

A Straightforward and Flexible [4+2] Route to β -C-Naphthyl-2-Deoxy-glycosides through Tandem Hydroboration-Ketal Reduction : *De novo* Access to C-Naphthyl-6-Fluoro and 6,6-Difluoro 2-Deoxyglycosides

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Supporting Information

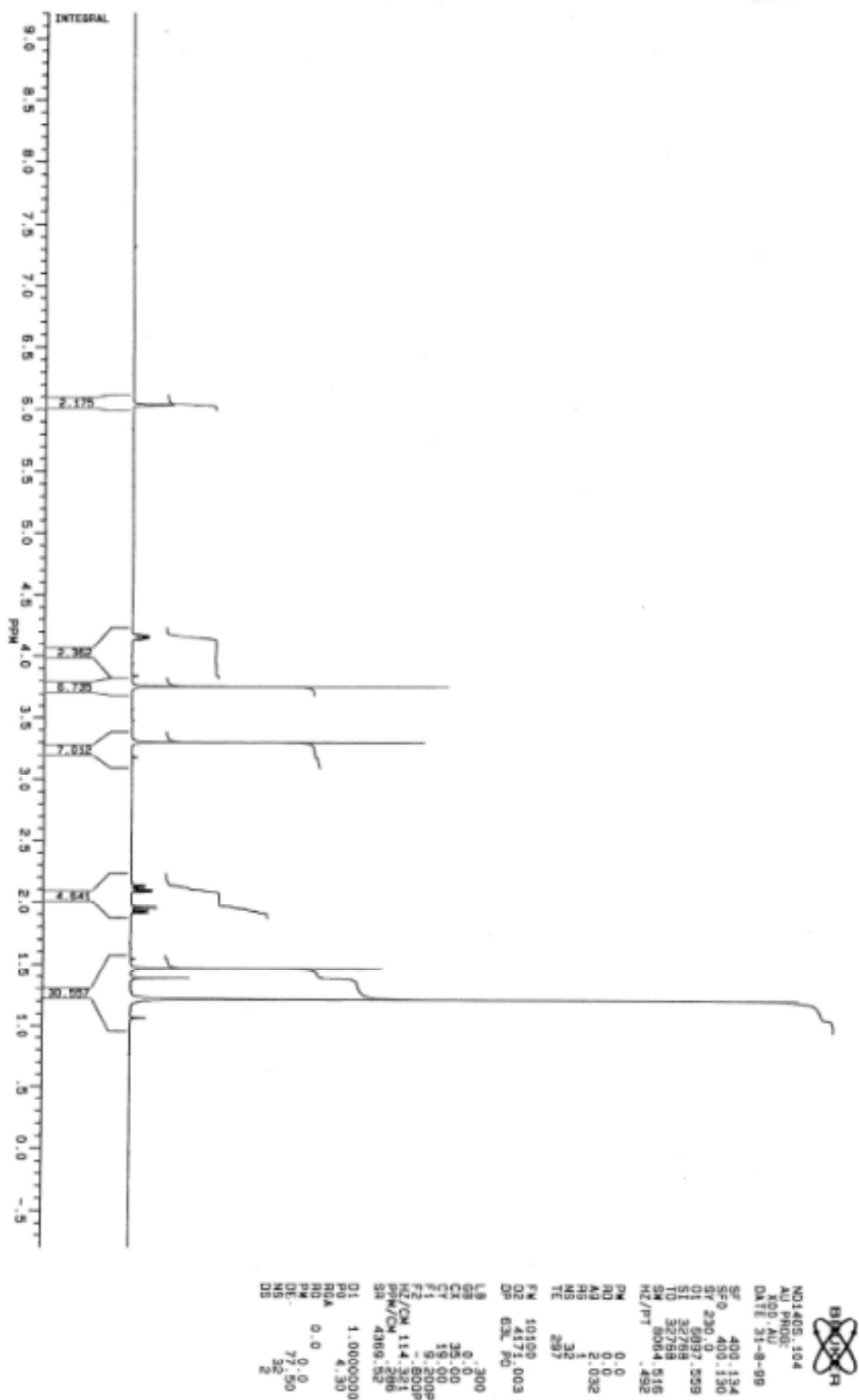
Summary :

SI : General Methods for the Experimental Section

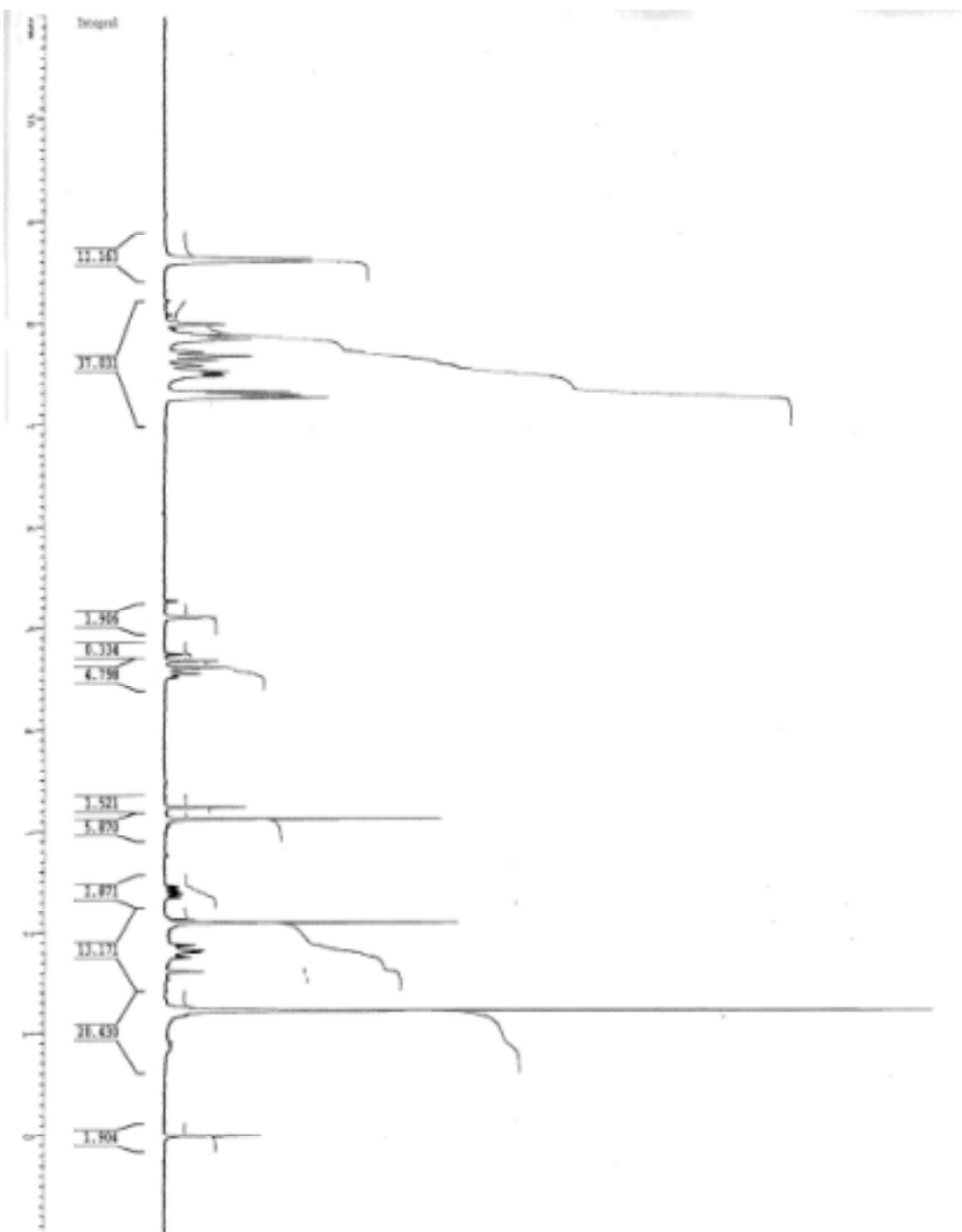
S-2/S-24 : Copies of ¹H NMR spectra : Figure S-2: (**6**); Figure S-3: (**epi-6**); Figure S-4: (**4b**); Figure S-5: (**epi-4b**); Figure S-6: (**7b**); Figure S-7: (**4c**); Figure S-8: (**9**); Figure S-9: (**10**); Figure S-10: (**11**); Figure S-11: (**12**); Figure S-12: (**4d**); Figure S-13: (**4e**); Figure S-14: (**4f**); Figure S-15: (**4g**); Figure S-16: (**4h**); Figure S-17: (**5a**); Figure S-18: (**8a**); Figure S-19: (**5c**); Figure S-20: (**5d**); Figure S-21: (**5e**); Figure S-22: (**5f**);); Figure S-23: (**5g**); Figure S-24: (**5h**).

General Methods for the Experimental Section. The reagents were purchased from commercial suppliers and used without purification. All solvents were dried using standard procedures. Column chromatography was performed with 40-60 μ m silica gel under medium pressure (1 bar). All melting points are uncorrected. Infrared spectra were performed on an FT spectrophotometer. ¹H and ¹³C NMR spectra were recorded on 400 MHz spectrometers in CDCl₃ with TMS as reference. LCMS (EI or CI) were performed on a particle beam mass spectrometer.

Ester epi-6

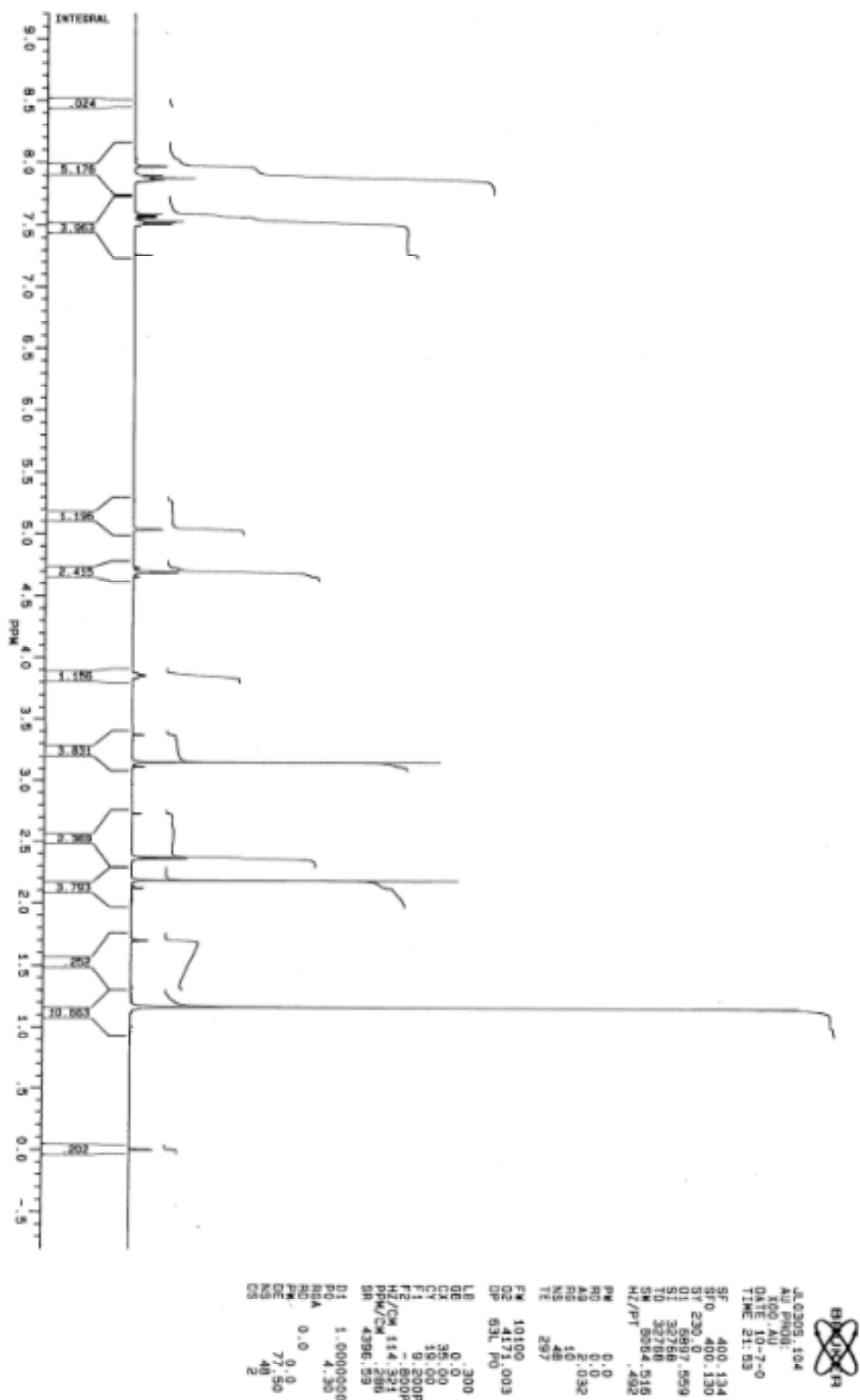


Alcohol 4b

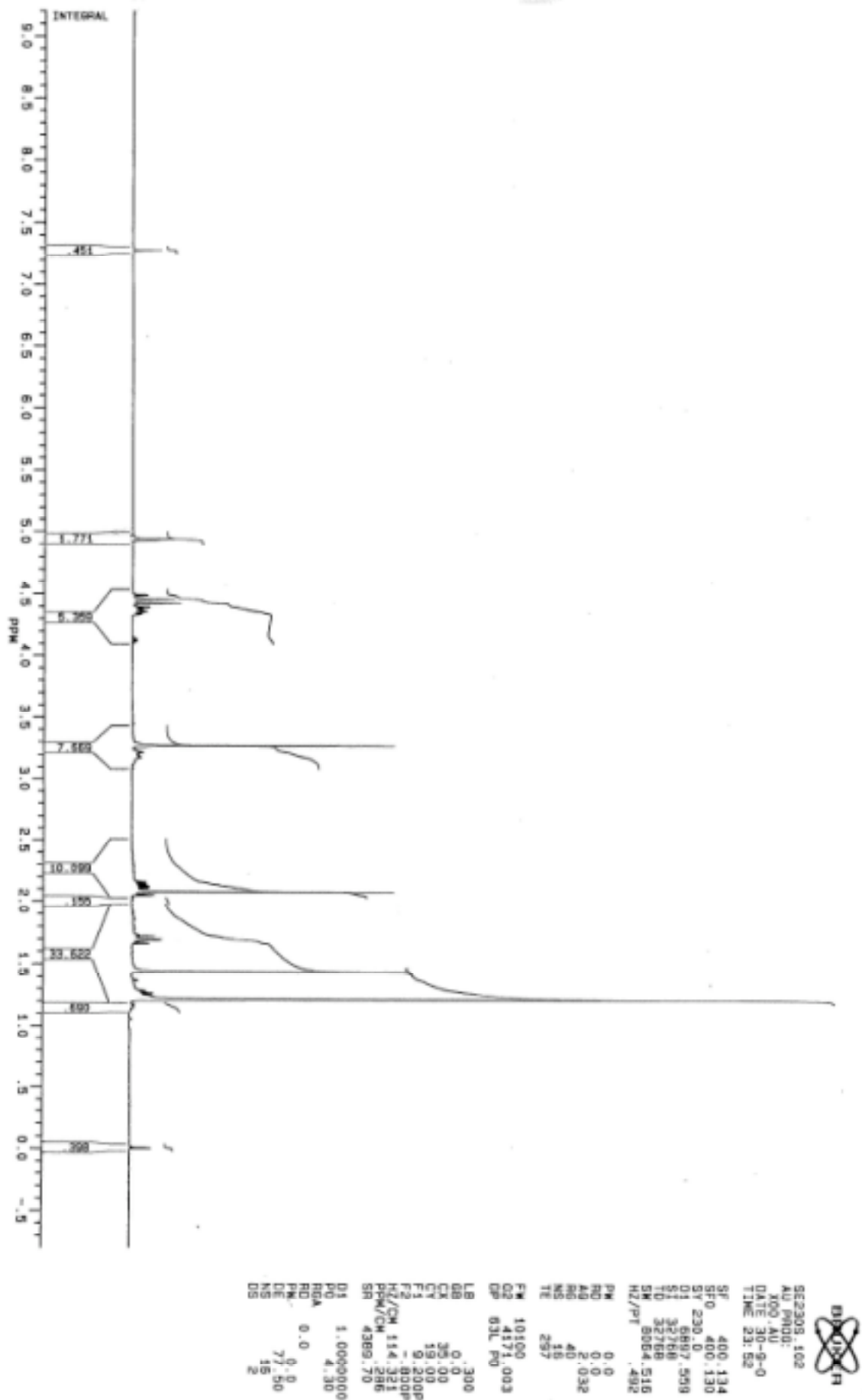


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TD	32768
ACQPROG	zgpg30
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RG2	2
RG3	4139.073 Hz
RG4	9.136514 Hz
RG5	3.958423 sec
RG6	5160.6
RG7	128.870 kHz
RG8	9.50 kHz
RG9	303.0 K
RG10	1.0000000 sec
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PL1	-4.00 dB
PR1	200.131259 MHz
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LB	0.50 Hz
GB	0
PC	1.00
1D NMR plot parameters	
CA	36.00 cm
F1P	11.000 ppm
F1	2281.43 Hz
F2P	-1.000 ppm
F2	-200.11 Hz
PRINCM	E-6010 exp/cm
ISCM	81.8510 Hz/cm

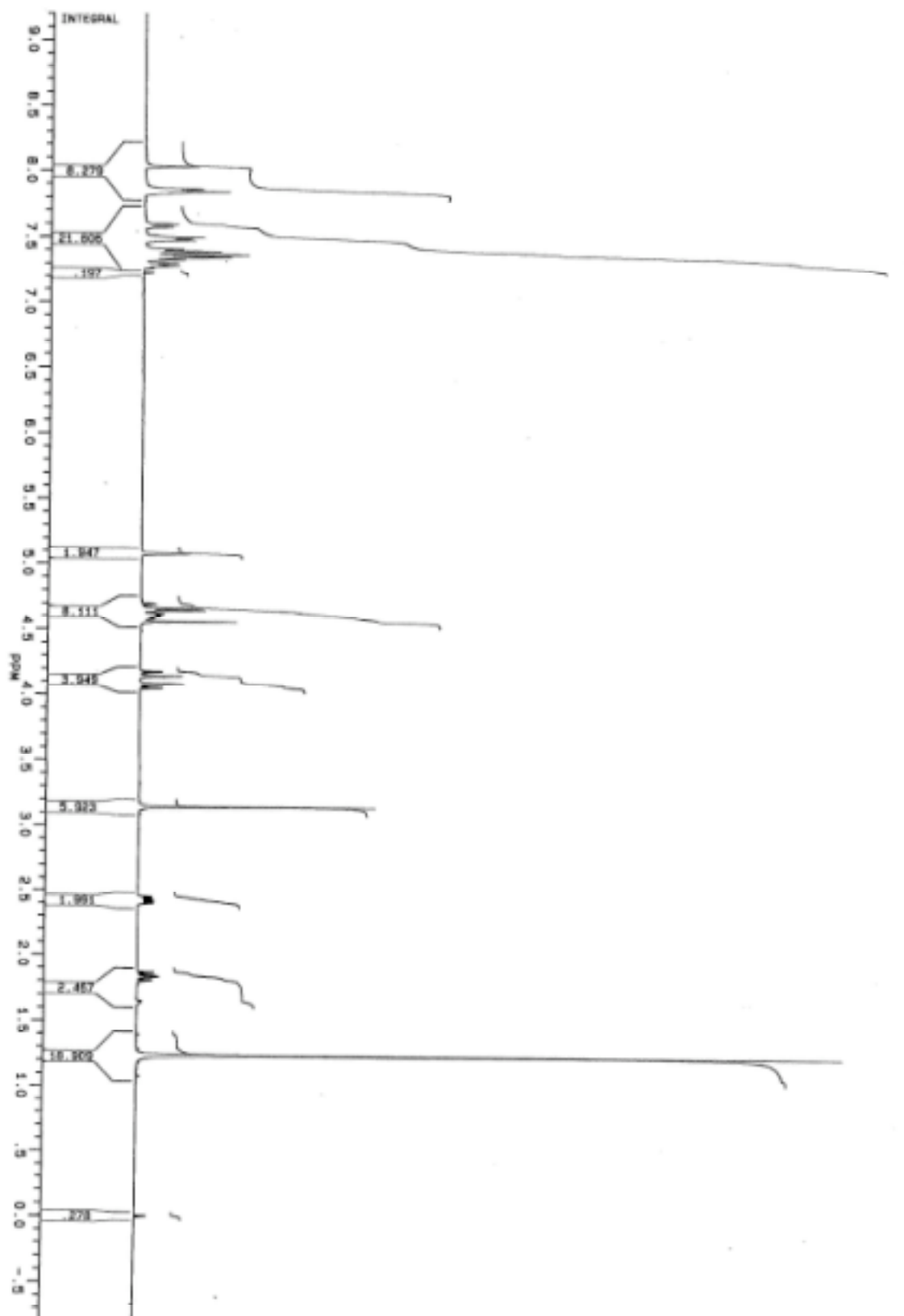
Alcohol epi-4b



Acetate 7b

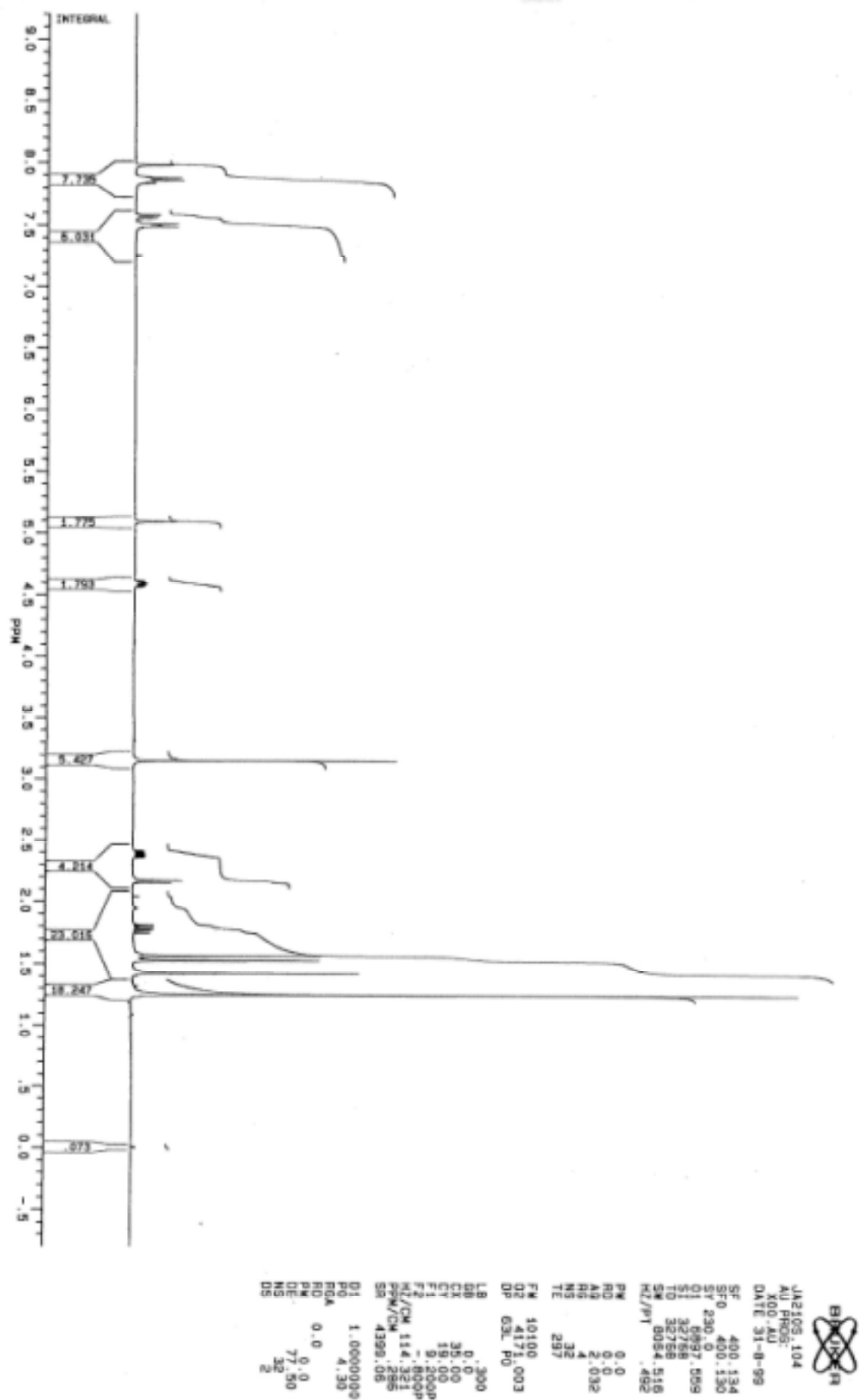


Ether 4c

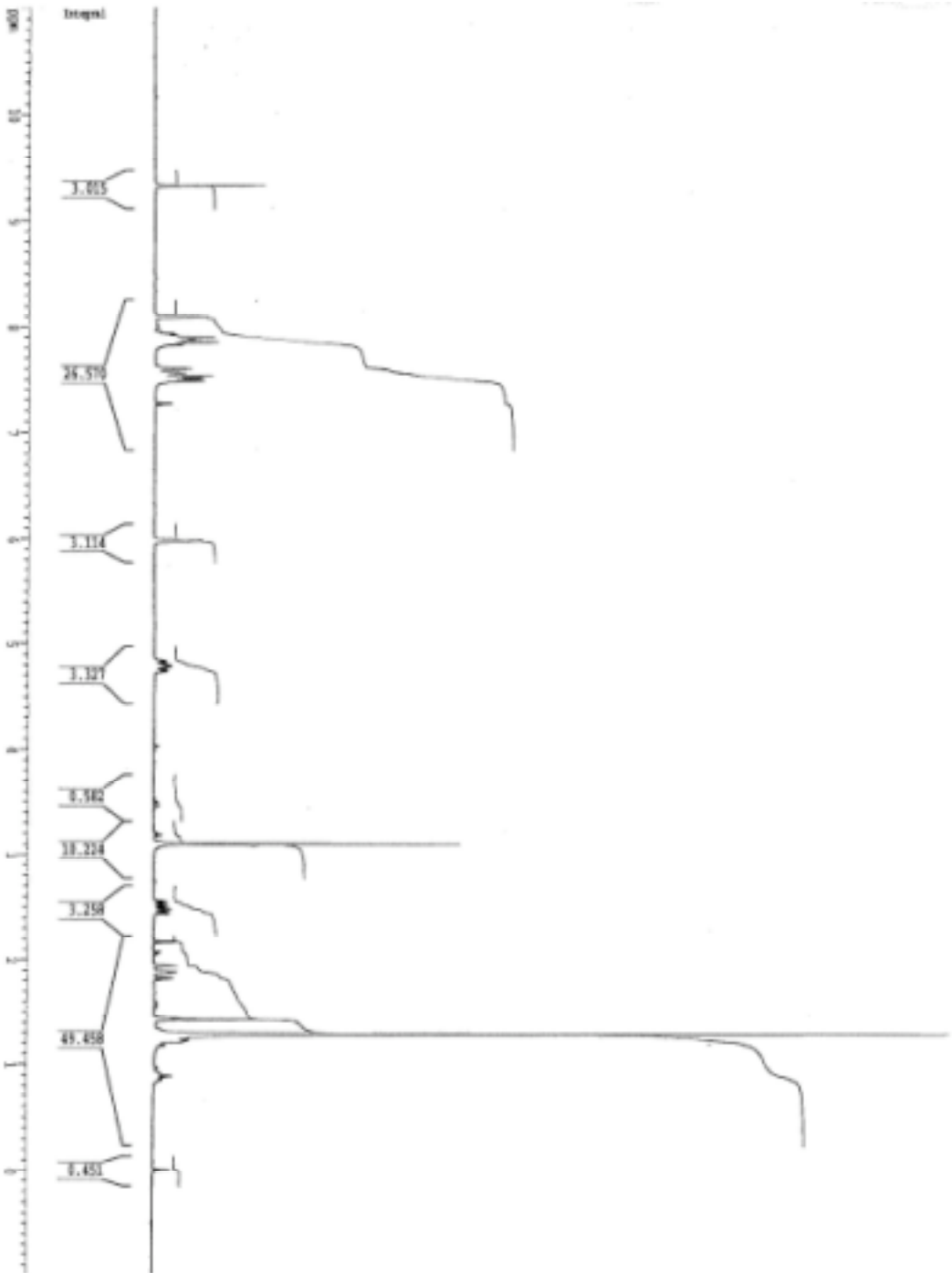



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 T0 32768
 SW 8064.516
 HZ/P1 .492
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 R0 0.0
 AU 2.032
 N0 4
 NS 10
 TE 297
 FM 10100
 D2 4171.003
 DP 63L P0
 LB .300
 GB 0.0
 CX 35.00
 CY 19.00
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 F2 -.800P
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 PPM/CW .266
 SR 4409.35
 O1 1.0000000
 P0 4.33
 R0A
 RD 0.0
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 DS 2

Alcohol 9



Aldehyde 10



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PROCNO: 1

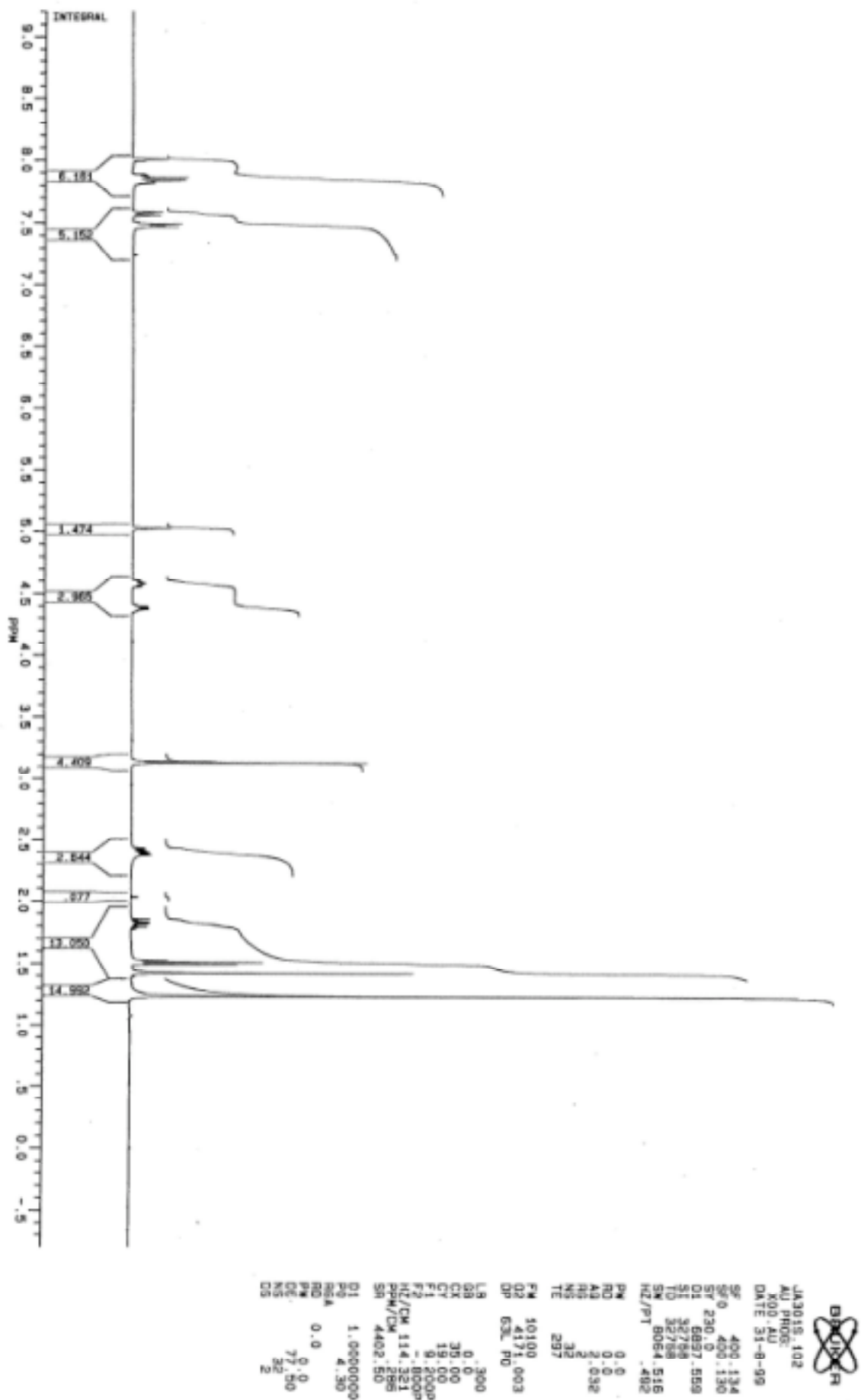
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NS: 12
DS: 2
SWH: 4139.873 Hz
FIDRES: 0.124314 Hz
AQ: 1.958424 sec
RG: 2048
SW: 120.800 MHz
WDW: 9.00 usec
SSB: 380.0 K
GB: 1.0000000 sec

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PC1: -6.00 dB
RFPO: 200.132259 MHz

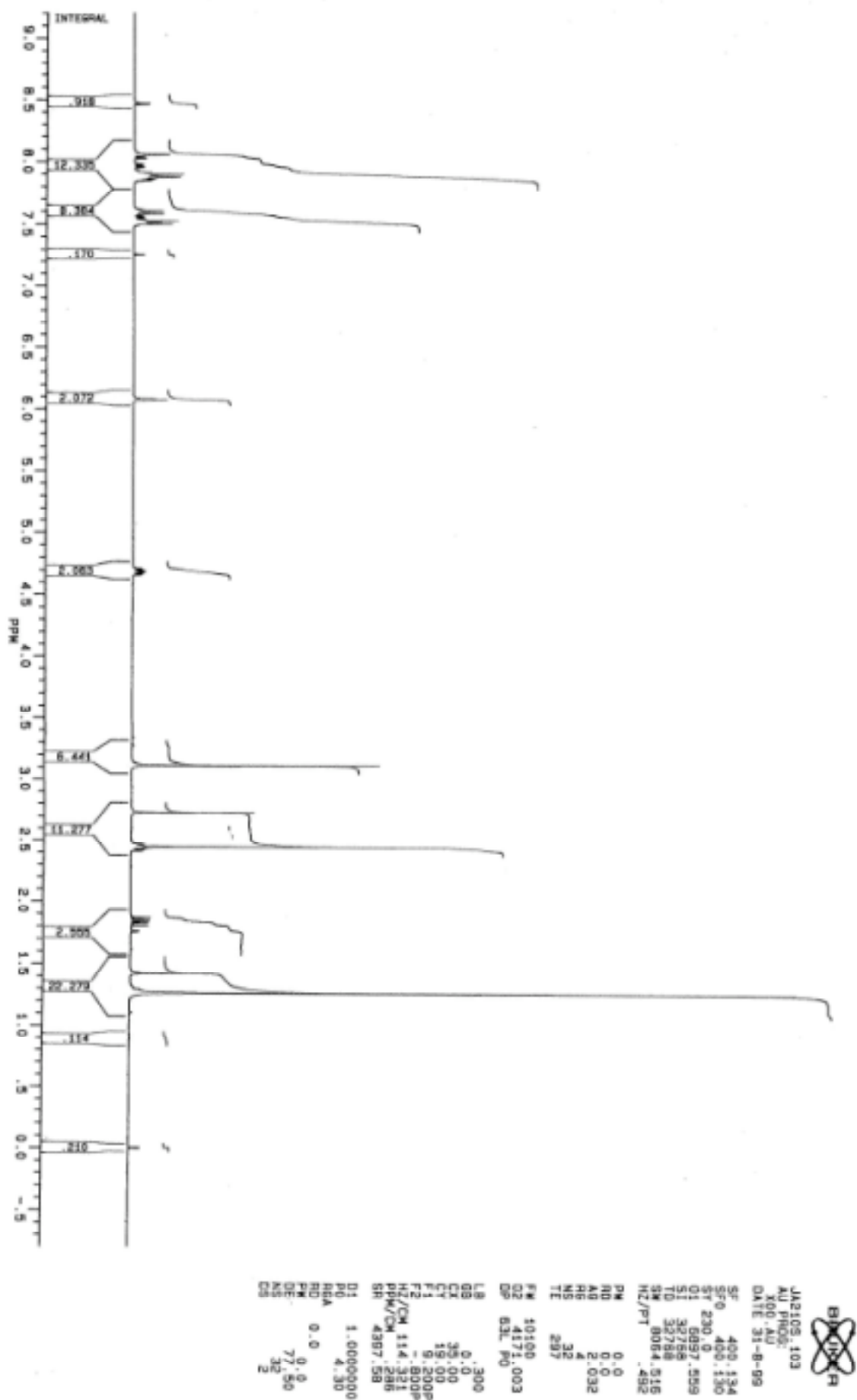
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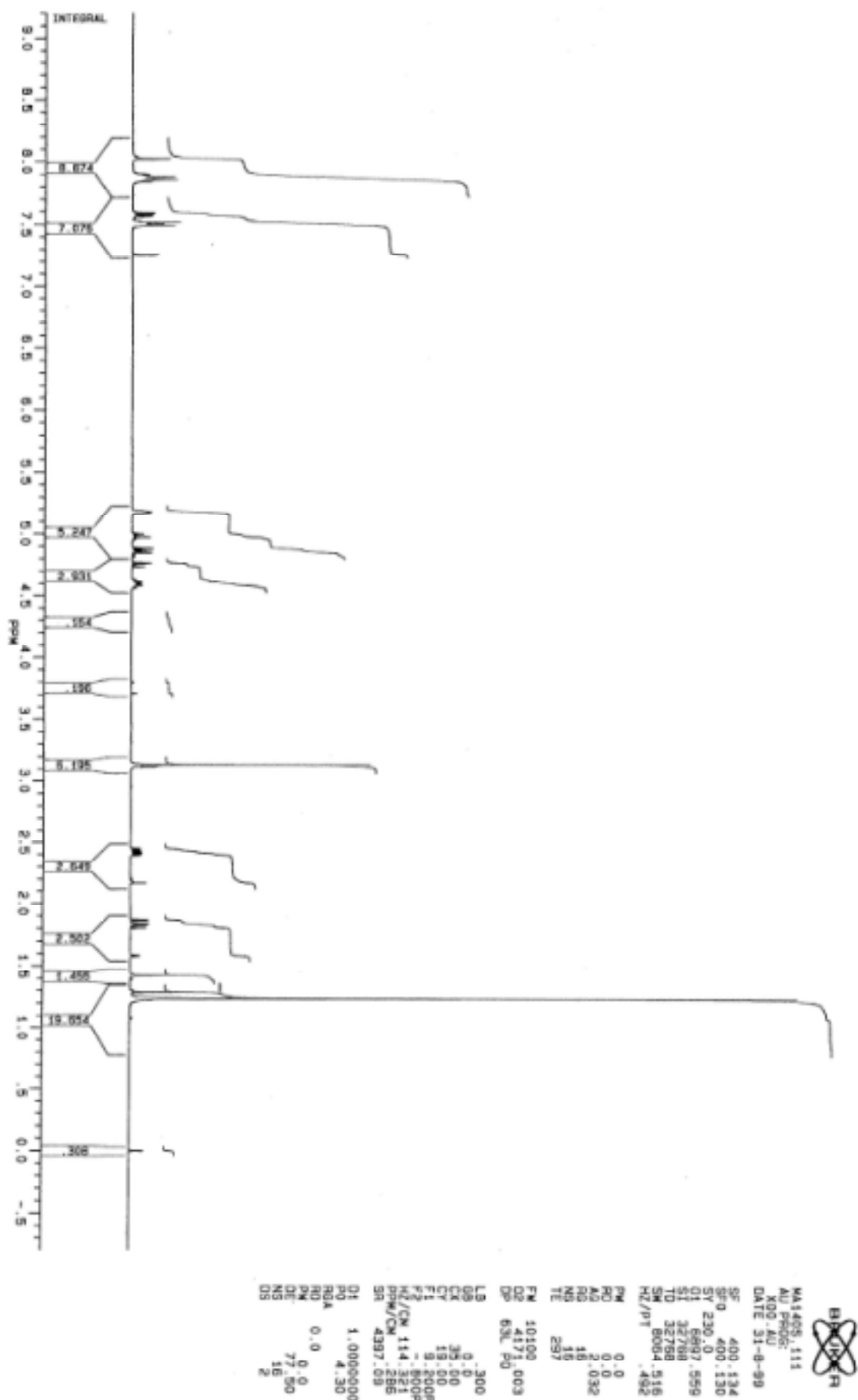
Alcohol 11



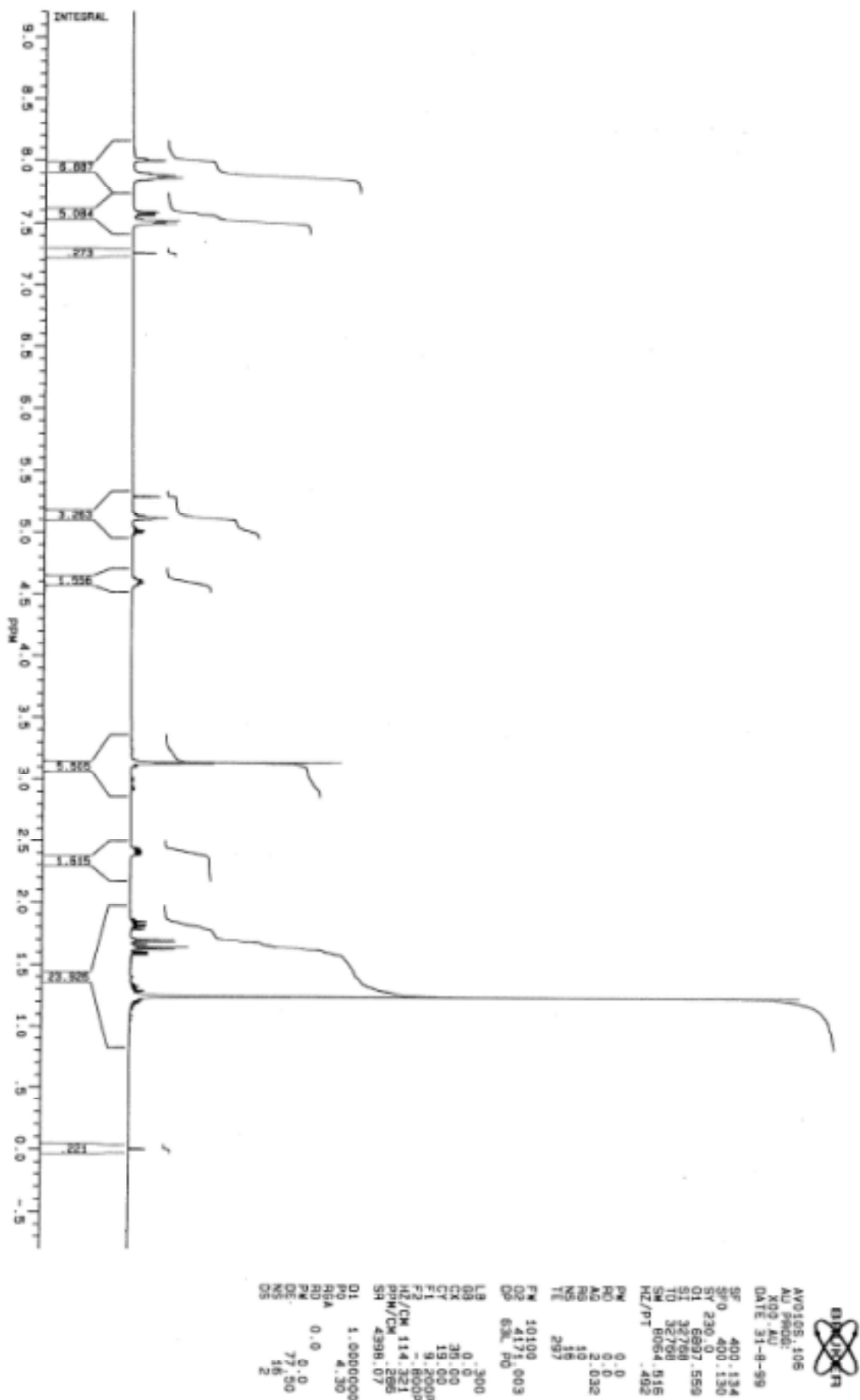
Ketone 12



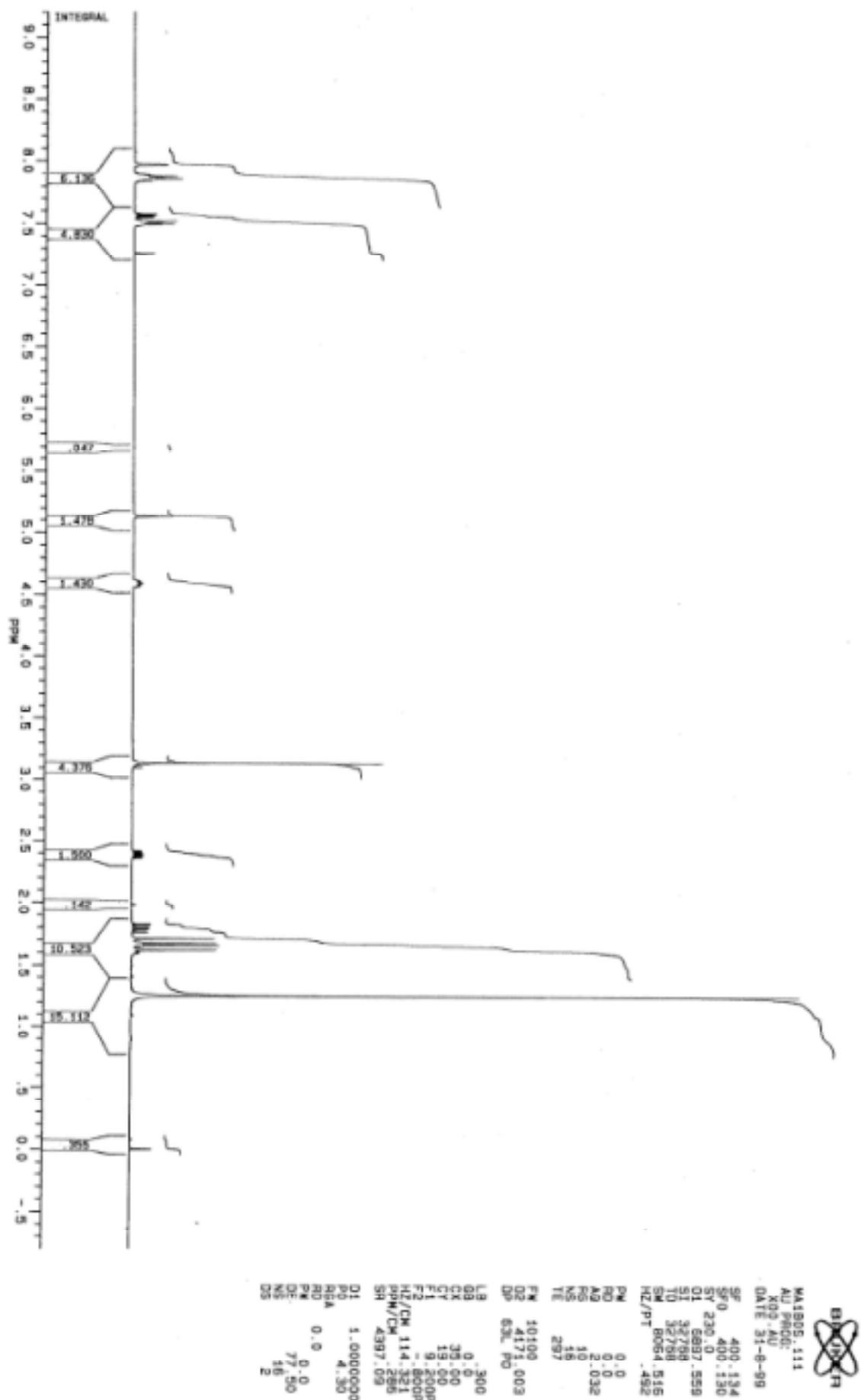
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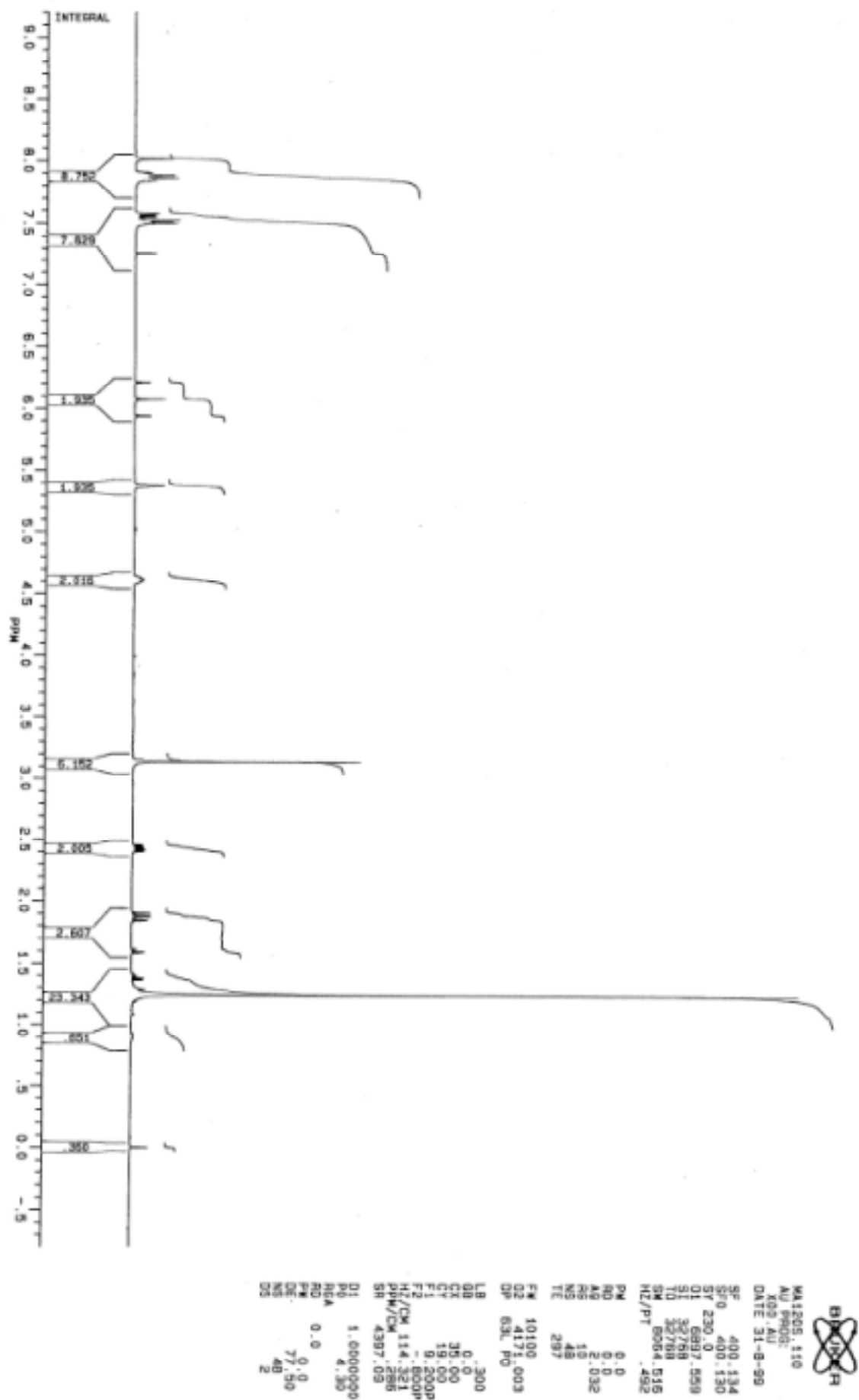
Monofluoride 4e



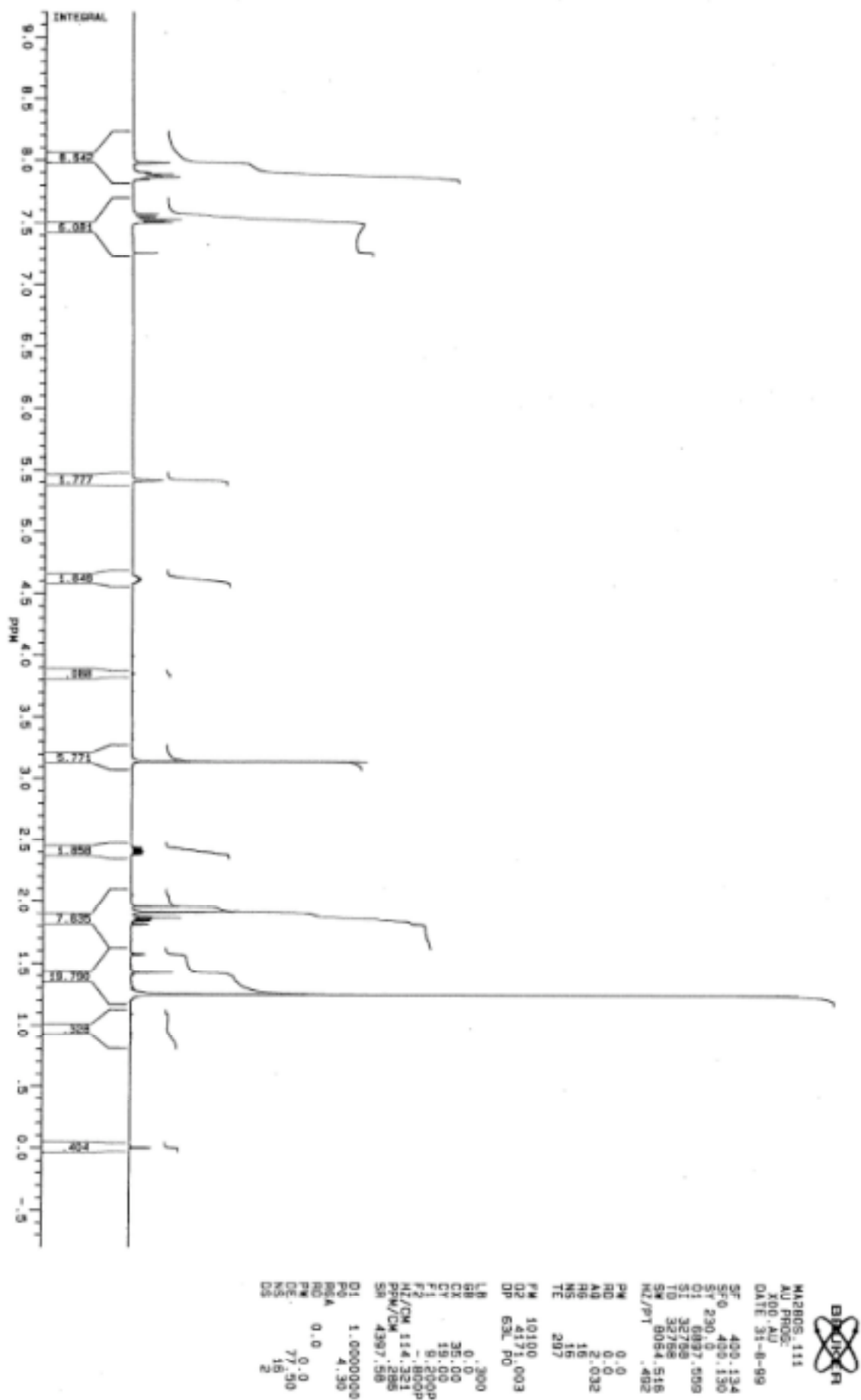
Monofluoride 4f



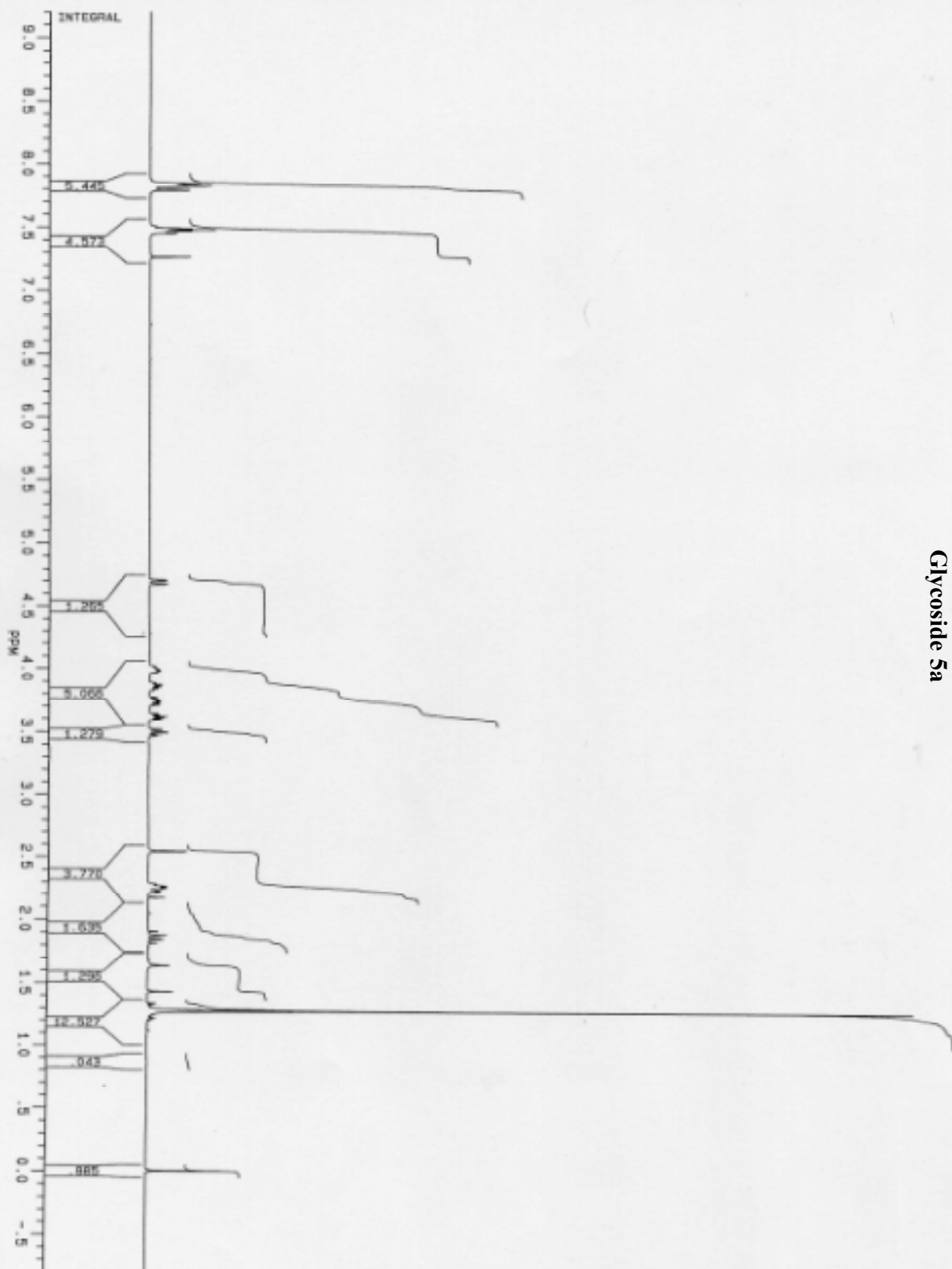
Difluoride 4g




Diffuoride 4h



Glycoside 5a





 J40625.101

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 DATE 31-8-99

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 O1 6897.559

 Y1 32768

 T0 32768

 SM 8064.515

 HZ/PT .492

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 RD 0.0

 AG 2.032

 RG 40

 NS 16

 TE 297

 FM 10100

 D2 4171.003

 DP 63L PO

 LB -300

 GB 0.0

 CX 38.00

 CY 19.00

 F1 9.200P

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 SR 4395.12

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 RQA

 RD 0.0

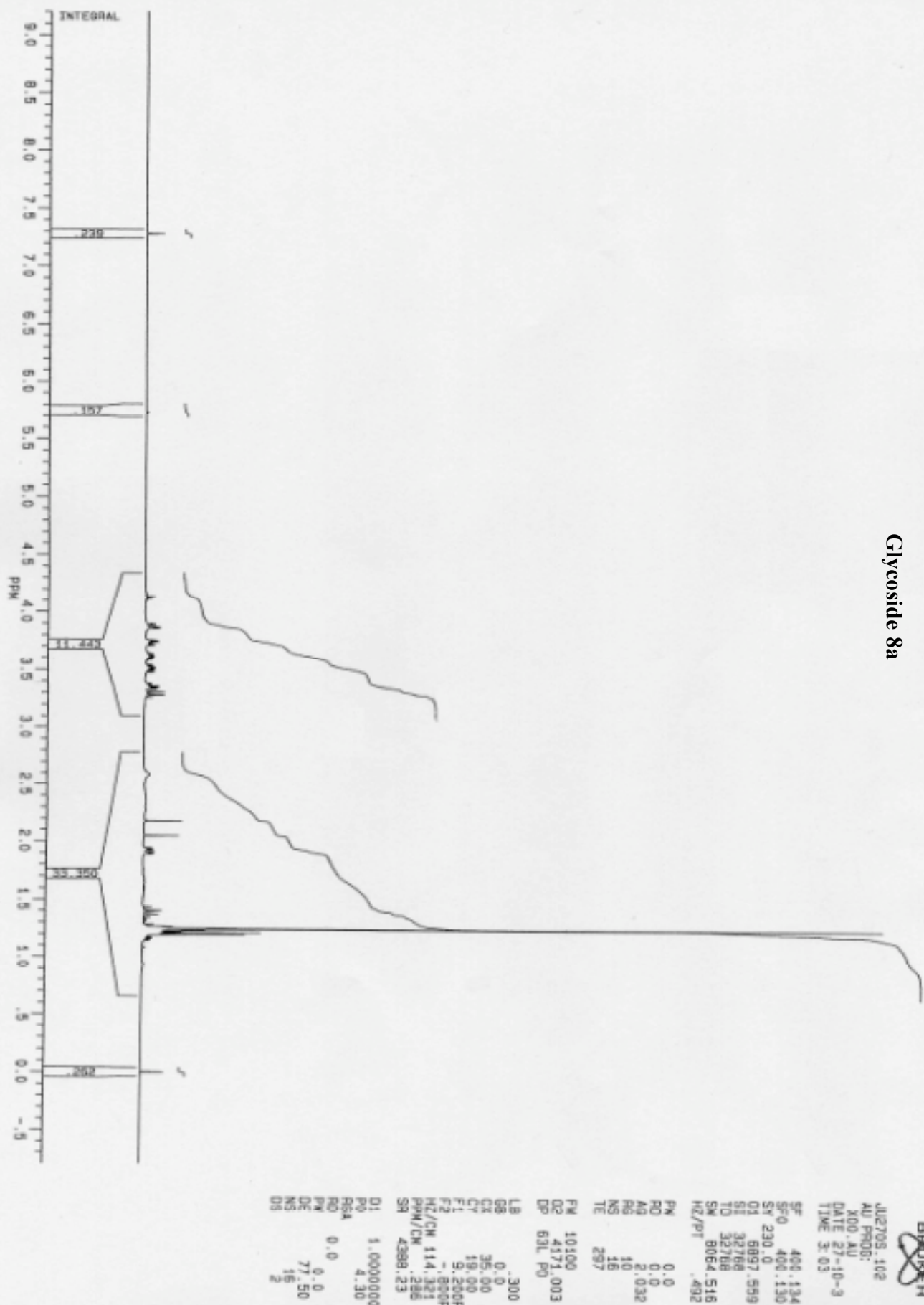
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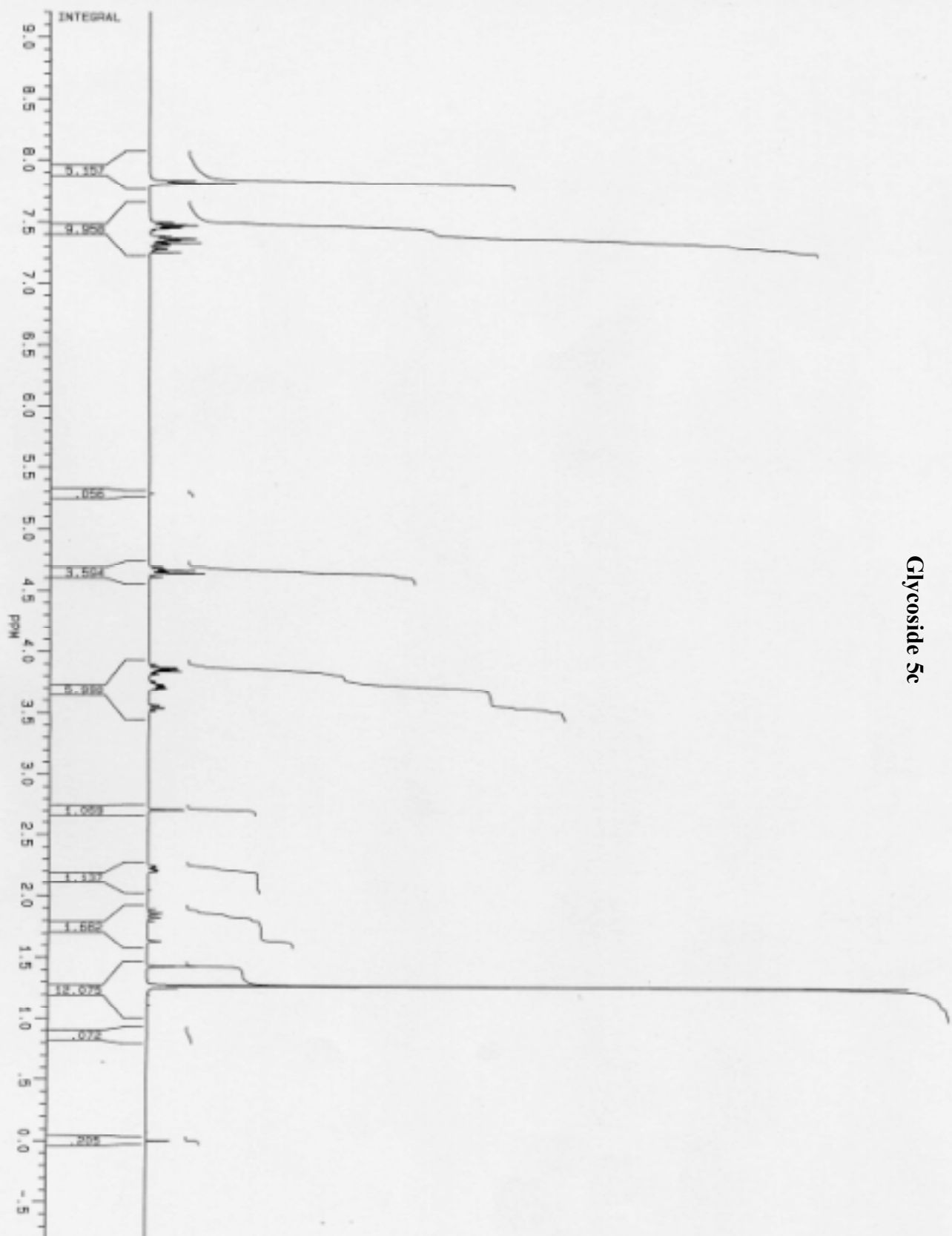
 NS 16

 DS 2

Glycoside 8a

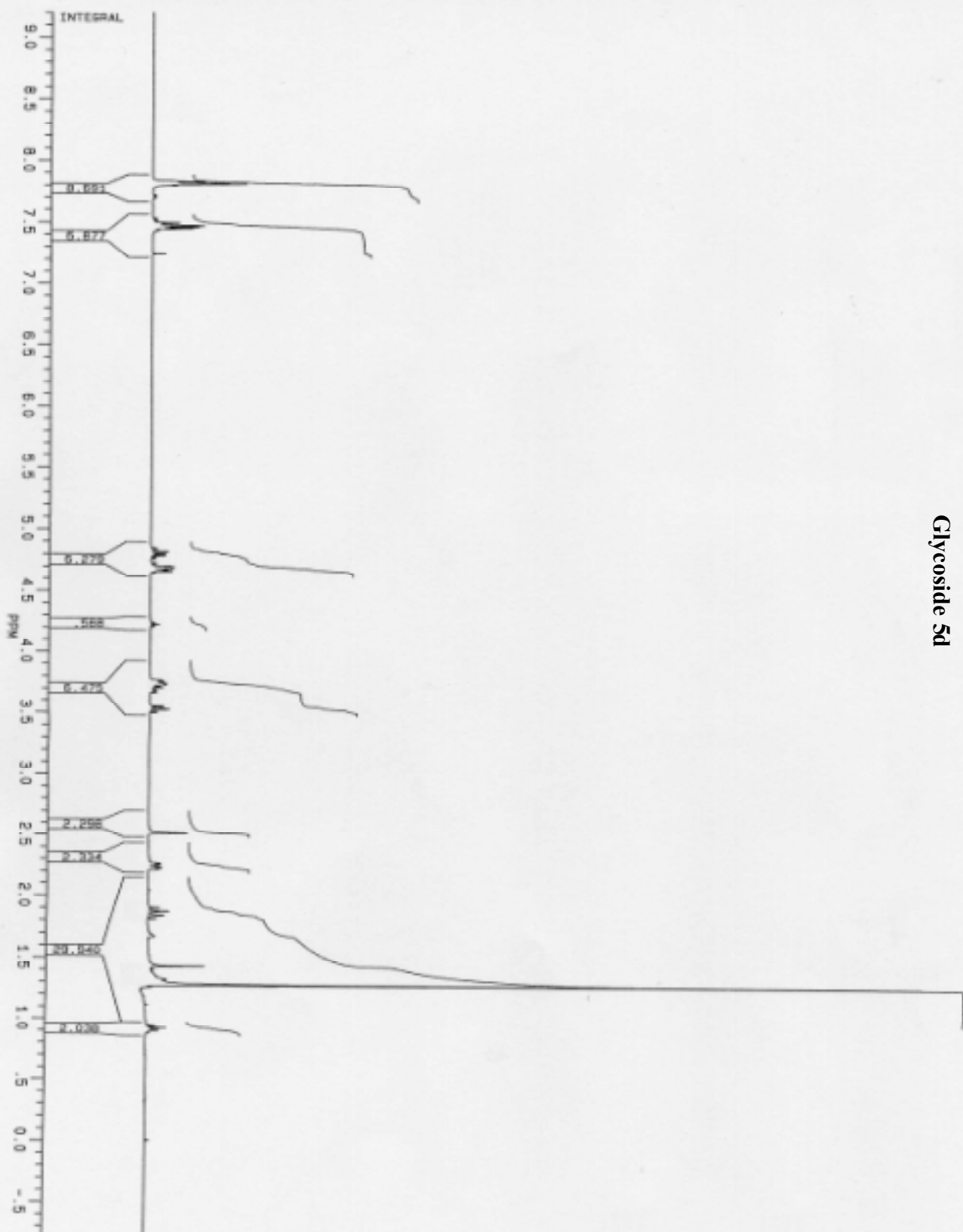



Glycoside 5c



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 T0 32769
 SM 8064.516
 HZ/PT .492
 PM 0.0
 RD 0.0
 AD 2.032
 RS 10
 NS 16
 TE 297
 FM 10100
 D2 4171.003
 DP 63L PO
 LB .300
 GB 0.0
 CX 35.00
 CY 19.00
 F1 9.200P
 F2 -800P
 HZ/CW 114.821
 PPM/CW .295
 SR 4399.55
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 P0 4.30
 R0A 0.0
 RD 0.0
 PW 0.0
 DE 77.90
 NS 16
 DS 2

Glycoside 5d



 MA2005.109
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 HL/PT .492
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 RD 0.0
 AQ 2.032
 RG 4
 NS 32
 TE 297
 F# 10100
 Q2 4171.003
 DP 63L P0
 LB .300
 GB 0.0
 CX 35.00
 CY 18.00
 F1 9.200P
 F2 .800P
 H2/CW 114.321
 PPM/CW 286
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 DS 2

Glycoside 5c

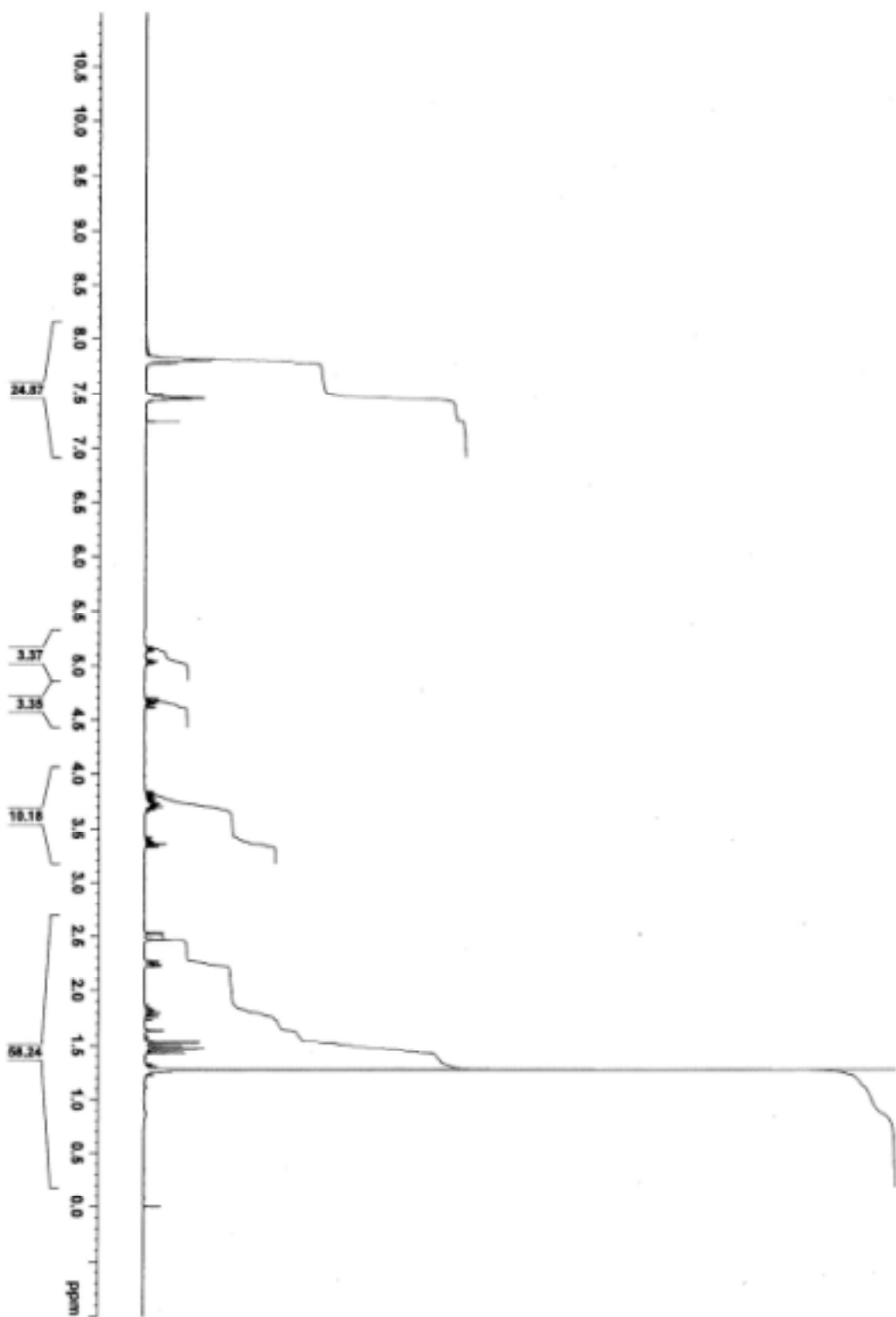


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DA 60.401 use
DE 18.00 use
TE 298.2 K
D1 1.6000000 sec
TOS 1

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F2 - Processing parameters
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Glycoside 5f



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TIME 6:26

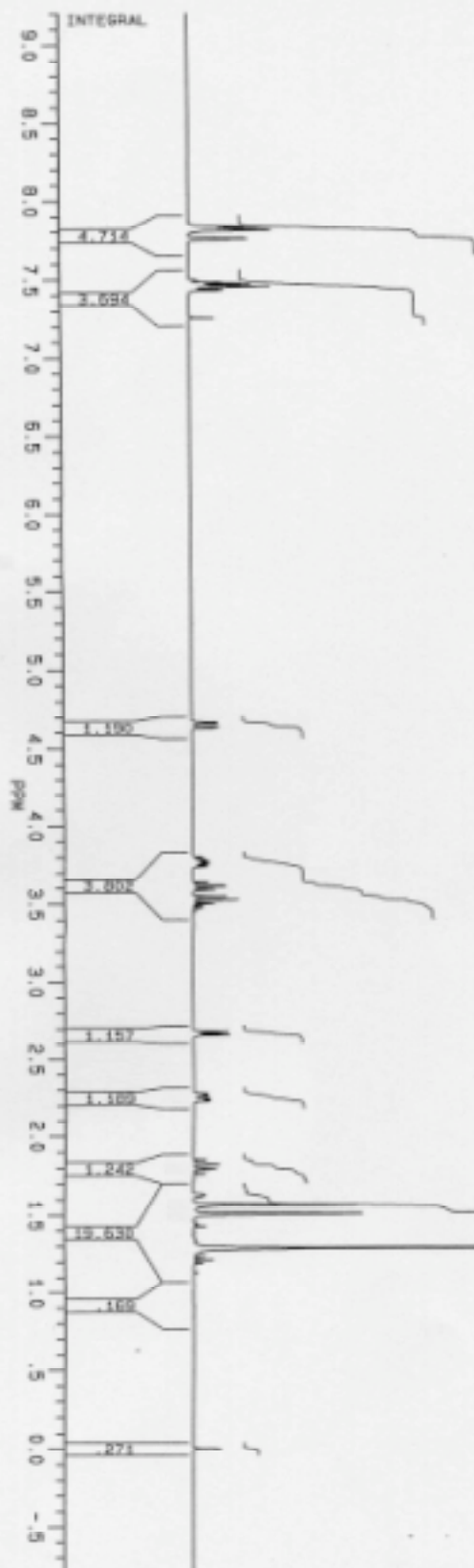
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FM 10100
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CY 19.00
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PPM/CW 286
SR 4397.56

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NS 48
DS 2



Glycoside 5g



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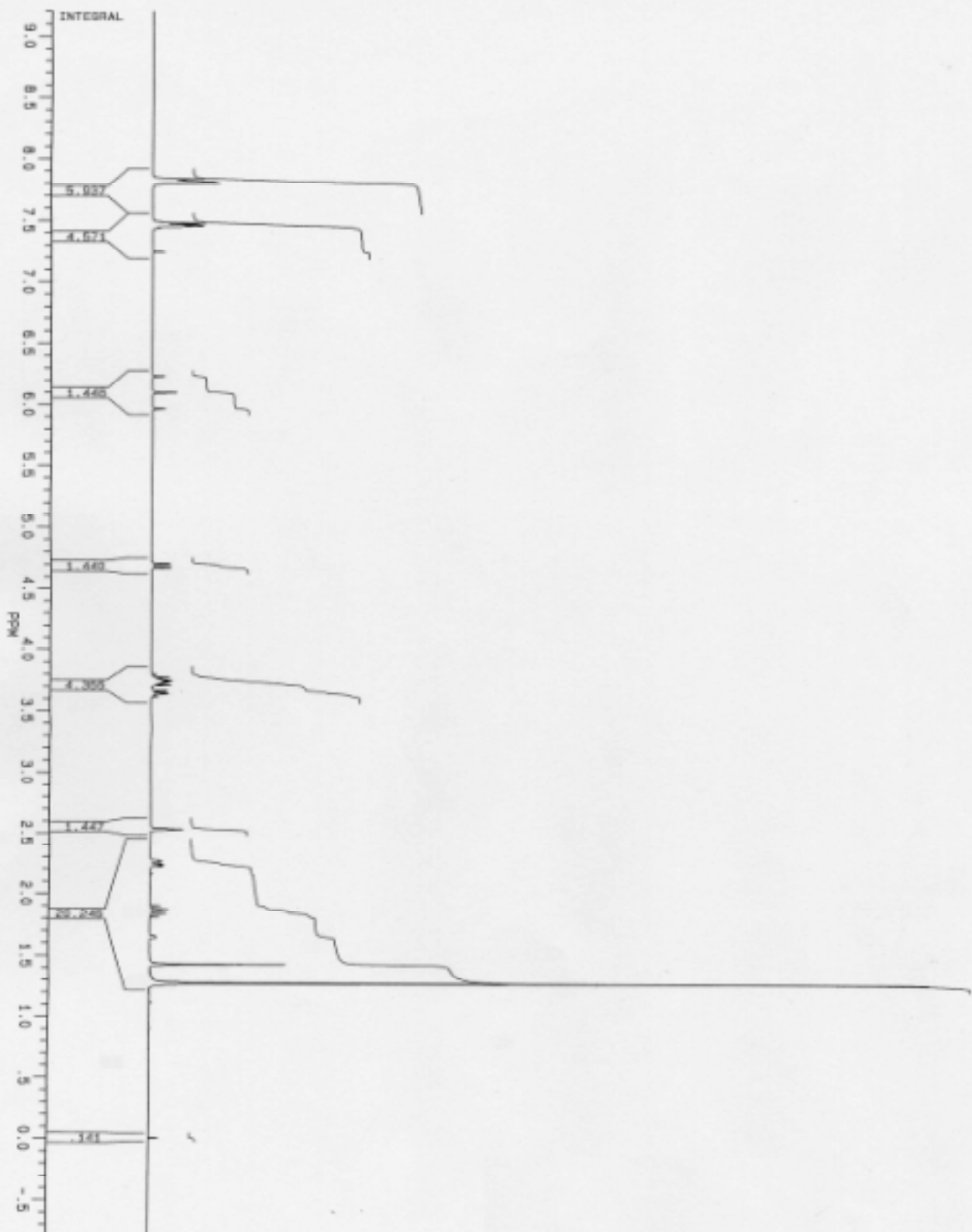
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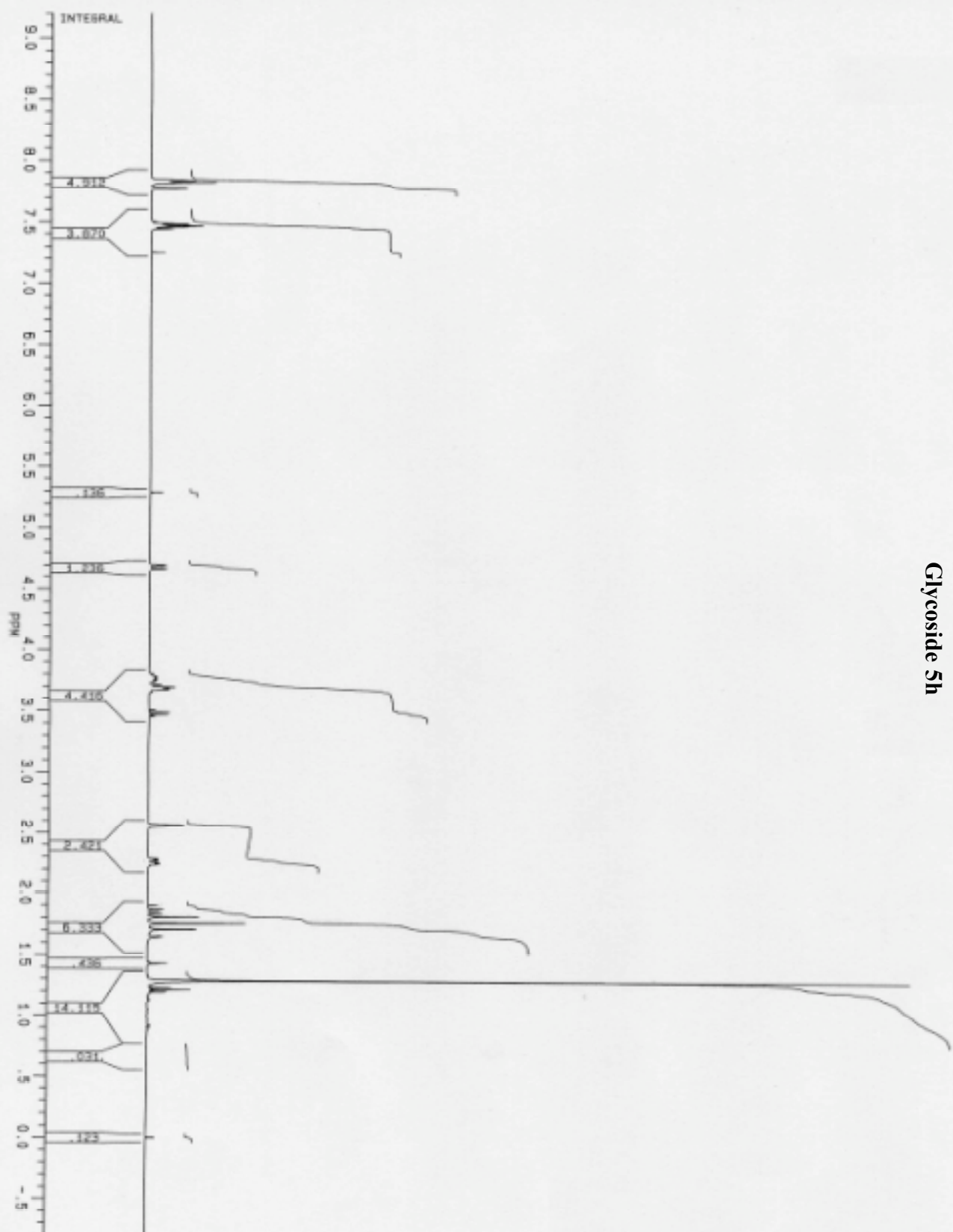
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PM 0.0
DE 77.50
NS 48
OS 2



Glycoside 5h



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 T0 32768
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 RO 0.0
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 RG 0
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 GB 0.0
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