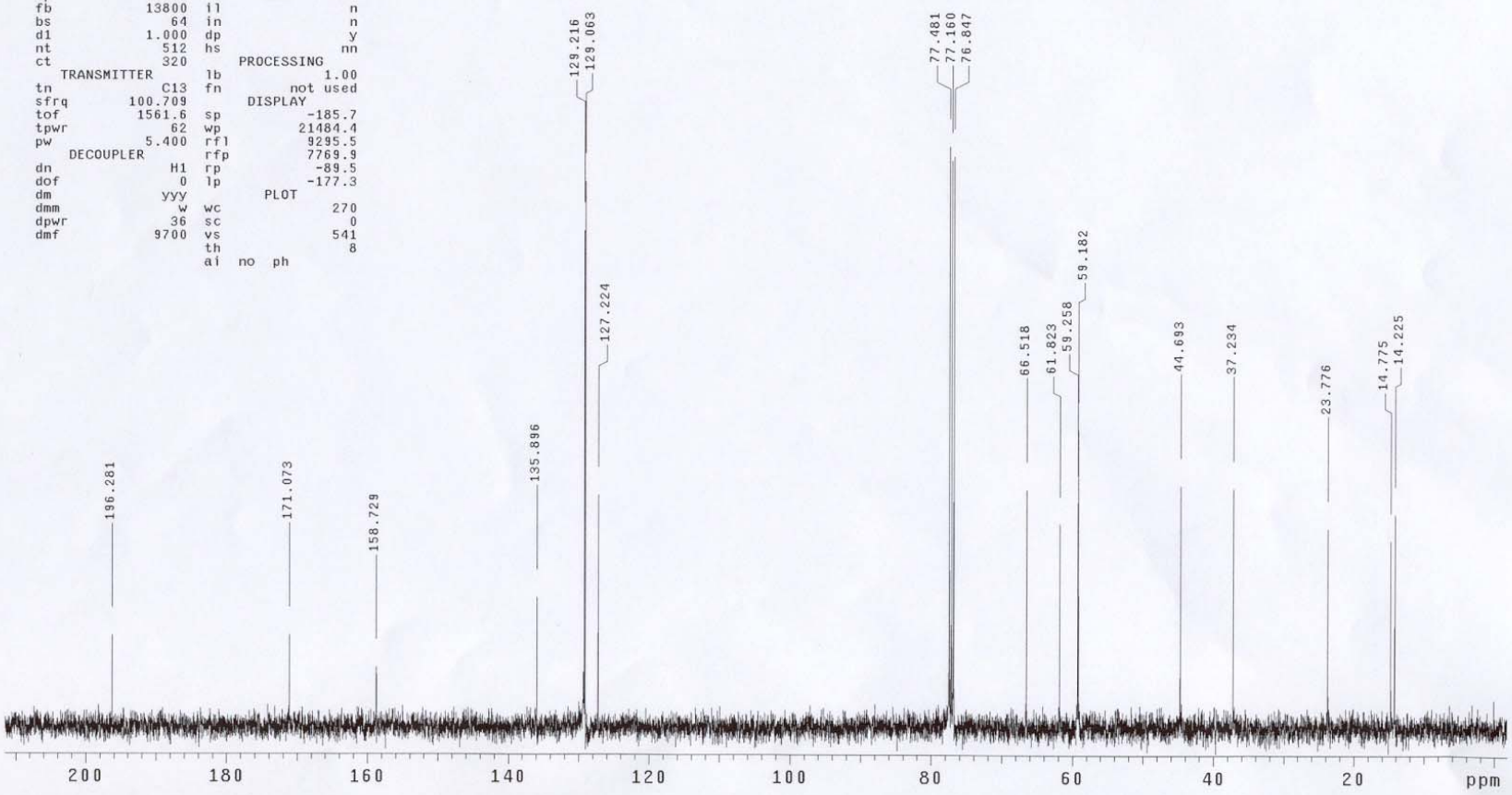

MFJ-687 325 A
exp1 s2pul
SAMPLE
date Oct 6 2003
solvent CDCl3
file exp
ACQUISITION
sw 6410.3
at 1.994
np 25560
fb not used
bs 16
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 400.472
tof 454.8
tpwr 56
pw 5.400
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 46
dmf 17100
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa -21.025
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn not used
DISPLAY
sp -180.8
wp 3402.5
rfl 800.2
rfp 0
rp 67.2
lp 9.7
PLOT
wc 270
sc 0
vs 121
th 2
ai cdc ph
Bn
NH
O
EtO2C
SEt
2h
8
7
6
5
4
3
2
1
0
ppm
69.36
39.20
1.00
18.39
60.23
40.38
20.98
20.27
81.27
21.46
119.22

2h

MFJ-687 325 A

exp1 s2pul

SAMPLE		SPECIAL	
date	Oct 6 2003	temp	26.0
solvent	CDCl3	gain	not used
file	exp	spin	20
ACQUISITION		hst	0.008
sw	25188.9	pw90	10.800
at	1.199	alfa	9.550
np	60422	FLAGS	
fb	13800	il	n
bs	64	in	n
d1	1.000	dp	y
nt	512	hs	nn
ct	320	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	100.709	DISPLAY	
tof	1561.6	sp	-185.7
tpwr	62	wp	21484.4
pw	5.400	rfl	9295.5
DECOUPLER		rfp	7769.9
dn	H1	rp	-89.5
dof	0	lp	-177.3
dm	yyy	PLOT	
dmm	w	wc	270
dpwr	36	sc	0
dmf	9700	vs	541
		th	8
		ai no ph	

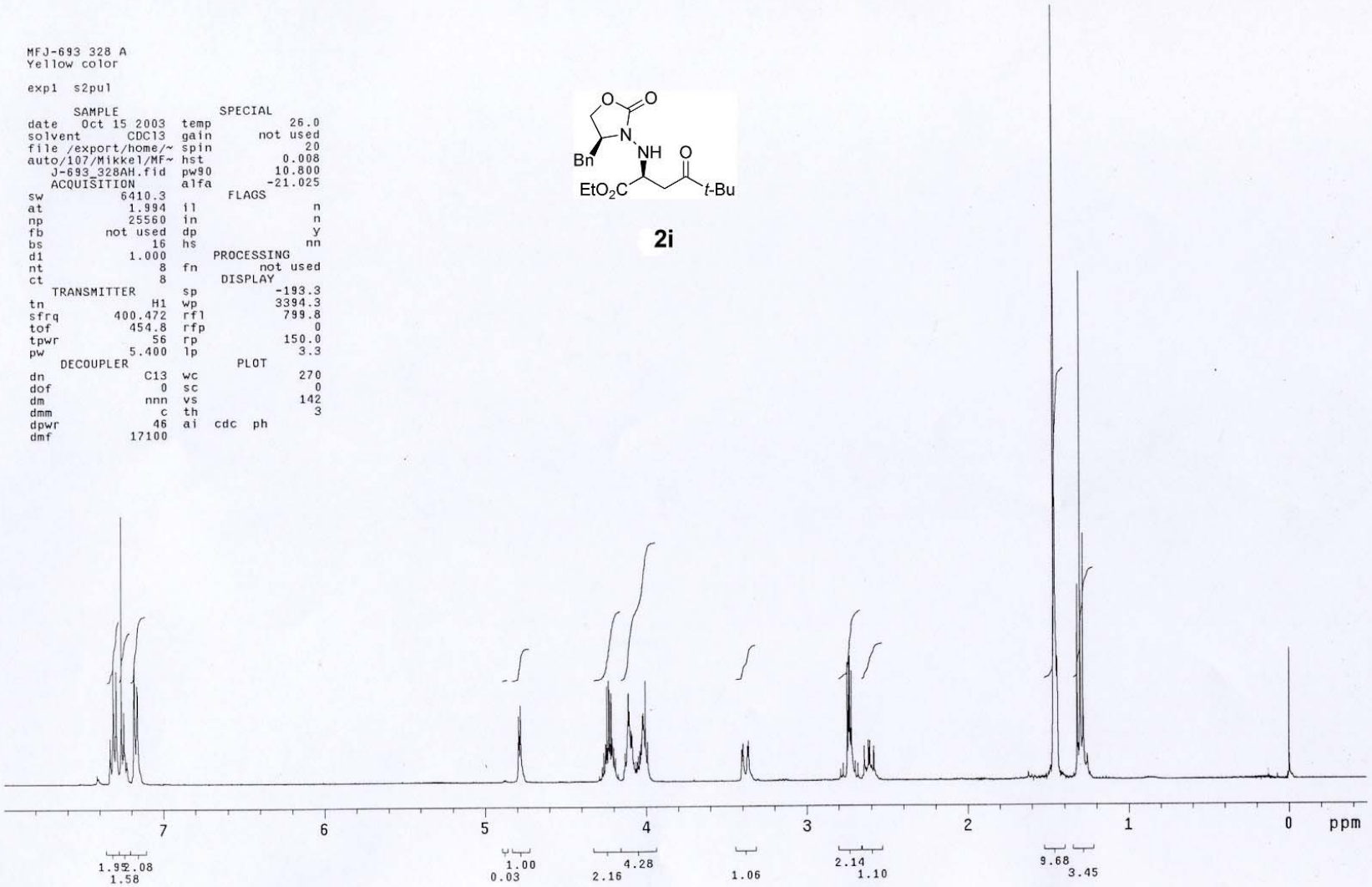


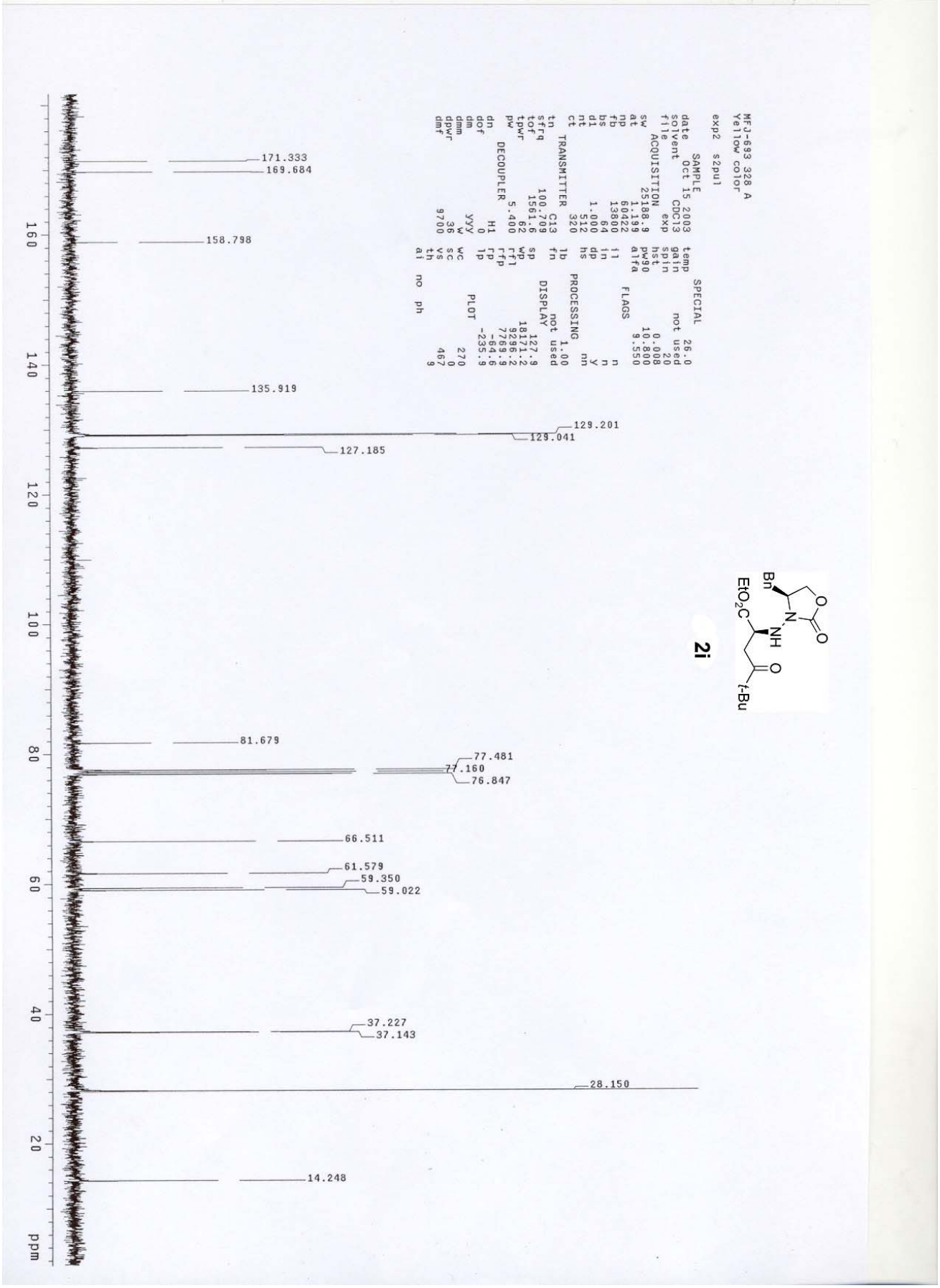
MFJ-693 328 A
Yellow color

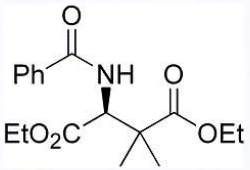
exp1 s2pul

SAMPLE		SPECIAL	
date	Oct 15 2003	temp	26.0
solvent	CDCl3	gain	not used
file	/export/home/~	spin	20
auto/107/Mikkel/MF~		hst	0.008
J-693_328AH.fid		pw90	10.800
ACQUISITION		alfa	-21.025
sw	6410.3	FLAGS	
at	1.994	il	n
np	25560	in	n
fb	not used	dp	y
bs	16	hs	nn
d1	1.000	PROCESSING	
nt	8	fn	not used
ct	8	DISPLAY	
TRANSMITTER		sp	-193.3
tn	H1	wp	3394.3
sfrq	400.472	rfl	799.8
tof	454.8	rfp	0
tpwr	56	rp	150.0
pw	5.400	lp	3.3
DECOUPLER		PLOT	
dn	C13	wc	270
dof	0	sc	0
dm	nnn	vs	142
dmm	c	th	3
dpwr	46	ai	cdc ph
dmf	17100		

2i




MFJ-693 328 A
Yellow color
exp2 s2pul
SAMPLE
date Oct 15 2003
solvent CDCl3
file exp
ACQUISITION
sw 25188.9
at 1.199
np 60422
fb 13800
bs 64
ds 1.000
d1 512
nt 320
ct
TRANSMITTER
tn C13
sfrq 100.709
tof 1561.6
tpwr 62
pw 5.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dmf 36
dpwr 9700
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa 9.550
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 127.9
wp 1811.2
rf1 926.2
rf2 728.3
rp -94.6
lp -235.9
PLOT
wc 270
sc 0
vs 462
th 9
ai no ph
171.333
169.684
158.798
135.919
129.201
129.041
127.185
81.679
77.481
77.160
76.847
66.511
61.579
59.350
59.022
37.227
37.143
28.150
14.248
160
140
120
100
80
60
40
20
ppm
Bn
EtO2C
t-Bu
2i

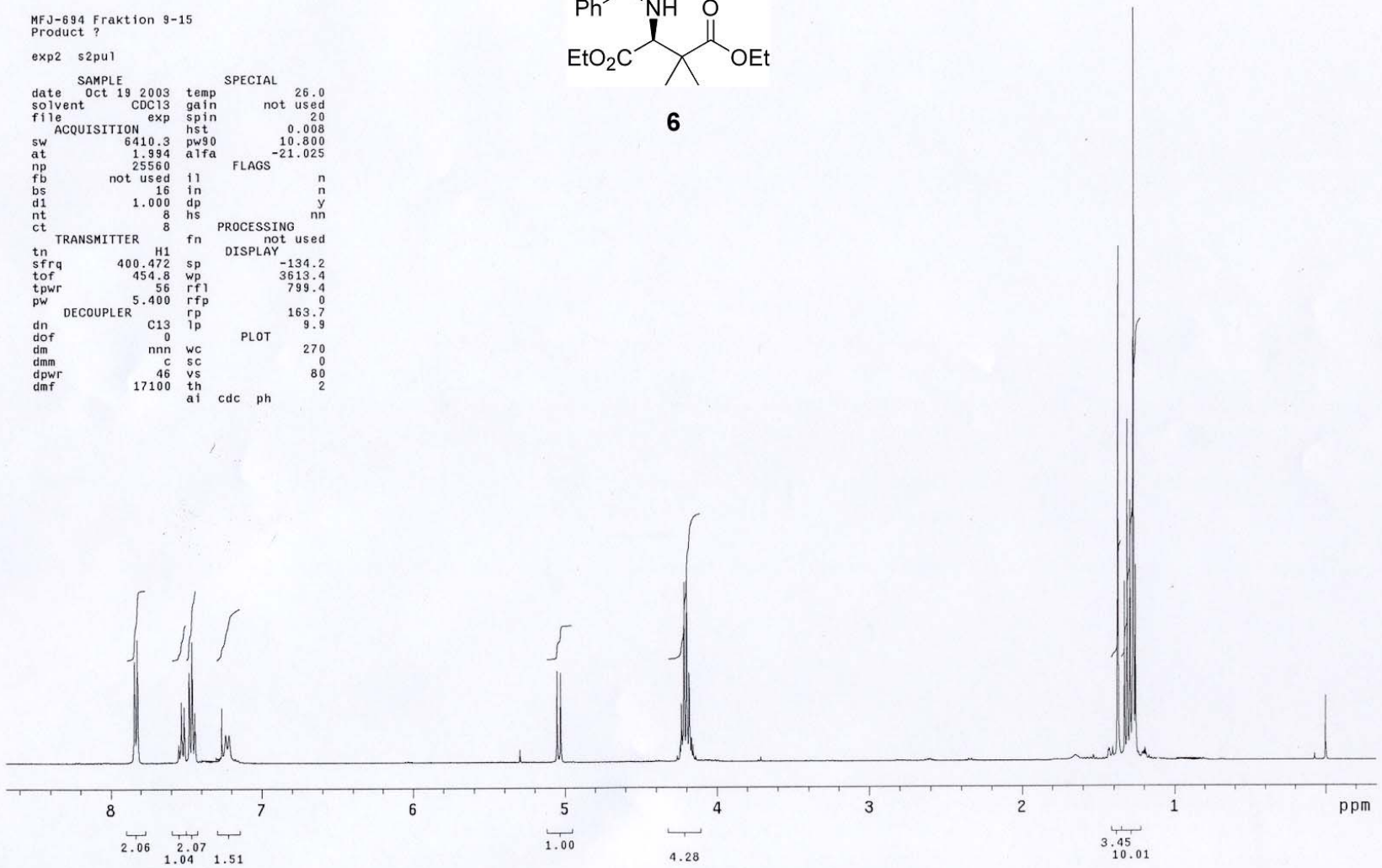


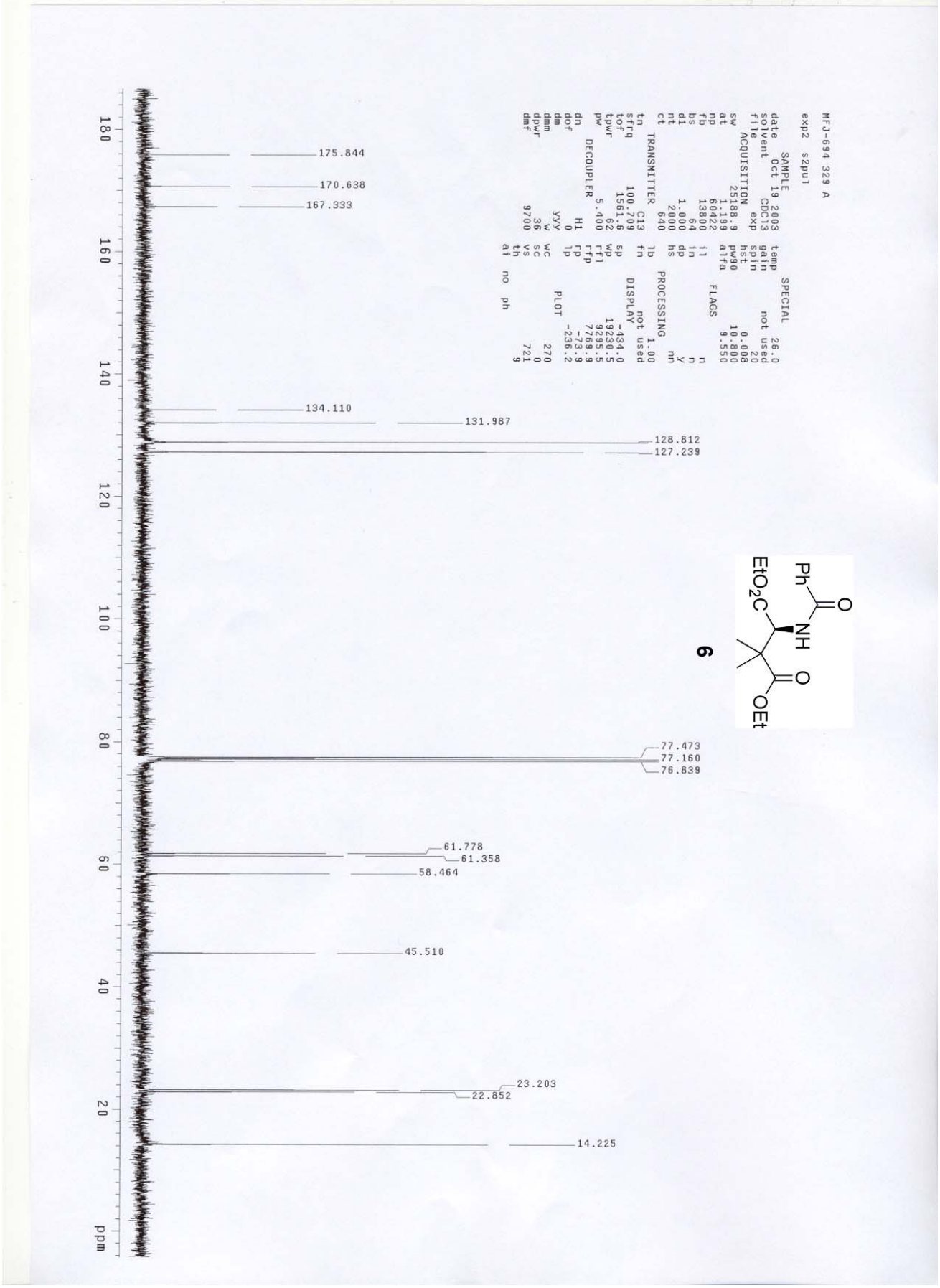
6

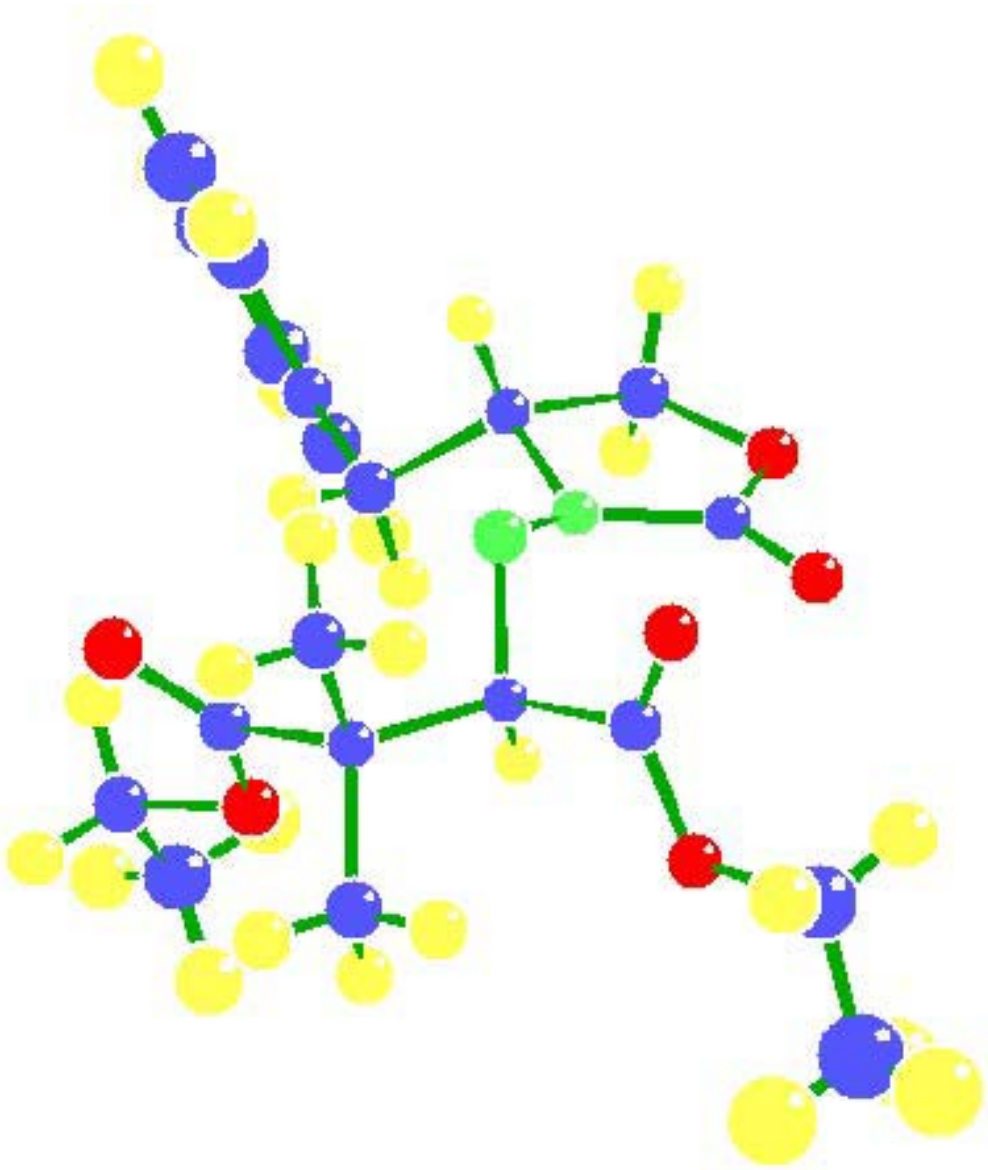
```
MFJ-694 Fraktion 9-15
Product ?

exp2  s2pul

      SAMPLE                SPECIAL
date   Oct 19 2003  temp            26.0
solvent       CDCl3  gain        not used
file            exp  spin            20
   ACQUISITION       hst           0.008
sw           6410.3  pw90         10.800
at            1.994  alfa        -21.025
np            25560          FLAGS
fb         not used  il                n
bs               16  in                n
d1            1.000  dp                y
nt                8  hs               nn
ct                8          PROCESSING
   TRANSMITTER      fn         not used
tn               H1         DISPLAY
sfrq        400.472  sp           -134.2
tof           454.8  wp           3613.4
tpwr             56  rfl           799.4
pw            5.400  rfp               0
    DECOUPLER        rp            163.7
dn               C13  lp              9.9
dof                0          PLOT
dm               nnn  wc              270
dmm                c  sc                0
dpwr              46  vs               80
dmf           17100  th                2
                     ai  cdc  ph
```




MFJ-694 329 A
exp2 s2pul
SAMPLE
date Oct 19 2003
solvent CDCl3
file exp
ACQUISITION
sw 29188.9
at 1.199
np 60422
fb 13800
bs 64
d1 1.000
nt 2000
ct 640
TRANSMITTER
tn C13
sfrq 100.709
tof 1561.6
tpwr 62
pw 5.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 36
dmf 9700
temp
gain
spin
hst
pw90
alfa
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -434.0
wp 19230.5
rfl 9295.5
rfp 7769.9
rp -73.9
lp -236.2
PLOT
wc 270
sc 0
vs 721
th 9
SPECIAL
temp 26.0
gain not used
spin 20
hst 0.008
pw90 10.800
alfa 9.550
ai no ph
Ph
O
NH
O
EtO2C
OEt
6
175.844
170.638
167.333
134.110
131.987
128.812
127.239
77.473
77.160
76.839
61.778
61.358
58.464
45.510
23.203
22.852
14.225
180
160
140
120
100
80
60
40
20
ppm



Spherical-atom plot of X-ray structure of compound **2a**

```
#===============================================================================

data_global
#===============================================================================

# 1. SUBMISSION DETAILS

_publ_contact_author           # Name and address of author for correspondence
;
;
_publ_contact_author_phone        '             '
_publ_contact_author_fax          '             '
_publ_contact_author_email        ts@chem.au.dk

_publ_requested_journal           'Journal of Organic Chemistry'
_publ_requested_coeditor_name     ?

#===============================================================================

# 3. TITLE AND AUTHOR LIST

_publ_section_title
;
 Highly Diastereoselective Mannich-Type Reactions of Chiral N-Acylhydrazones
;

# The loop structure below should contain the names and addresses of all
# authors, in the required order of publication. Repeat as necessary.

loop_
           _publ_author_name
'Mikkel Fog Jakobsen'
'Liviu Ionita'
'Troels Skrydstrup'

           _publ_author_address
;     Department of Chemistry
      Aarhus University
      Langelandsgade 140
      DK-8000 \%Arhus C
      Denmark
;

#===============================================================================

_publ_section_exptl
; The crystals available were of rather poor quality, flaky needles, likely
to be multiple crystals. The small specimens selected gave little intensity
and yielded low resolution data only. The underlying reason seems to be
that the ethyl ester groups have plenty of room, so that they show large
displacement parameters, possibly due to static as well as dynamic disorder.
Since these groups are of little chemical interest no further work seemed
warranted; the following complaints are derived from this:
poor internal agreement
few observations per parameter
unreliable (unphysical) displacement parameters for ethyl groups
low precision of the geometry, especially of these groups
foreshortening of C-C bonds in the most floppy regions, especially C6-C7.
;

_publ_section_references
;
```

Altomare,A., Cascarano,G., Giacovazzo,C., Guagliardi,A.,
Moliterni,.A,G,G., Burla,M.C., Polidori,G., Camalli,M.
& Spagna,R. (1997). SIR97. University of Bari, Italy.

Becker,P.J. & Coppens, P. (1974). Acta Cryst. A30, 129-153.

Burnett,M.N. & Johnson,C.K. (1996). ORTEP-III. Report ORNL-6895.
Oak Ridge National Laboratory, Tennessee, USA.

Busing,W.R., Martin,K.O. & Levy,H.A. (1962). ORFLS. Report
ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Hazell,A. (1995). KRYSTAL, An integrated system of
crystallographic programs. Aarhus University, Denmark.

Siemens (1995) SMART, SAINT and XPREP Area-Detector Control and
Integration Software. Siemens Analytical X-ray Instruments Inc.
Madison, Wisconsin, USA.

;

#==========

data_mfj

#==========

5. CHEMICAL DATA

_chemical_name_systematic
;
(S)-diethyl 3-((S)-4-benzyl-2-oxooxazolidin-3-ylamino)-2,2-dimethylsuccinate
;
_chemical_formula_sum 'C20 H28 N2 O6'
_chemical_formula_moiety 'C20 H28 N2 O6'
_chemical_formula_weight 392.46

#==========
6. CRYSTAL DATA

_symmetry_cell_setting orthorhombic
_symmetry_space_group_name_H-M 'P 21 21 21'
_symmetry_space_group_name_Hall 'P 2ac 2ab'

loop_
_symmetry_equiv_pos_as_xyz
'+x,+y,+z'
'1/2-x,-y,1/2+z'
'-x,1/2+y,1/2-z'
'1/2+x,1/2-y,-z'

_cell_length_a 6.5307(7)
_cell_length_b 14.195(2)
_cell_length_c 22.832(3)
_cell_angle_alpha 90.000
_cell_angle_beta 90.000
_cell_angle_gamma 90.000
_cell_volume 2116.7(4)
_cell_formula_units_Z 4
_cell_measurement_temperature 300
_cell_measurement_reflns_used 6196
_cell_measurement_theta_min 2.9

```
_cell_measurement_theta_max         27.5
_exptl_crystal_description          needle
_exptl_crystal_colour               colourless
_exptl_crystal_size_max             0.60
_exptl_crystal_size_mid             0.25
_exptl_crystal_size_min             0.20
_exptl_crystal_density_meas         'not measured'
_exptl_crystal_density_diffrn       1.231
_exptl_crystal_density_method       'not measured'
_exptl_crystal_F_000                 840
_exptl_absorpt_coefficient_mu       0.091
_exptl_absorpt_correction_type      'none'
_exptl_absorpt_process_details      'none'

#===================================

# 7. EXPERIMENTAL DATA
_diffrn_ambient_temperature         300
_diffrn_radiation_wavelength        0.71073
_diffrn_radiation_type              'Mo K\a'
_diffrn_radiation_source            'x-ray tube'
_diffrn_radiation_monochromator     'graphite'
_diffrn_measurement_device          'Siemens SMART CCD diffractometer'
_diffrn_measurement_method          '\w rotation scans with narrow frames'
_diffrn_standards_decay_%           0
_diffrn_reflns_number               18751
_diffrn_reflns_av_R_equivalents     0.117
_diffrn_reflns_limit_h_min          -8
_diffrn_reflns_limit_h_max           8
_diffrn_reflns_limit_k_min          -17
_diffrn_reflns_limit_k_max           18
_diffrn_reflns_limit_l_min          -28
_diffrn_reflns_limit_l_max           29
_diffrn_reflns_theta_min            2.9
_diffrn_reflns_theta_max            27.5
_diffrn_reflns_reduction_process    18751
_reflns_number_total                2791
_diffrn_measured_fraction_theta_max 100.0
_diffrn_measured_fraction_theta_full 100.0
_diffrn_reflns_theta_full           27.5
_reflns_number_gt                   1857
_reflns_threshold_expression        I>3\s(I)
_computing_data_collection          'SMART (Siemens, 1995)'
_computing_cell_refinement          'SAINT (Siemens, 1995)'
_computing_data_reduction           'SAINT (Siemens, 1995)'
_computing_structure_solution
;
     SIR97 (Altomare et al., 1997 ), KRYSTAL
;
_computing_structure_refinement     'modified ORFLS(1962), KRYSTAL'
_computing_molecular_graphics
;
      ORTEP-III (Burnett & Johnson,  1996), KRYSTAL
;
_computing_publication_material      KRYSTAL
_atom_type_scat_source              IntTabIV

#===================================

# 8. REFINEMENT DATA

_refine_special_details
```

```
;
;
_refine_ls_structure_factor_coef    F

_refine_ls_matrix_type              full
_refine_ls_weighting_scheme         calc
_refine_ls_weighting_details
;
w= 1/{[\s~cs~(F^2^)+B+(1+A)F^2^]^1/2^- |F|}^2^
where A = 0.04   and B = 0.1
;
_refine_ls_hydrogen_treatment       constr
_refine_ls_extinction_method
;
 Type 1 Lorentzian isotropic ( Becker and Coppens, 1974)
;
_refine_ls_extinction_coef          329(71)
_refine_ls_number_reflns            1857
_refine_ls_number_parameters        254
_refine_ls_number_restraints        0
_refine_ls_number_constraints       0
_refine_ls_R_factor_gt              0.061
_refine_ls_wR_factor_ref            0.072
_refine_ls_goodness_of_fit_ref      1.65
_refine_ls_shift/su_max             0.0010
_refine_ls_shift/su_mean            0.0002
_refine_diff_density_max            0.33(5)
_refine_diff_density_min            -0.20(5)

 #=========================================

 # 9. ATOMIC COORDINATES AND THERMAL PARAMETERS

 loop_
 _atom_site_label
 _atom_site_fract_x
 _atom_site_fract_y
 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_thermal_displace_type
   O1       0.4747(6)   0.3081(2)   0.4777(1)   0.055(2)     Uij
   O2       0.4604(5)   0.2331(2)   0.5637(1)   0.057(2)     Uij
   O3       0.6372(6)   0.0504(3)   0.6332(1)   0.067(2)     Uij
   O4       0.2957(6)   0.0486(3)   0.6197(2)   0.073(3)     Uij
   O5       0.7592(6)  -0.0727(3)   0.4520(1)   0.065(2)     Uij
   O6       0.4756(7)  -0.1546(3)   0.4318(2)   0.082(3)     Uij
   N1       0.4413(6)   0.1538(2)   0.4764(1)   0.047(2)     Uij
   N2       0.3724(6)   0.0656(2)   0.4974(1)   0.046(2)     Uij
   C1       0.4680(8)   0.2815(3)   0.4160(2)   0.054(3)     Uij
   C2       0.4100(7)   0.1771(3)   0.4149(2)   0.046(2)     Uij
   C3       0.4561(7)   0.2309(3)   0.5109(2)   0.047(2)     Uij
   C4       0.5194(7)   0.0213(3)   0.5376(2)   0.043(2)     Uij
   C5       0.4659(9)   0.0427(3)   0.6011(2)   0.053(3)     Uij
   C6       0.6083(14)  0.0668(6)   0.6952(2)   0.110(6)     Uij
   C7       0.8046(21)  0.0716(7)   0.7218(3)   0.160(9)     Uij
   C8       0.5137(8)  -0.0879(3)   0.5280(2)   0.050(3)     Uij
   C9       0.3004(10) -0.1280(4)   0.5380(2)   0.073(4)     Uij
   C10      0.6706(11) -0.1364(4)   0.5683(2)   0.072(4)     Uij
   C11      0.5752(8)  -0.1091(3)   0.4654(2)   0.054(3)     Uij
   C12      0.8372(11) -0.0977(4)   0.3942(2)   0.078(4)     Uij
   C13      1.0209(11) -0.0401(6)   0.3830(3)   0.095(5)     Uij
   C14      0.5439(9)   0.1187(3)   0.3755(2)   0.060(3)     Uij
```

```
  C15      0.5339(10)  0.1509(3)   0.3124(2)   0.060(3)     Uij
  C16      0.3626(13)  0.1343(5)   0.2787(2)   0.095(5)     Uij
  C17      0.3540(15)  0.1657(7)   0.2210(3)   0.114(6)     Uij
  C18      0.5152(19)  0.2125(6)   0.1970(3)   0.109(6)     Uij
  C19      0.6842(15)  0.2298(5)   0.2300(3)   0.107(6)     Uij
  C20      0.6931(12)  0.1993(5)   0.2882(2)   0.084(4)     Uij
  H2n      0.2466      0.0746      0.5175      0.055        Uiso
  H1a      0.5982      0.2907      0.3984      0.065        Uiso
  H1b      0.3683      0.3178      0.3959      0.065        Uiso
  H2       0.2700      0.1697      0.4045      0.056        Uiso
  H4       0.6531      0.0441      0.5294      0.052        Uiso
  H6a      0.5318      0.0165      0.7118      0.132        Uiso
  H6b      0.5371      0.1244      0.7010      0.132        Uiso
  H7a      0.7855      0.0824      0.7625      0.192        Uiso
  H7b      0.8809      0.1219      0.7052      0.192        Uiso
  H7c      0.8756      0.0140      0.7160      0.192        Uiso
  H9a      0.2969     -0.1942      0.5322      0.087        Uiso
  H9b      0.2080     -0.0990      0.5114      0.087        Uiso
  H9c      0.2593     -0.1145      0.5770      0.087        Uiso
  H10a     0.6671     -0.2027      0.5625      0.086        Uiso
  H10b     0.6384     -0.1227      0.6079      0.086        Uiso
  H10c     0.8038     -0.1136      0.5595      0.086        Uiso
  H12a     0.7362     -0.0851      0.3653      0.093        Uiso
  H12b     0.8720     -0.1627      0.3933      0.093        Uiso
  H13a     1.0717     -0.0564      0.3453      0.114        Uiso
  H13b     1.1219     -0.0527      0.4119      0.114        Uiso
  H13c     0.9861      0.0248      0.3839      0.114        Uiso
  H14a     0.5003      0.0549      0.3775      0.072        Uiso
  H14b     0.6814      0.1233      0.3887      0.072        Uiso
  H16      0.2496      0.1013      0.2950      0.114        Uiso
  H17      0.2347      0.1545      0.1982      0.137        Uiso
  H18      0.5097      0.2330      0.1574      0.131        Uiso
  H19      0.7970      0.2626      0.2134      0.128        Uiso
  H20      0.8110      0.2125      0.3110      0.101        Uiso

loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_12
_atom_site_aniso_U_13
_atom_site_aniso_U_23
  O1    0.069(2)   0.044(2)   0.053(2)  -0.005(2)   0.002(2)   0.001(1)
  O2    0.063(2)   0.065(2)   0.043(2)  -0.009(2)   0.000(2)  -0.006(1)
  O3    0.089(3)   0.080(2)   0.032(2)  -0.005(2)  -0.007(2)  -0.002(2)
  O4    0.076(3)   0.086(3)   0.056(2)   0.002(2)   0.022(2)   0.005(2)
  O5    0.079(3)   0.077(2)   0.039(2)  -0.003(2)   0.005(2)  -0.007(2)
  O6    0.100(3)   0.083(2)   0.064(2)  -0.019(3)   0.000(2)  -0.027(2)
  N1    0.062(2)   0.048(2)   0.032(2)  -0.005(2)   0.001(2)   0.002(2)
  N2    0.054(2)   0.044(2)   0.039(2)  -0.003(2)   0.001(2)   0.005(2)
  C1    0.063(3)   0.058(3)   0.041(2)  -0.002(3)  -0.001(2)   0.005(2)
  C2    0.057(3)   0.046(2)   0.037(2)   0.001(2)   0.000(2)   0.004(2)
  C3    0.048(3)   0.047(2)   0.046(3)  -0.006(2)   0.002(2)  -0.003(2)
  C4    0.054(3)   0.042(2)   0.034(2)   0.000(2)  -0.002(2)   0.003(2)
  C5    0.073(4)   0.047(2)   0.040(2)  -0.001(3)   0.002(3)   0.004(2)
  C6    0.149(7)   0.149(6)   0.032(3)  -0.001(6)  -0.009(4)  -0.013(3)
  C7    0.243(12)  0.182(9)   0.054(4)  -0.049(10) -0.038(6)   0.001(5)
  C8    0.073(3)   0.039(2)   0.038(2)   0.001(2)  -0.001(2)   0.001(2)
  C9    0.093(4)   0.058(3)   0.068(3)  -0.023(3)   0.009(3)   0.009(3)
  C10   0.105(5)   0.057(3)   0.054(3)   0.020(3)  -0.008(3)   0.005(2)
  C11   0.068(4)   0.041(2)   0.053(3)   0.004(2)   0.001(3)   0.001(2)
```

```
  C12   0.104(5)   0.077(4)   0.052(3)   0.006(4)   0.020(3)  -0.005(3)
  C13   0.081(4)   0.132(6)   0.072(4)   0.003(5)   0.008(4)   0.002(4)
  C14   0.079(4)   0.054(3)   0.046(2)   0.012(3)   0.007(3)   0.005(2)
  C15   0.088(4)   0.049(3)   0.042(2)   0.010(3)   0.011(3)   0.000(2)
  C16   0.123(6)   0.113(5)   0.048(3)  -0.024(5)  -0.001(4)   0.002(3)
  C17   0.144(7)   0.151(7)   0.047(3)  -0.012(7)  -0.015(4)   0.003(4)
  C18   0.180(9)   0.103(5)   0.044(3)   0.026(6)   0.022(5)   0.008(3)
  C19   0.143(7)   0.104(5)   0.073(4)  -0.003(6)   0.043(5)   0.015(4)
  C20   0.103(5)   0.091(5)   0.058(3)  -0.006(4)   0.018(3)   0.003(3)

#==================================

# 10. MOLECULAR GEOMETRY

loop_
    _geom_bond_atom_site_label_1
    _geom_bond_atom_site_label_2
    _geom_bond_distance
 O1      C3        1.339(5)
 O1      C1        1.458(5)
 O2      C3        1.204(5)
 O3      C5        1.342(6)
 O3      C6        1.447(6)
 O4      C5        1.192(6)
 O5      C11       1.343(6)
 O5      C12       1.458(6)
 O6      C11       1.195(6)
 N1      C3        1.352(6)
 N1      N2        1.415(5)
 N1      C2        1.457(5)
 N2      C4        1.469(5)
 C1      C2        1.530(6)
 C2      C14       1.504(7)
 C4      C5        1.523(6)
 C4      C8        1.566(6)
 C6      C7        1.421(14)
 C8      C11       1.515(7)
 C8      C9        1.523(8)
 C8      C10       1.539(7)
 C12     C13       1.474(10)
 C14     C15       1.514(6)
 C15     C20       1.363(8)
 C15     C16       1.378(9)
 C16     C17       1.392(9)
 C17     C18       1.360(12)
 C18     C19       1.358(12)
 C19     C20       1.399(9)
 N2      H2n       0.95
 C1      H1a       0.95
 C1      H1b       0.95
 C2      H2        0.95
 C4      H4        0.95
 C6      H6a       0.95
 C6      H6b       0.95
 C7      H7a       0.95
 C7      H7c       0.95
 C7      H7b       0.95
 C9      H9c       0.95
 C9      H9a       0.95
 C9      H9b       0.95
 C10     H10c      0.95
 C10     H10a      0.95
```

```
 C10     H10b      0.95
 C12     H12b      0.95
 C12     H12a      0.95
 C13     H13b      0.95
 C13     H13c      0.95
 C13     H13a      0.95
 C14     H14b      0.95
 C14     H14a      0.95
 C16     H16       0.95
 C17     H17       0.95
 C18     H18       0.95
 C19     H19       0.95
 C20     H20       0.95

loop_
    _geom_angle_atom_site_label_1
    _geom_angle_atom_site_label_2
    _geom_angle_atom_site_label_3
    _geom_angle
 C1      O1      C3         109.4(3)
 C5      O3      C6         116.0(5)
 C11     O5      C12        115.1(4)
 N2      N1      C3         122.7(3)
 C2      N1      C3         112.9(3)
 N2      N1      C2         118.9(3)
 N1      N2      C4         112.5(3)
 O1      C1      C2         105.9(3)
 N1      C2      C14        111.7(4)
 N1      C2      C1          99.7(3)
 C1      C2      C14        113.6(4)
 O1      C3      O2         122.9(4)
 O2      C3      N1         127.3(4)
 O1      C3      N1         109.7(3)
 N2      C4      C5         111.1(4)
 N2      C4      C8         108.7(3)
 C5      C4      C8         108.9(3)
 O3      C5      O4         125.3(4)
 O4      C5      C4         124.5(5)
 O3      C5      C4         110.2(4)
 O3      C6      C7         108.0(7)
 C9      C8      C11        108.0(4)
 C10     C8      C11        107.3(4)
 C4      C8      C11        108.8(3)
 C9      C8      C10        110.6(4)
 C4      C8      C9         111.8(4)
 C4      C8      C10        110.1(4)
 O5      C11     O6         123.3(5)
 O6      C11     C8         124.7(5)
 O5      C11     C8         112.0(4)
 O5      C12     C13        107.9(5)
 C2      C14     C15        112.2(4)
 C16     C15     C20        118.6(5)
 C14     C15     C20        120.4(6)
 C14     C15     C16        121.0(5)
 C15     C16     C17        120.4(7)
 C16     C17     C18        120.4(8)
 C17     C18     C19        119.6(6)
 C18     C19     C20        120.3(7)
 C15     C20     C19        120.6(7)
 N1      N2      H2n        108.7
 C4      N2      H2n        108.7
 H1a     C1      H1b        109.5
```

```
  O1      C1      H1a        110.3
  C2      C1      H1a        110.4
  O1      C1      H1b        110.3
  C2      C1      H1b        110.4
  N1      C2      H2         110.5
  C14     C2      H2         110.5
  C1      C2      H2         110.5
  N2      C4      H4         109.4
  C5      C4      H4         109.4
  C8      C4      H4         109.4
  H6a     C6      H6b        109.5
  C7      C6      H6a        109.9
  O3      C6      H6a        109.8
  C7      C6      H6b        109.9
  O3      C6      H6b        109.8
  H7a     C7      H7c        109.9
  H7a     C7      H7b        109.9
  C6      C7      H7a        107.9
  H7b     C7      H7c        109.5
  C6      C7      H7c        109.8
  C6      C7      H7b        109.8
  H9a     C9      H9c        108.9
  H9b     C9      H9c        109.5
  C8      C9      H9c        108.9
  H9a     C9      H9b        108.9
  C8      C9      H9a        111.8
  C8      C9      H9b        108.9
  H10a    C10     H10c       109.3
  H10b    C10     H10c       109.5
  C8      C10     H10c       109.3
  H10a    C10     H10b       109.3
  C8      C10     H10a       110.1
  C8      C10     H10b       109.3
  H12a    C12     H12b       109.5
  O5      C12     H12b       109.9
  C13     C12     H12b       109.9
  O5      C12     H12a       109.9
  C13     C12     H12a       109.9
  H13b    C13     H13c       109.5
  H13a    C13     H13b       109.9
  C12     C13     H13b       109.9
  H13a    C13     H13c       109.9
  C12     C13     H13c       109.9
  C12     C13     H13a       107.9
  H14a    C14     H14b       109.5
  C2      C14     H14b       108.8
  C15     C14     H14b       108.8
  C2      C14     H14a       108.8
  C15     C14     H14a       108.8
  C15     C16     H16        119.8
  C17     C16     H16        119.8
  C18     C17     H17        119.8
  C16     C17     H17        119.8
  C19     C18     H18        120.2
  C17     C18     H18        120.2
  C18     C19     H19        119.9
  C20     C19     H19        119.8
  C15     C20     H20        119.7
  C19     C20     H20        119.7

#===END
```