SUPPORTING INFORMATION

General experimental methods

^{1}H and ^{13}C NMR were recorded at 300 (or 500) and 75 (or 125) MHz respectively. MS spectra were recorded on a chromatograph equipped with a MS capillary column (30 m x 0.25 mm i.d. x 0.25 μm film thickness; injection temperature: 250°C, column temperature program: 100°C for 3 min, then 10°C min^{-1} until 250°C) and a mass selective detector (mass range: 15-800 a.m.u.; scan rate: 1.9 scans s^{-1}; EM voltage: 1435). Commercially available reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Column chromatography was carried out using 60-240 mesh silica gel at atmospheric pressure.

General procedure for the synthesis of epoxides 5(a-d), 9 and 10.

NaOH (7.1 mL of 50% aqueous solution) was added dropwise at 0°C to a stirred solution of benzyldimethylsulfonium chloride (1.3 equiv., 10.5 mmol), the appropriate aldehyde (1 equiv.) and tetrabutylammonium hydrogensulfate (0.05 equiv.) in CH_2Cl_2 (15 mL). After 5h the reaction is quenched and worked up as usual.[13]

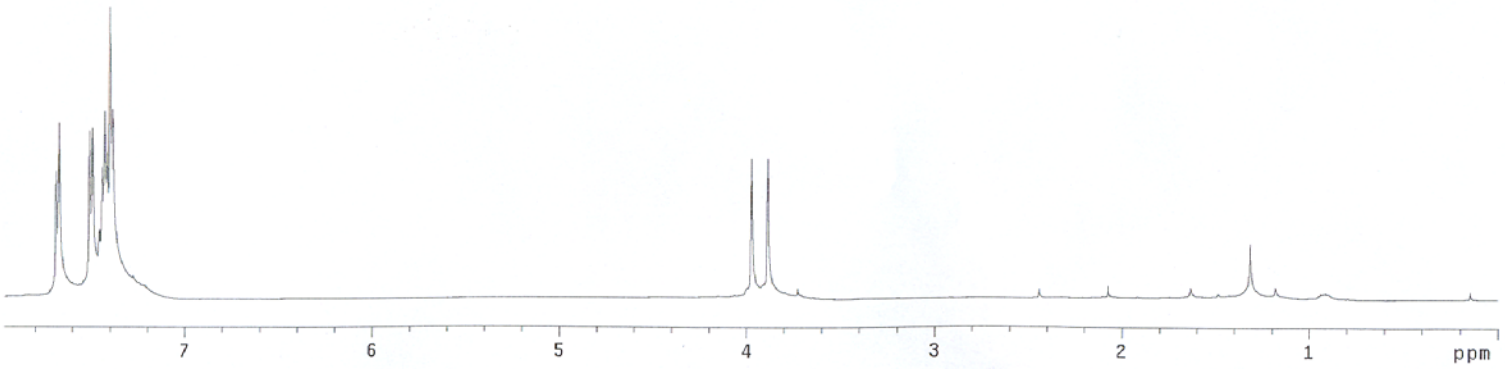
General procedure for the LiBr opening of (*E*)-2,3-diaryloxiranes. To a solution of the epoxide (0.50 mmol) in 10 mL of acetonitrile, kept at the desired temperature, were added solid LiBr (2-4 equiv.) and Amberlyst 15 (220-440 mg/mmol) consecutively in single portions. The mixture was stirred at the desired temperature and monitored by TLC until complete. The mixture was filtered and the filtrate was evaporated under vacuum. The residue was dissolved in Et_2O and the resulting organic layer was dried with Na_2SO_4. The solvent was evaporated under vacuum and the crude product was analyzed by NMR.

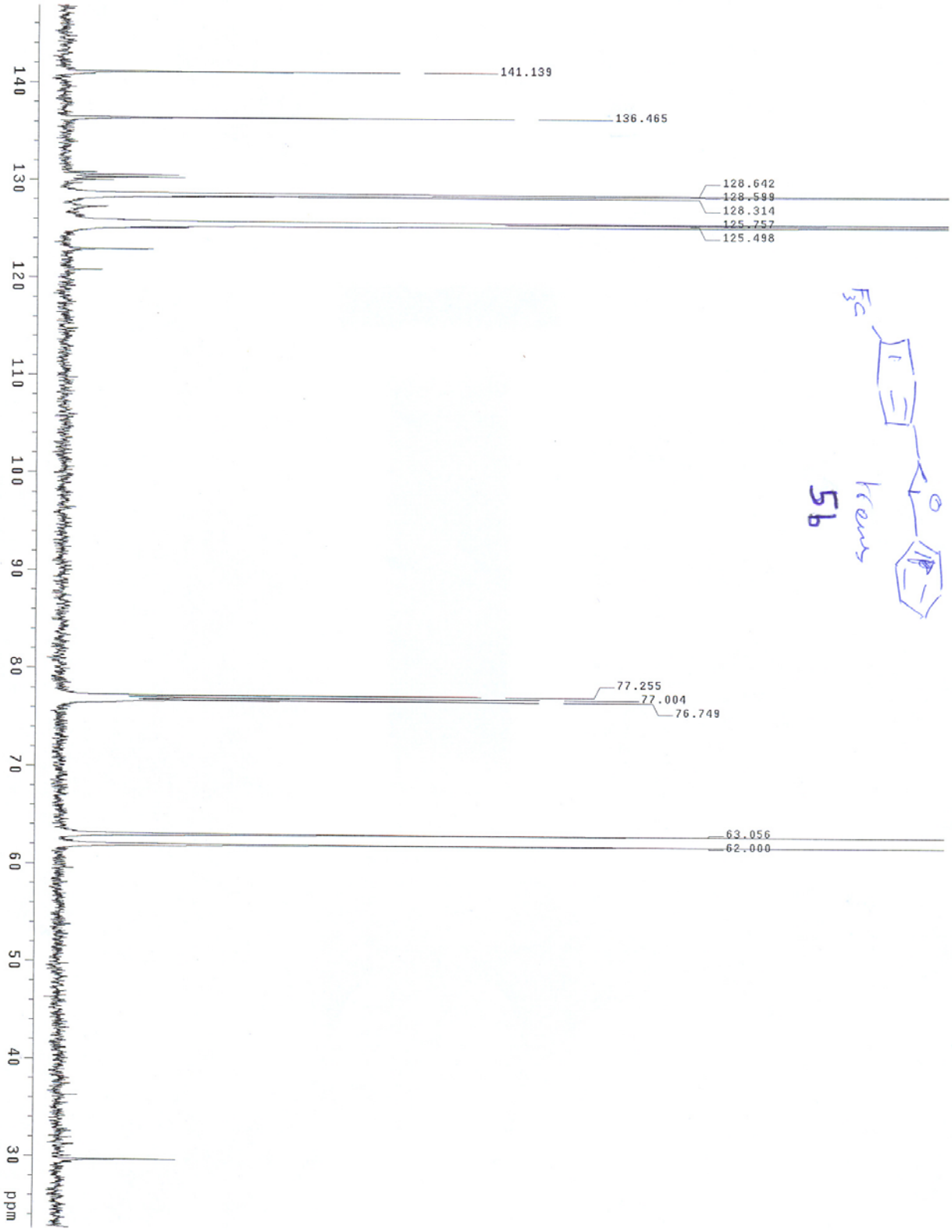
General procedure for the alkali ring closure of bromohydrins mixtures. To a solution of the bromohydrins (0.10 mmol) in 2 mL of anhydrous THF, kept at 0°C, was added NaH (1.5 equiv.) in a single portion. The mixture was stirred and monitored by TLC until complete. The mixture was quenched by cold water and the organic layer extracted by Et_2O, dried with Na_2SO_4. The solvent was evaporated under vacuum and the crude product was analyzed by ^{1}H NMR.

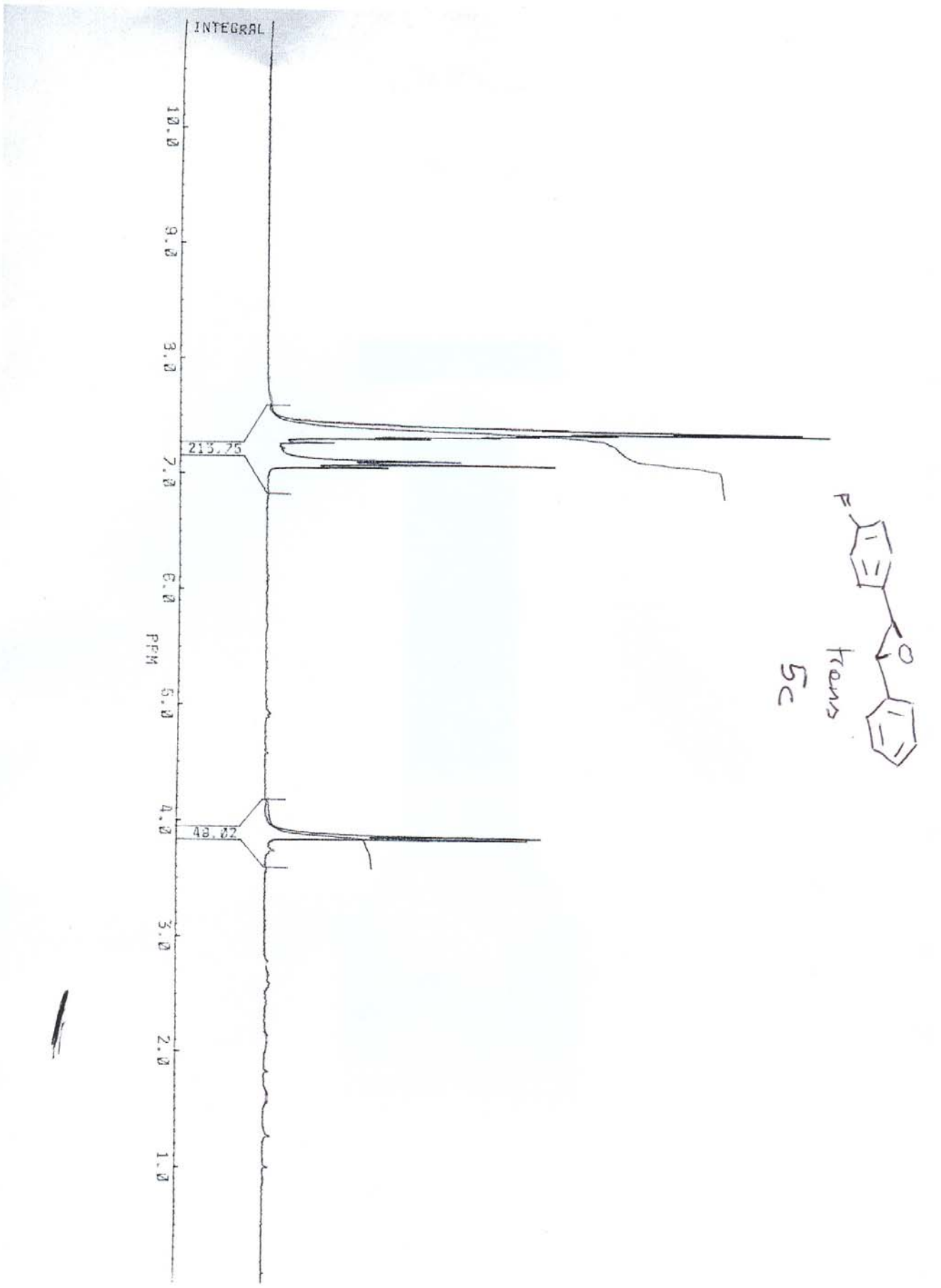
5b

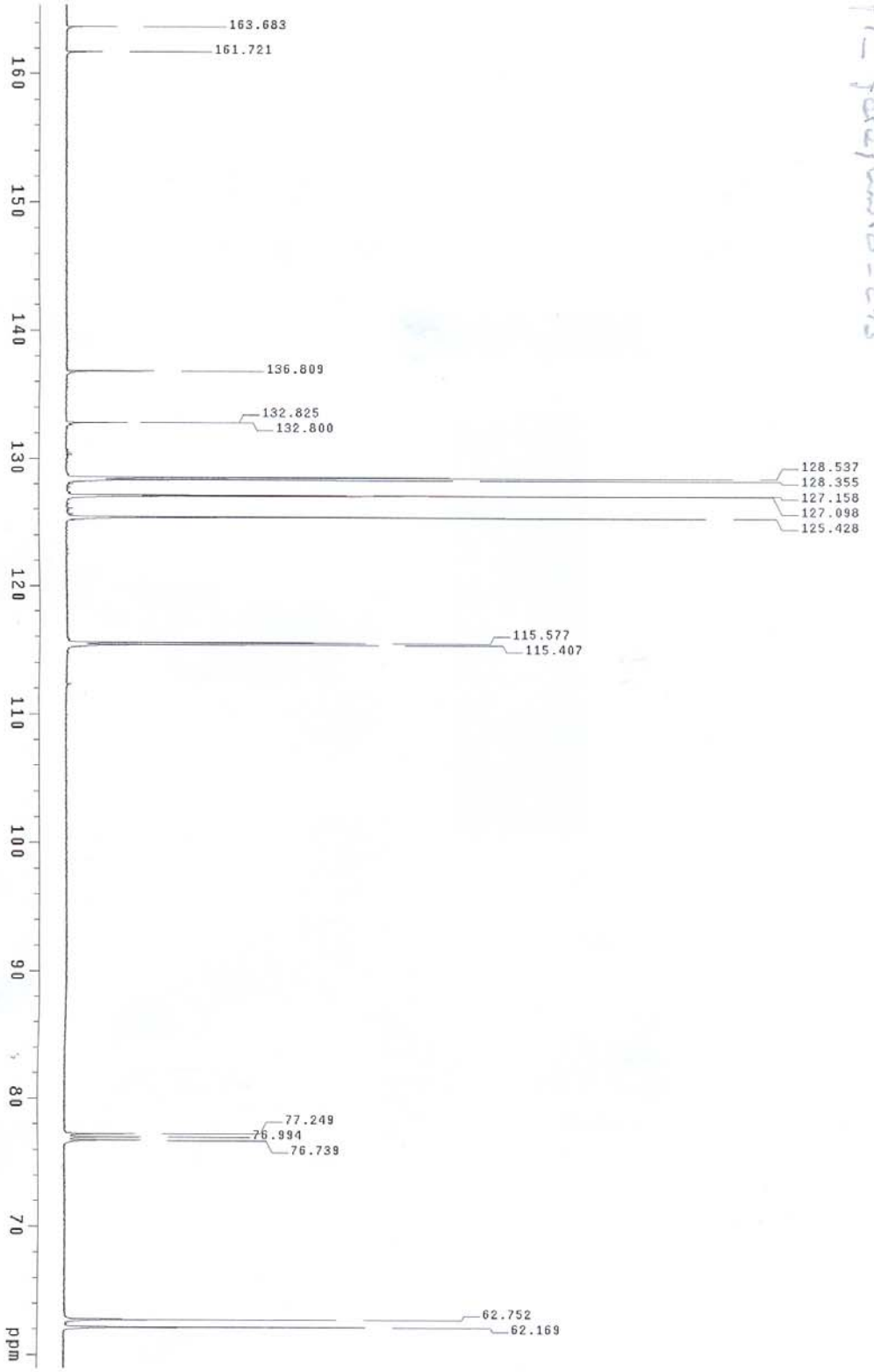
Ph_ para CF_3 – ^1H 500 MH_z

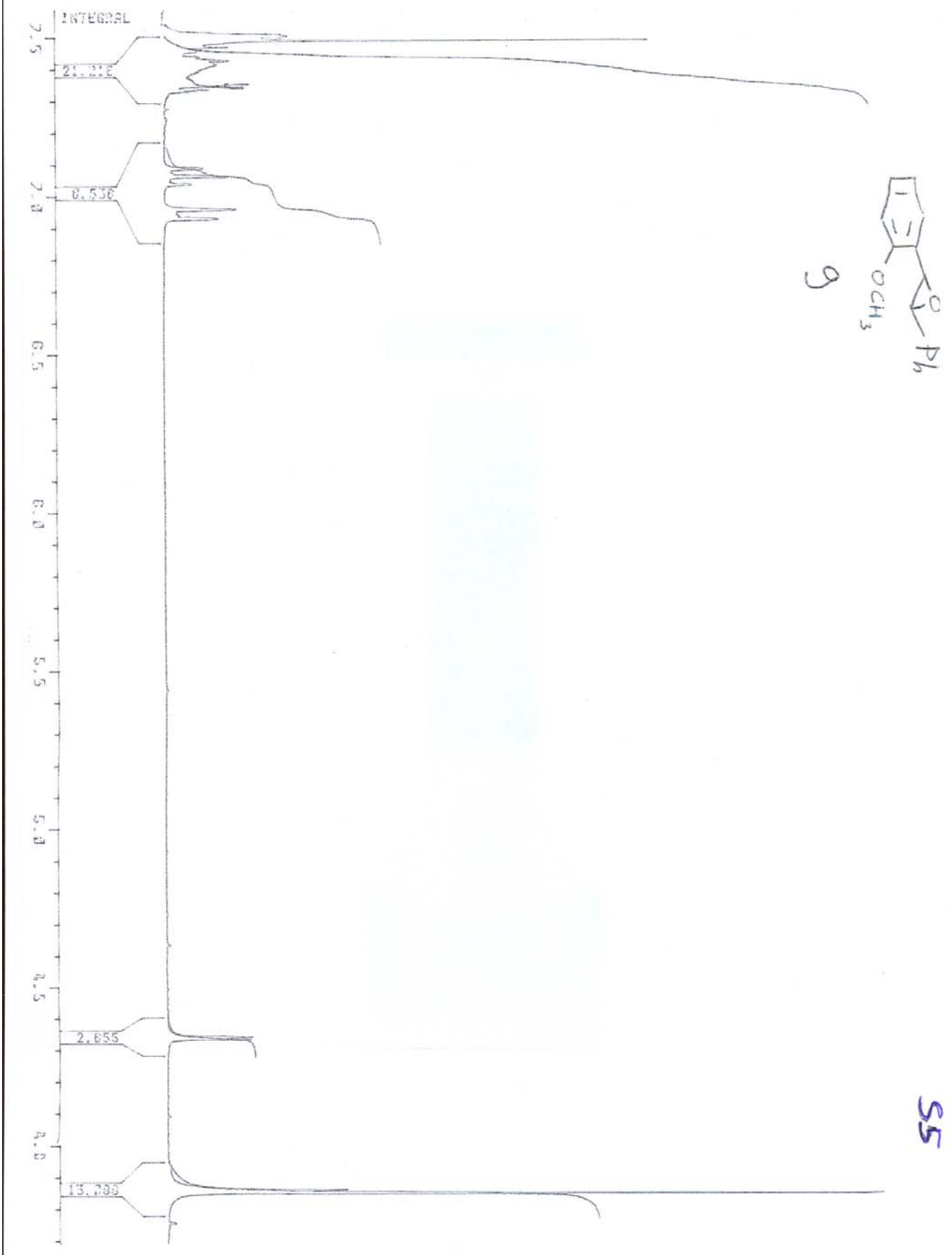
S1

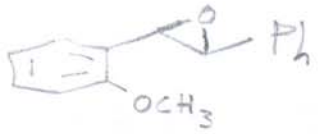



141.139
136.465
128.642
128.599
128.314
125.757
125.498
77.255
77.004
76.749
63.056
62.000
140
130
120
110
100
90
80
70
60
50
40
30
ppm
F3C
O
trans
5b


INTEGRAL
213.75
48.02
10.0
9.0
3.0
7.0
6.0
PPM
5.0
4.0
3.0
2.0
1.0
F
O
trans
5c


163.683
161.721
136.809
132.825
132.800
128.537
128.355
127.158
127.098
125.428
115.577
115.407
77.249
76.994
76.739
62.752
62.169
160
150
140
130
120
110
100
90
80
70
ppm

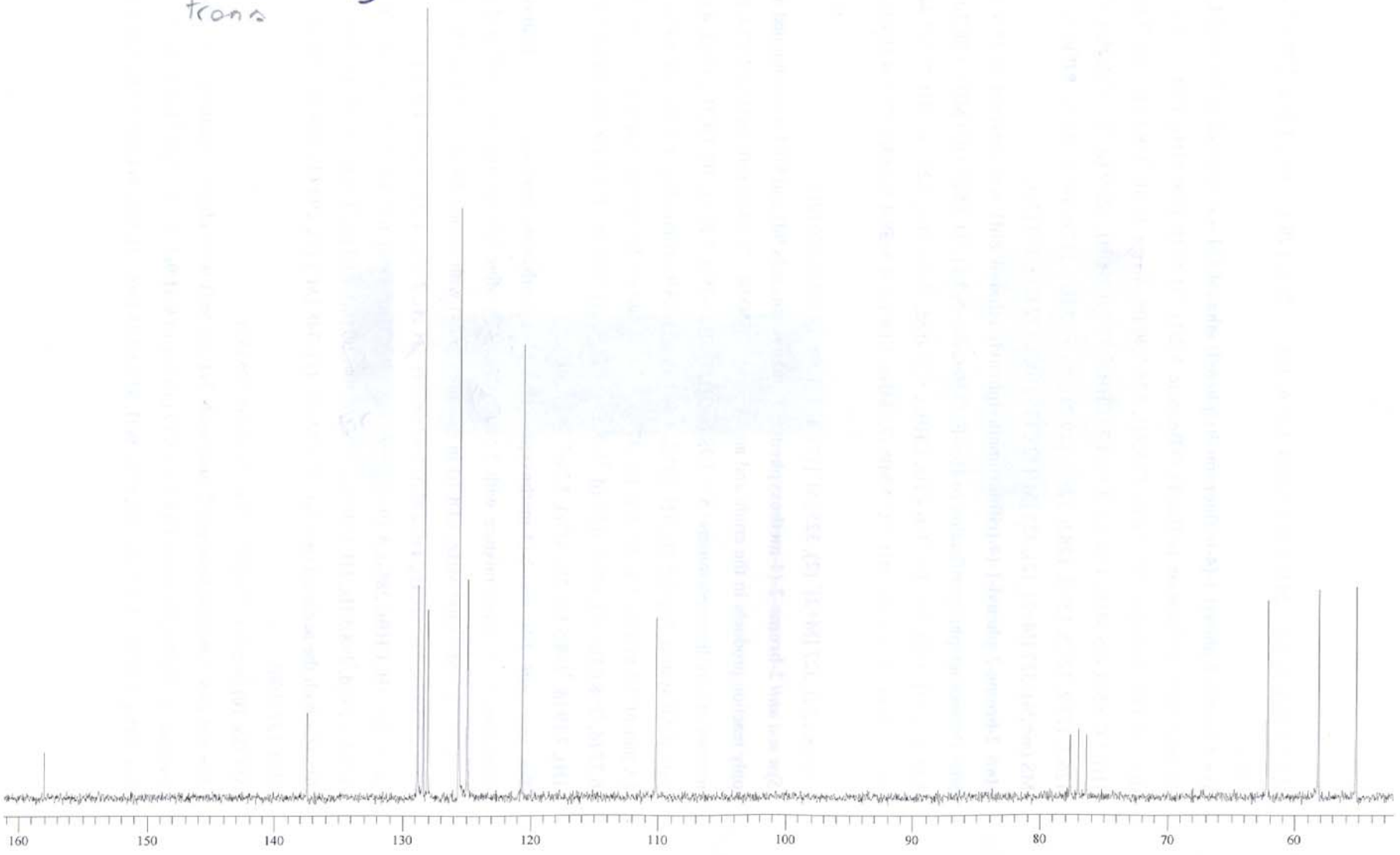

INTEGRAL
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
8.536
2.855
15.709
OCH3
Ph
9
S5

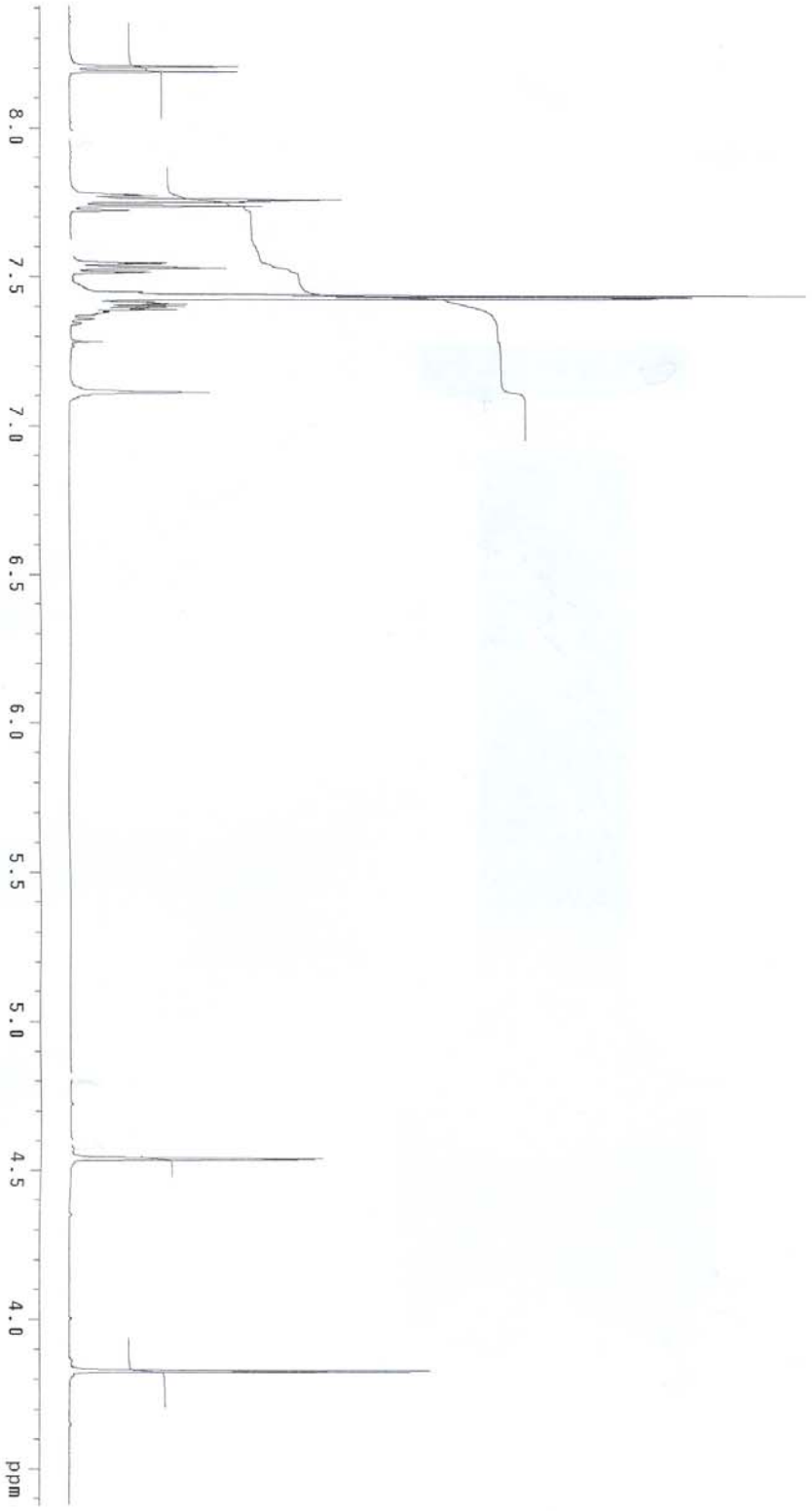


trans

9

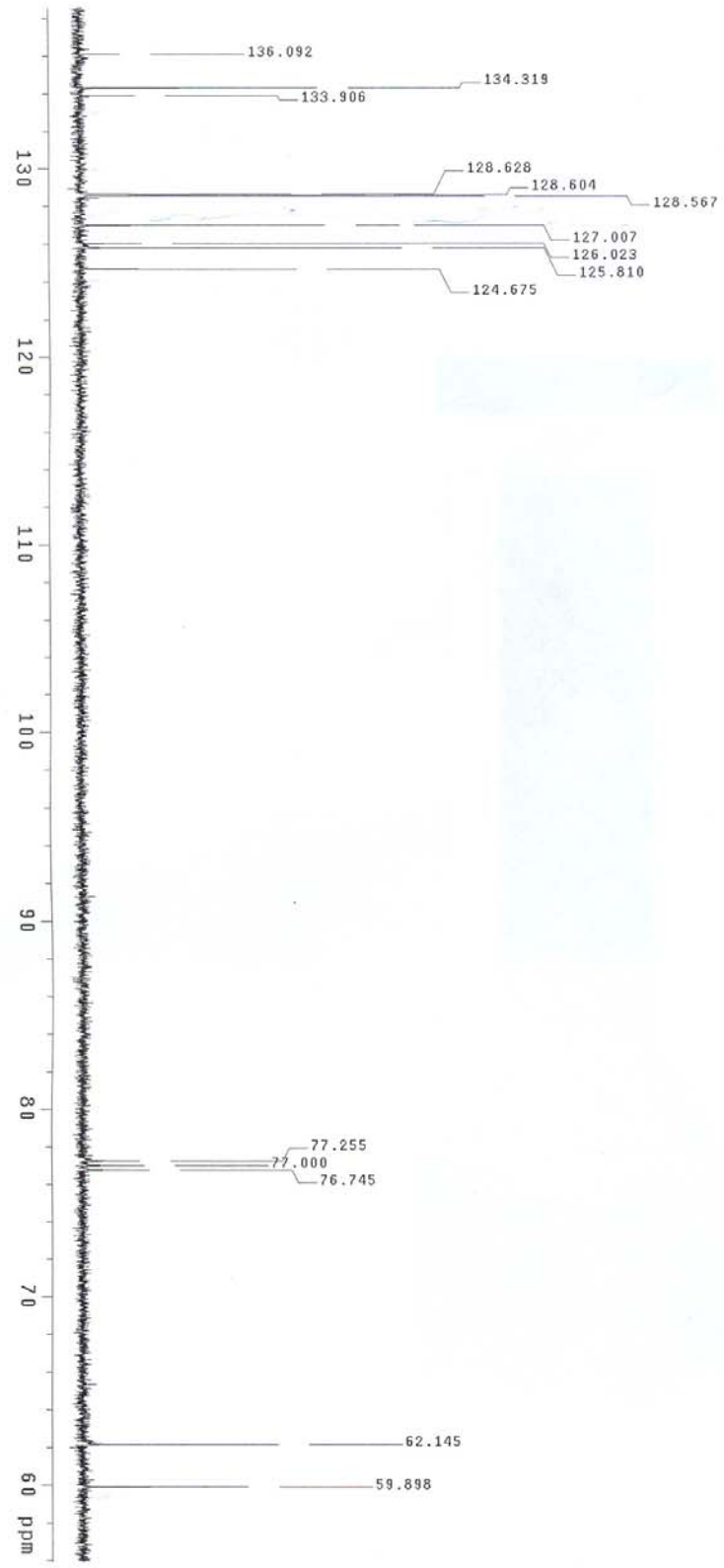
S6

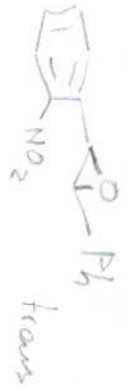




1e

S7

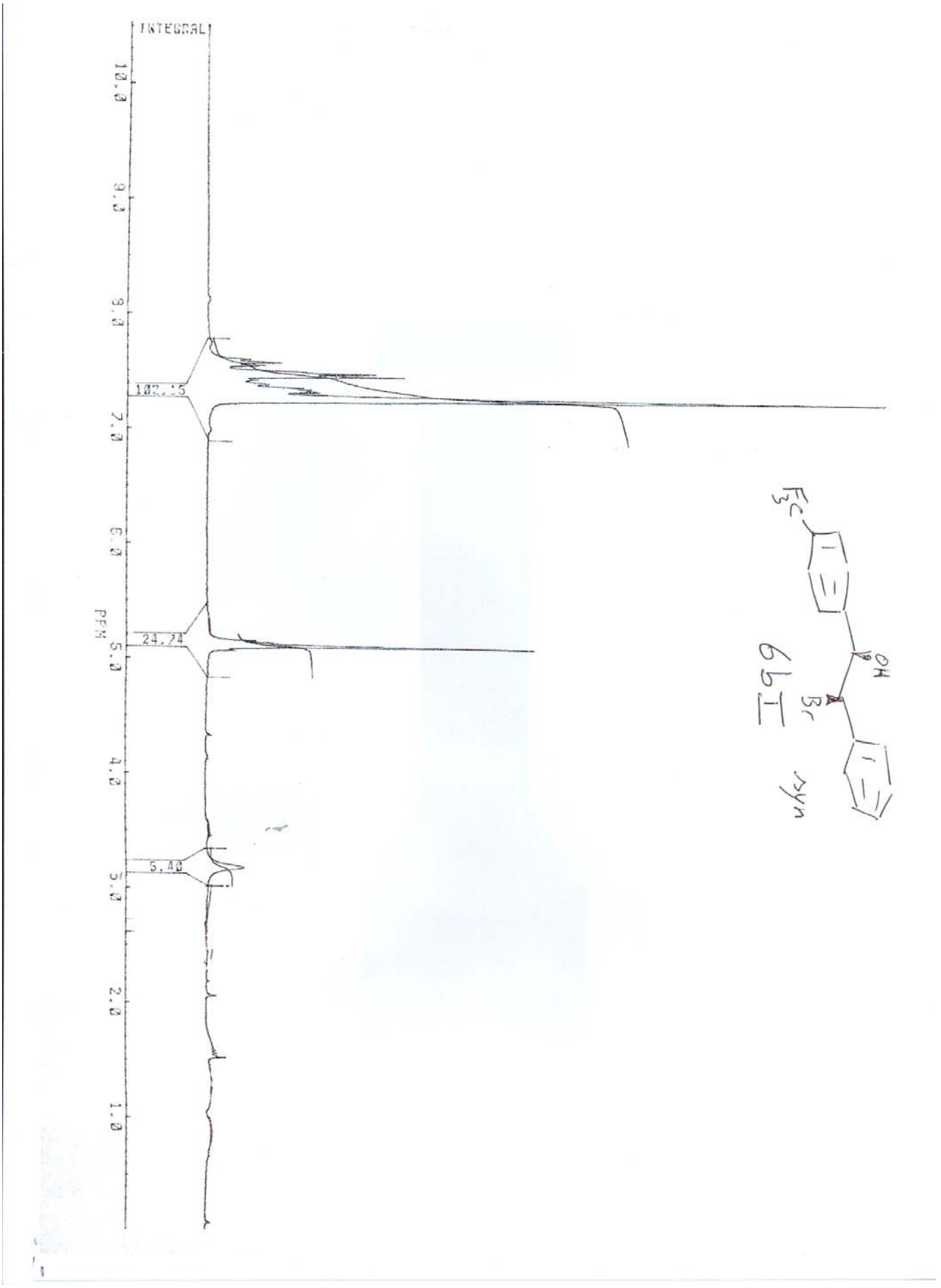

136.092
134.319
133.906
128.628
128.604
128.567
127.007
126.023
125.810
124.675
77.255
77.000
76.745
62.145
59.898
130
120
110
100
90
80
70
60 ppm

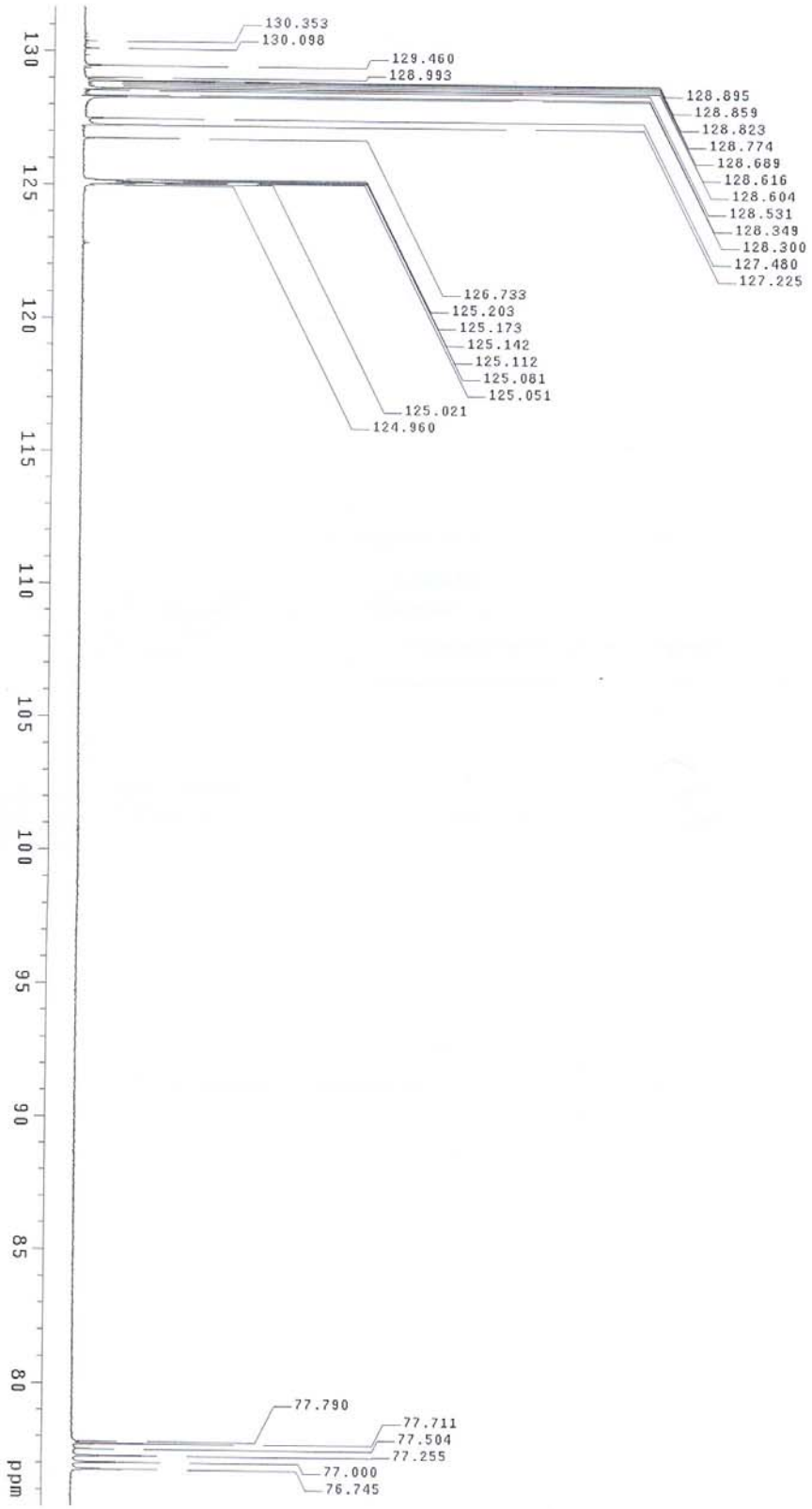

NO2
O
Ph

10

trans

S8


INTEGRAL
10.0
9.0
8.0
102.15
7.0
6.0
PPM
24.24
5.0
4.0
5.40
3.0
2.0
1.0
FC
3
OH
Br
I
6b
syn



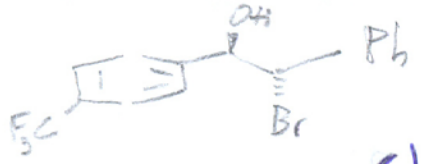
PCF3 Br OH meno polare
40 mg P. 68
syn

6bI

syn

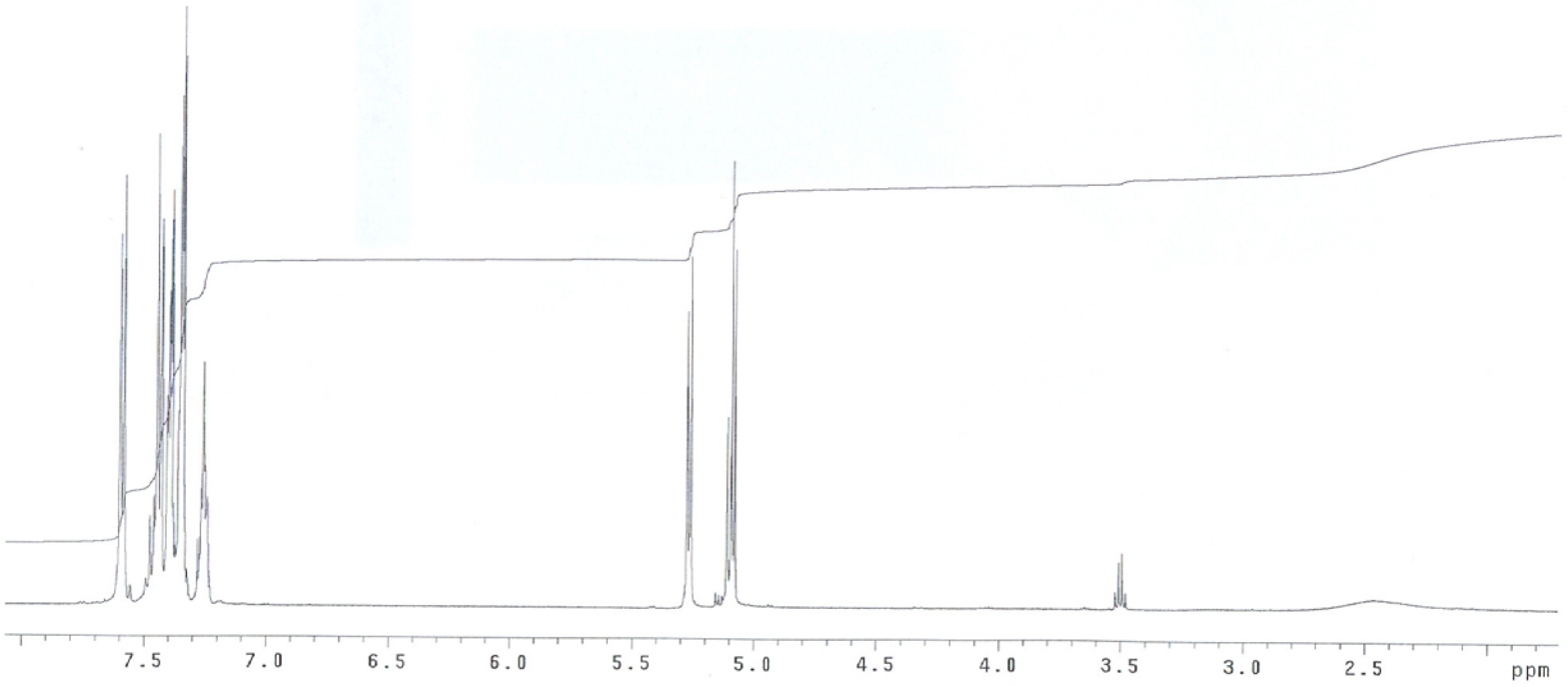
S10

PCF_3 BuOH
più polare



anti

6bII

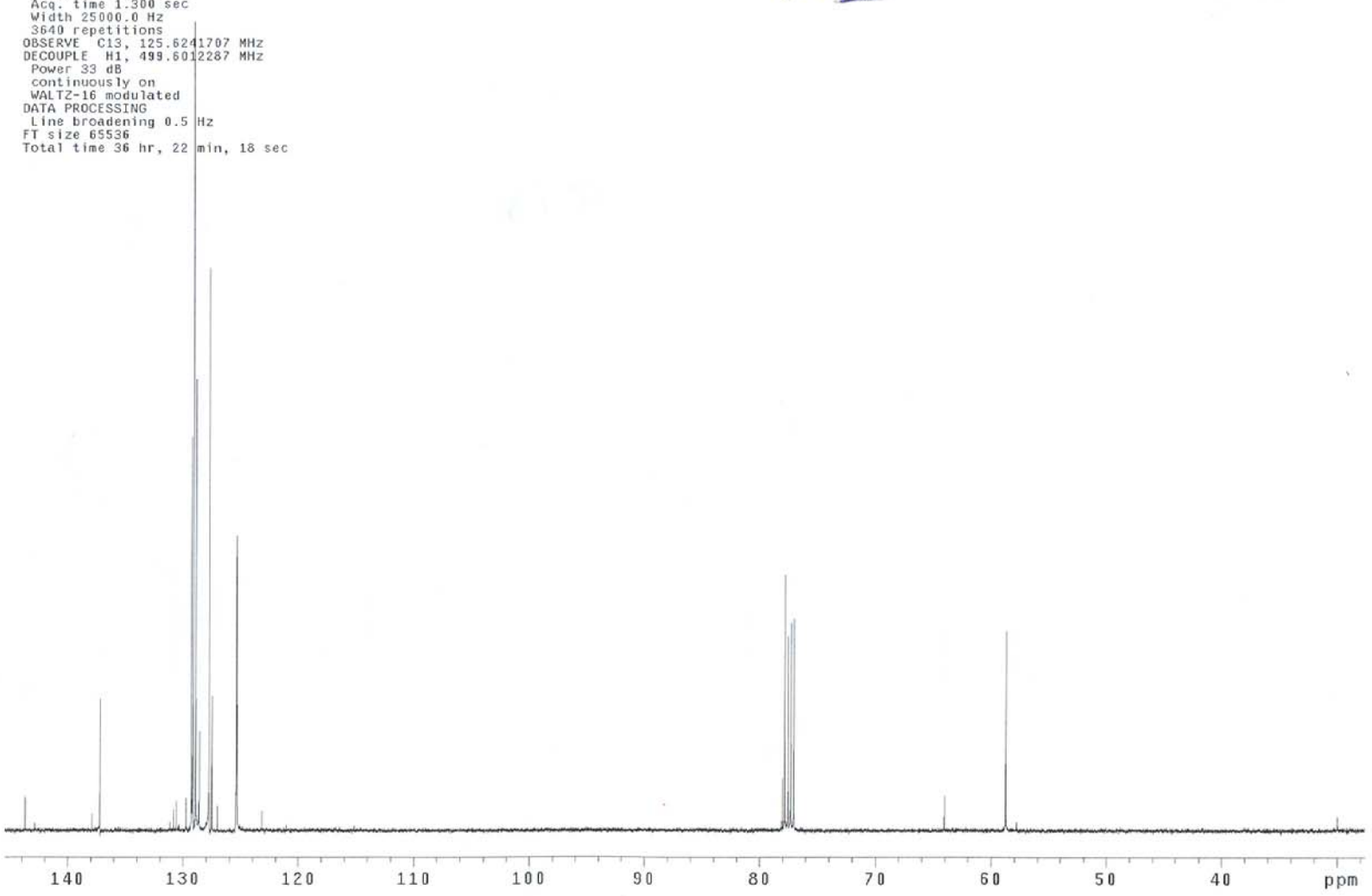


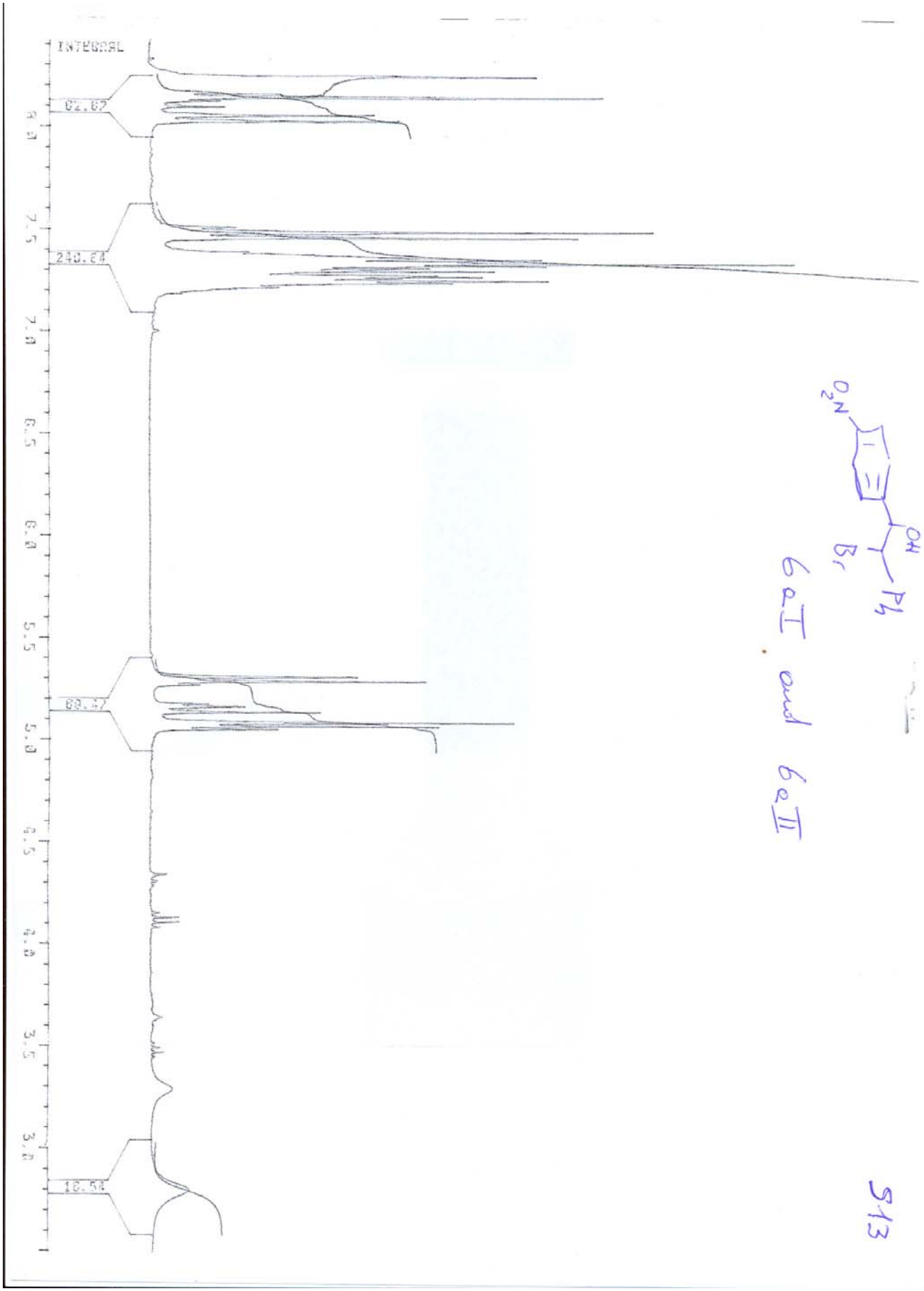
paolo

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "nmr500"

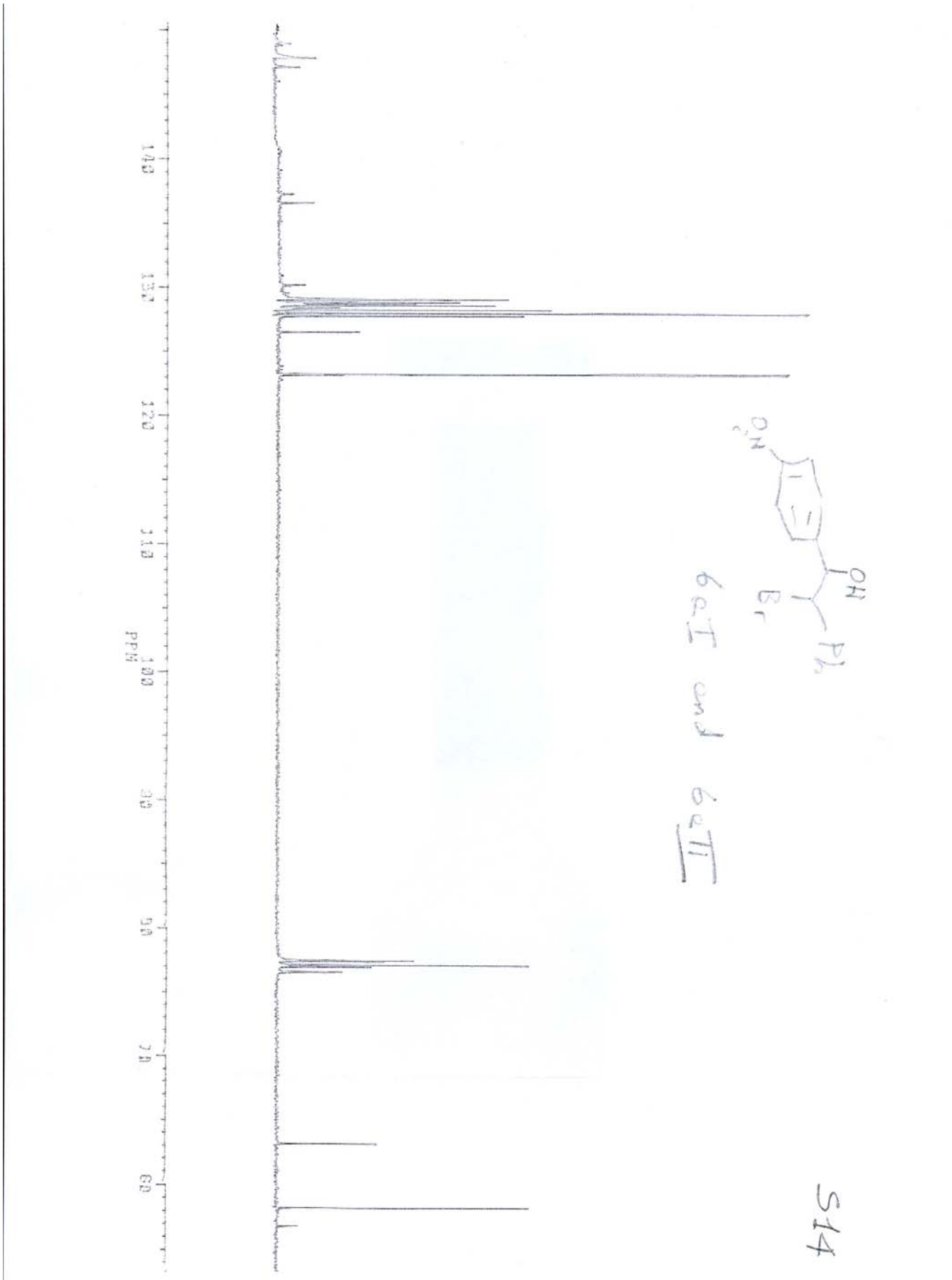
Pulse 71.1 degrees
Acq. time 1.300 sec
Width 25000.0 Hz
3640 repetitions
OBSERVE C13, 125.6241707 MHz
DECOUPLE H1, 499.6012287 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 36 hr, 22 min, 18 sec





6aI and 6aII

S13



S14

p13

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "nmr500"

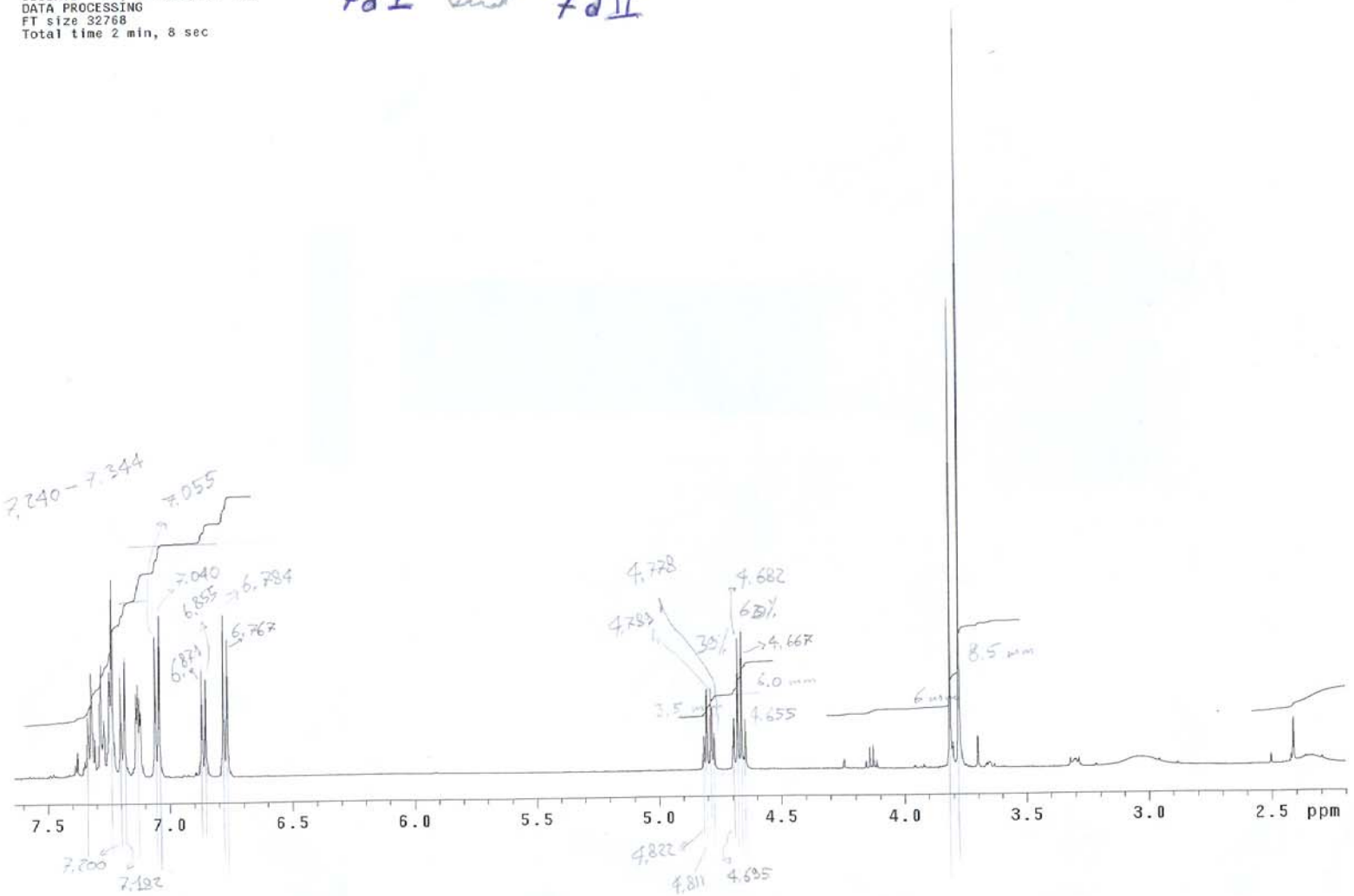
Pulse 65.5 degrees
Acq. time 2.000 sec
Width 8000.0 Hz
56 repetitions
OBSERVE H1, 499.5987306 MHz
DATA PROCESSING
FT size 32768
Total time 2 min, 8 sec

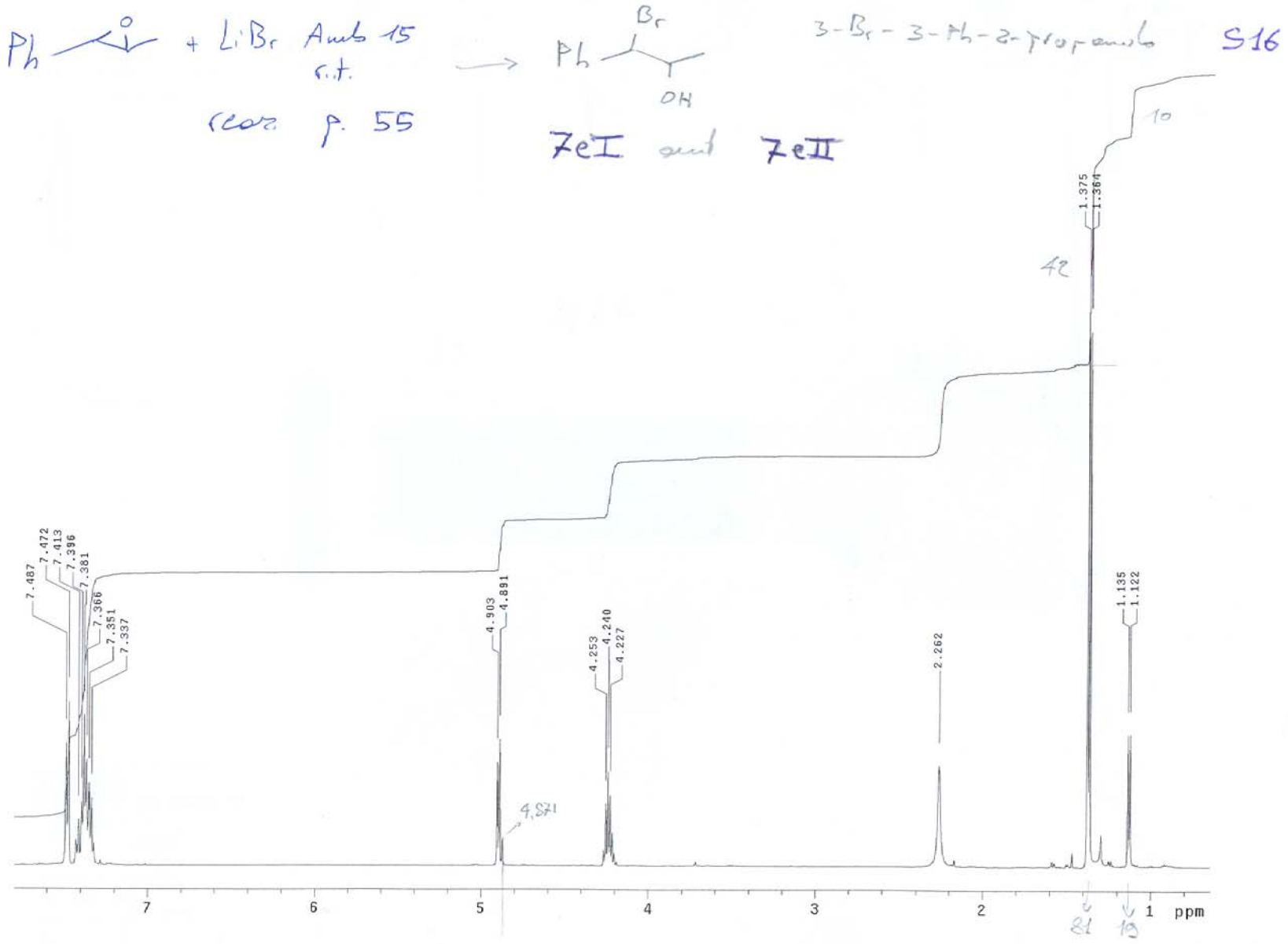
gcerco

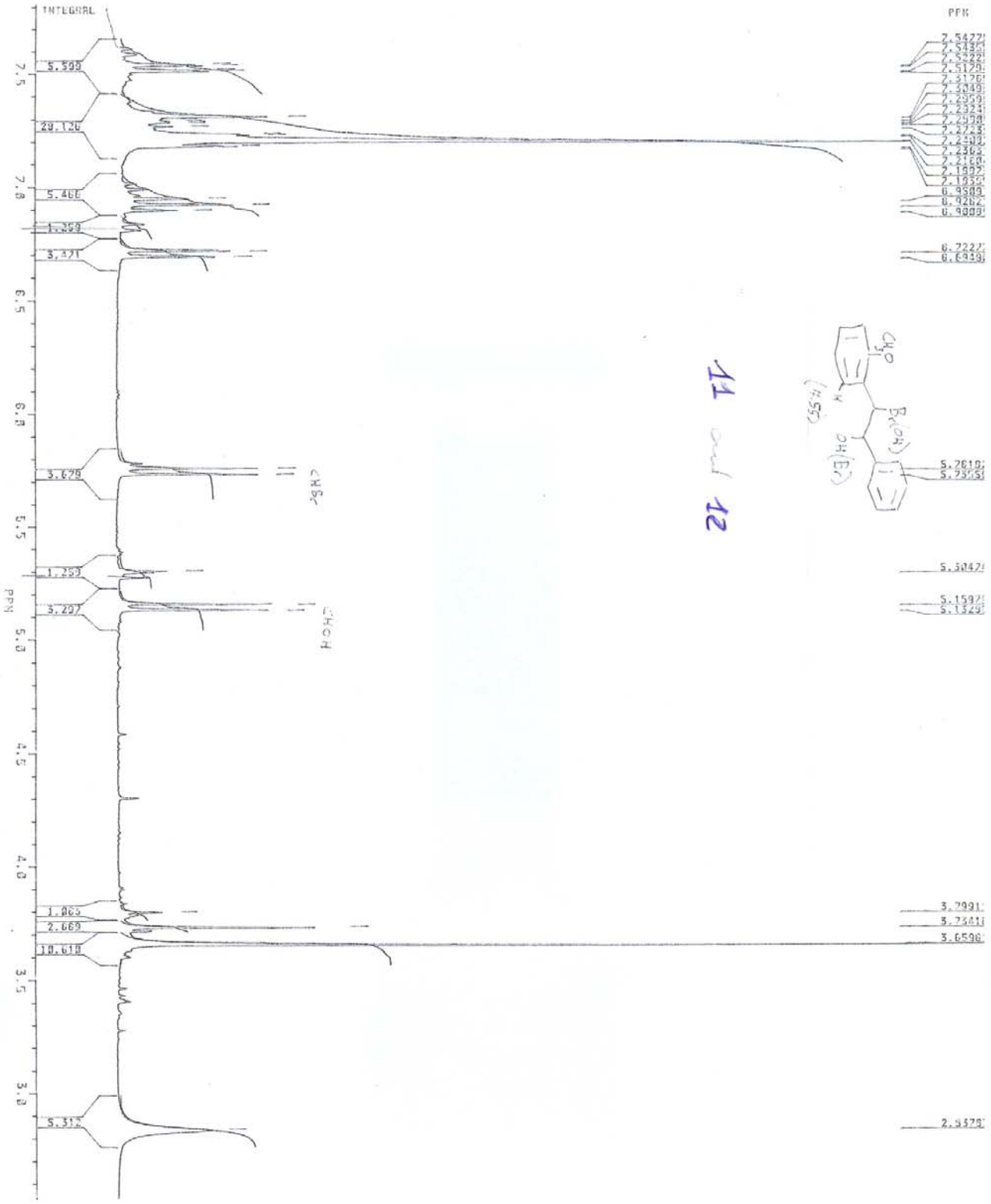
rear. p. 47

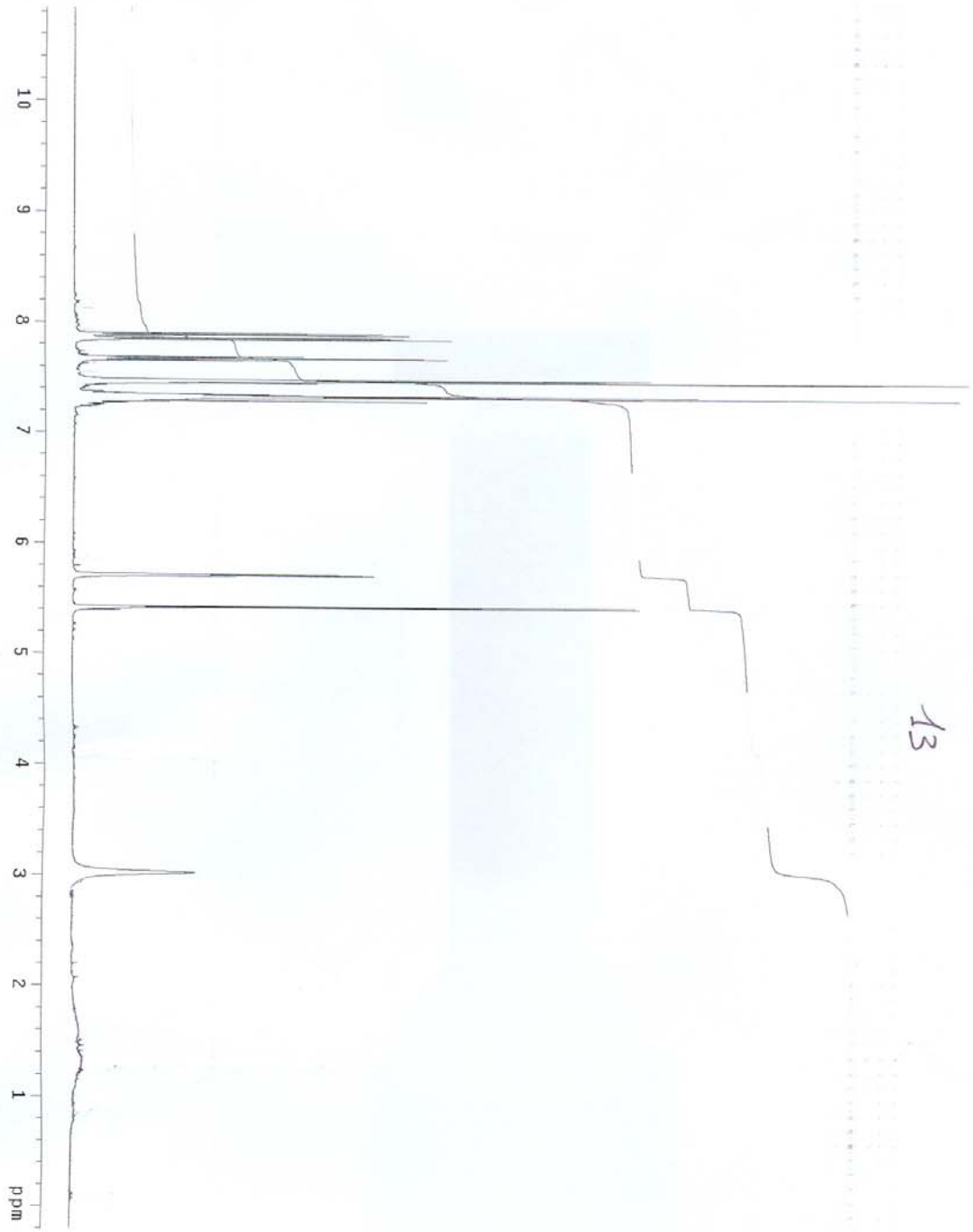
7dI and 7dII

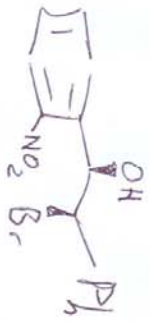
S15



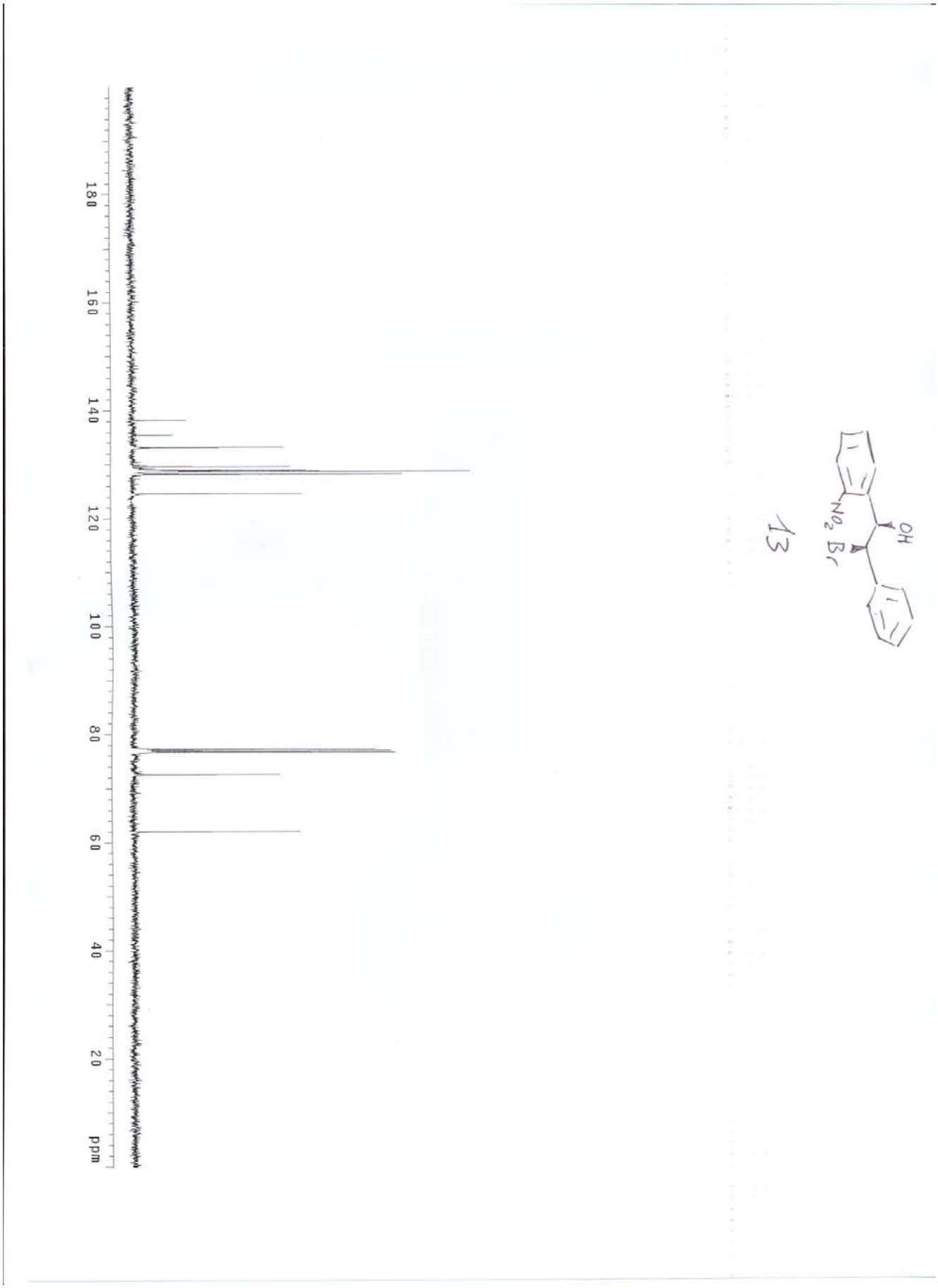

Ph
+ LiBr Amb 15
r.t.
rear. p. 55
Br
Ph
OH
3-Br-3-Ph-2-propanol
S16
ZeI and ZeII
10
42
1.375
1.364
7.487
7.472
7.413
7.396
7.381
7.366
7.351
7.337
4.903
4.891
4.253
4.240
4.227
2.262
1.135
1.122
4.871
7
6
5
4
3
2
1
ppm
8.1
1.9


INTEGRAL
PPM
5.599
20.120
5.466
1.399
3.471
3.679
1.259
3.297
1.865
2.669
10.618
5.312
11
12
S19





13


OH
NO2
Br
13
180
160
140
120
100
80
60
40
20
ppm

Geometry of structure 7a(H+)A

b3lyp/6-31g(d)

Sum of electronic and thermal Free Energies E=-820.560887(Hartree/Particle)

H	1.45495100	2.12756900	1.77615400
C	1.62786200	1.37471900	1.01132000
C	2.09555900	-0.53398400	-0.99318200
C	0.64299900	1.09363200	0.05411200
C	2.85114300	0.71207200	0.96669700
C	3.06072300	-0.23238800	-0.03598300
C	0.87234100	0.12842400	-0.93790400
H	3.63940800	0.91996800	1.68010800
H	0.10822100	-0.08381500	-1.67892800
H	2.31012000	-1.27454900	-1.75407300
C	-0.71434700	1.83625000	0.09020200
H	-0.59340500	2.72972100	0.72616500
N	4.36056600	-0.94260700	-0.08595300
O	4.50949900	-1.76990200	-0.97940800
O	5.18778900	-0.65236000	0.77182500
C	-1.57428100	0.88299000	0.83191300
H	-1.24779800	0.75871500	1.86354500
C	-2.65622100	0.09952500	0.43475700
C	-4.85700500	-1.51694700	-0.17242000
C	-3.19871800	-0.80356800	1.41308400
C	-3.26668800	0.16398500	-0.86448200
C	-4.35162500	-0.64077500	-1.14956500
C	-4.28299200	-1.59876000	1.10873700
H	-2.74086900	-0.85300000	2.39703000
H	-2.87243800	0.85439300	-1.59756300
H	-4.82120000	-0.59482300	-2.12658000
H	-4.69222500	-2.28051700	1.84667000
H	-5.71308600	-2.14217200	-0.41128000
O	-1.22812200	2.15926100	-1.17247500
H	-0.60145000	2.74971800	-1.62283000

Geometry of structure 7a(H+)B

b3lyp/6-31g(d)

Sum of electronic and thermal Free Energies E=-820.554404 (Hartree/Particle)

H	-3.93514200	0.26594900	-1.89432500
C	-3.72772500	-0.18558900	-0.92703100
C	-3.22109100	-1.31281000	1.59015600
C	-2.74104400	0.36284000	-0.08476800
C	-4.46938500	-1.27895500	-0.49606500
C	-4.21631600	-1.84321900	0.76102900
C	-2.46775000	-0.22405900	1.16490600
H	-5.24943100	-1.68771000	-1.13049500
H	-1.69647100	0.19540200	1.80279000
H	-3.03293900	-1.75219900	2.56468600
C	-1.95867200	1.63567100	-0.52867100
H	-2.54432900	2.16833400	-1.28907800
C	-0.89888500	0.83186000	-1.14983300
C	0.40645600	0.50363300	-0.70756300
C	3.01399100	-0.16283500	-0.05320000
C	1.13668000	-0.43594300	-1.49427900
C	1.03819300	1.10335200	0.42205400
C	2.34218900	0.76668300	0.74414000
C	2.43925700	-0.77150600	-1.17021600
H	0.66318700	-0.89298700	-2.35830400
H	0.49913300	1.83302100	1.01087500
H	2.85311400	1.20826600	1.59112500
H	3.01491400	-1.48144500	-1.75142100
H	-4.79642300	-2.69855800	1.09397600
N	4.41560300	-0.52037300	0.30384100
O	4.88632900	0.02152300	1.29625900
O	4.97964800	-1.32834400	-0.42367000
H	-1.20241100	0.38879600	-2.09532800
O	-1.52190800	2.46324000	0.50341000
H	-2.29037100	2.90965000	0.89665700

Geometry of structure 7d(H+)A

b3lyp/6-31g(d) geom=connectivity

Sum of electronic and thermal Free Energies E=-730.571423 (Hartree/Particle)

H	-1.57441300	2.19302900	1.83095600
C	-1.73683700	1.41233800	1.09149300
C	-2.17983100	-0.56856400	-0.84839700
C	-0.78707100	1.20111700	0.06536200
C	-2.89356500	0.66415400	1.13794900
C	-3.13198900	-0.33602100	0.16584400
C	-1.01493700	0.18243500	-0.87916800
H	-3.64725100	0.83167500	1.89989800
H	-0.28293300	0.00216800	-1.66023600
H	-2.34694000	-1.32775100	-1.60272000
O	-4.28488500	-0.99943400	0.29699000
C	-4.63317900	-2.02327300	-0.64488500
H	-4.70484000	-1.61225000	-1.65747000
H	-5.60854800	-2.38866600	-0.32597300
H	-3.90506800	-2.84099700	-0.61823700
C	0.48334700	2.07404100	-0.01924700
H	0.32373900	3.00509300	0.54072000
O	0.98101600	2.29755500	-1.30627800
H	0.35726000	2.86945000	-1.78341500
C	1.27333800	1.11764800	0.77508200
H	1.03516000	1.15683500	1.83538700
C	2.23162400	0.15039700	0.39637300
C	4.22393100	-1.74325200	-0.14644600
C	2.78561300	0.04226100	-0.91456300
C	2.71200300	-0.72020800	1.42032200
C	3.69610100	-1.65370600	1.14953800
C	3.76959000	-0.89714400	-1.16991900
H	2.44262900	0.71213700	-1.69159800
H	2.29709400	-0.64066100	2.42139900
H	4.05892000	-2.31034900	1.93344900
H	4.19813800	-0.97435700	-2.16400200
H	4.99917200	-2.47365800	-0.35988800

Geometry of structure 7d(H+)B

b3lyp/6-31g(d)

Sum of electronic and thermal Free Energies E=-730.583531 (Hartree/Particle)

H	1.27297500	-0.92952400	2.22905900
C	1.67247600	-0.46060300	1.33411600
C	2.65965800	0.77261800	-0.98745300
C	0.82308700	0.42629700	0.58054600
C	2.96063200	-0.72792300	0.95400100
C	3.47357100	-0.11169800	-0.22175100
C	1.37652400	1.04013500	-0.60376000
H	3.57598300	-1.39834000	1.54120800
H	0.75896200	1.72144200	-1.17302700
H	3.09702900	1.22523900	-1.87081500
O	4.69386900	-0.29308700	-0.68334100
C	5.63226200	-1.15721700	-0.00465300
H	5.83196000	-0.78216900	1.00284200
H	6.53836700	-1.11512000	-0.60626400
H	5.24967400	-2.18099200	0.02823800
C	-0.45793400	0.63874400	1.05784200
H	-0.71896100	0.12404400	1.98132000
C	-1.60588200	1.41071100	0.51197400
H	-2.01854300	2.00077200	1.34870200
O	-1.22433100	2.24124900	-0.55890300
H	-2.02936900	2.61675100	-0.95161100
C	-2.64434900	0.33771600	0.13670200
C	-4.52076000	-1.60742100	-0.56240200
C	-3.72028900	0.06449300	0.99049300
C	-2.49918400	-0.37774000	-1.06081200
C	-3.44421700	-1.34008100	-1.41219500
C	-4.65810500	-0.90514900	0.63815200
H	-3.83871400	0.62283100	1.91635400
H	-1.66449200	-0.16265000	-1.72176300
H	-3.33990200	-1.88293400	-2.34685000
H	-5.50140300	-1.10295300	1.29286500
H	-5.25480100	-2.35898900	-0.83711200