Supporting Information for

# Polymer precursors from catalytic reactions of natural oils

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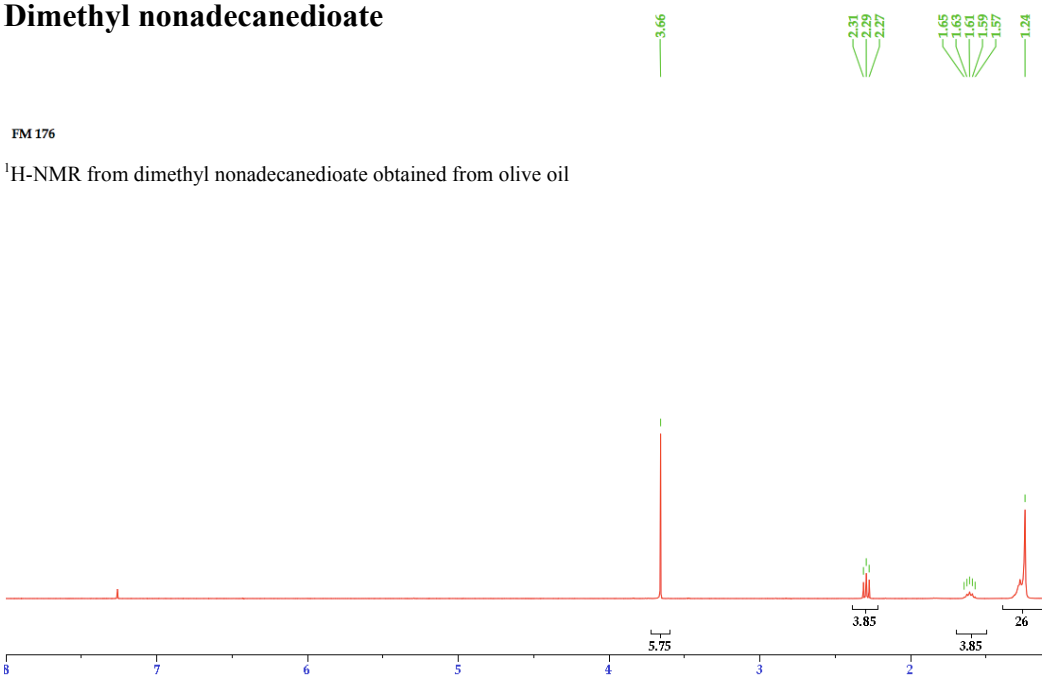
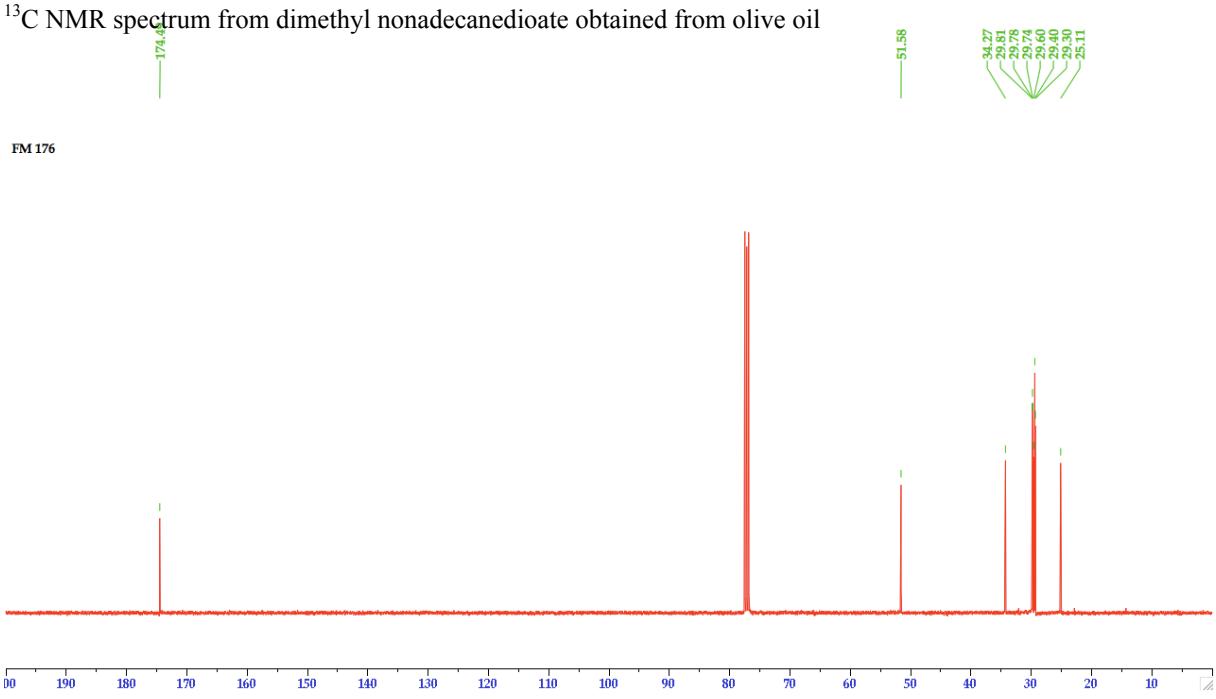
NMR and other spectra for the compounds formed during the study are shown below, together with GC analysis of the minor products obtained from the carbonylation of sunflower and olive oils.:

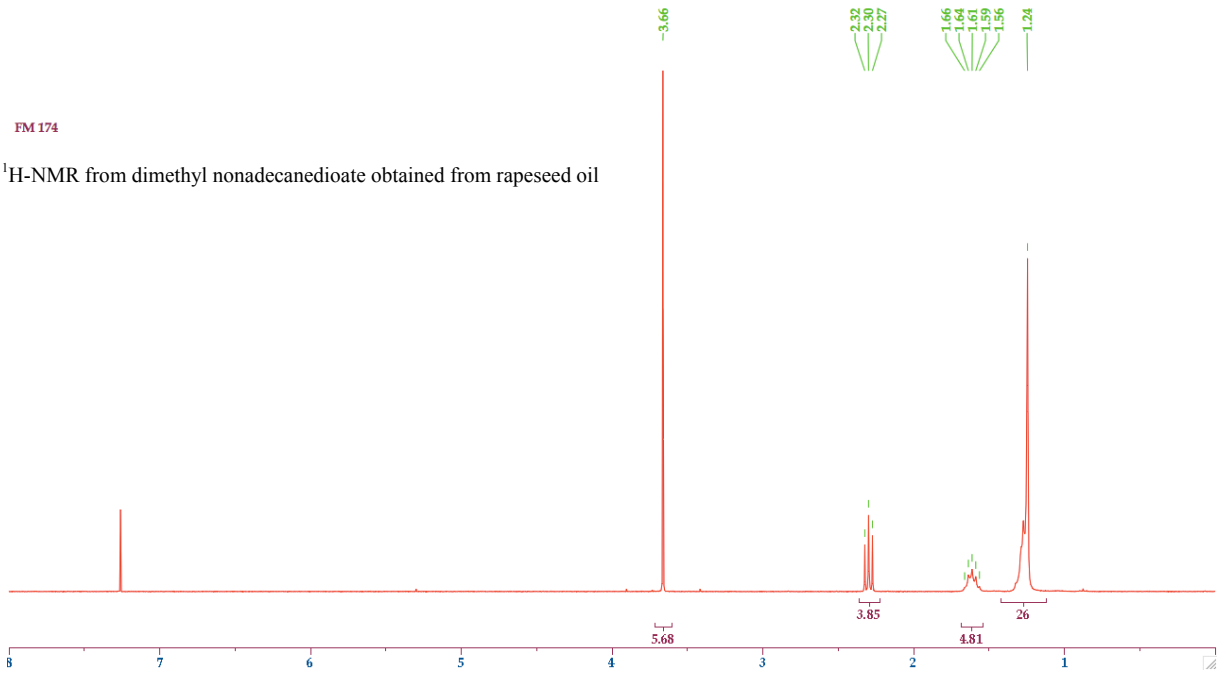
## Dimethyl nonadecanedioate



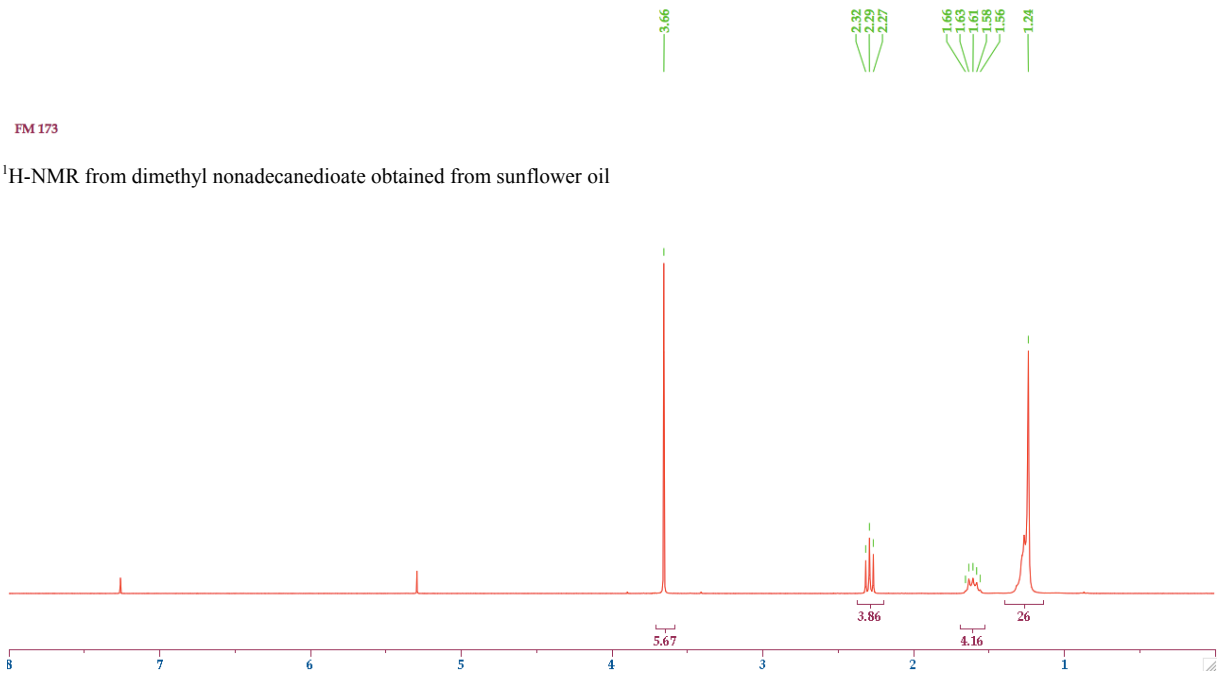

$^{1}$H-NMR from dimethyl nonadecanedioate obtained from olive oil




$^{13}$C NMR spectrum from dimethyl nonadecanedioate obtained from olive oil

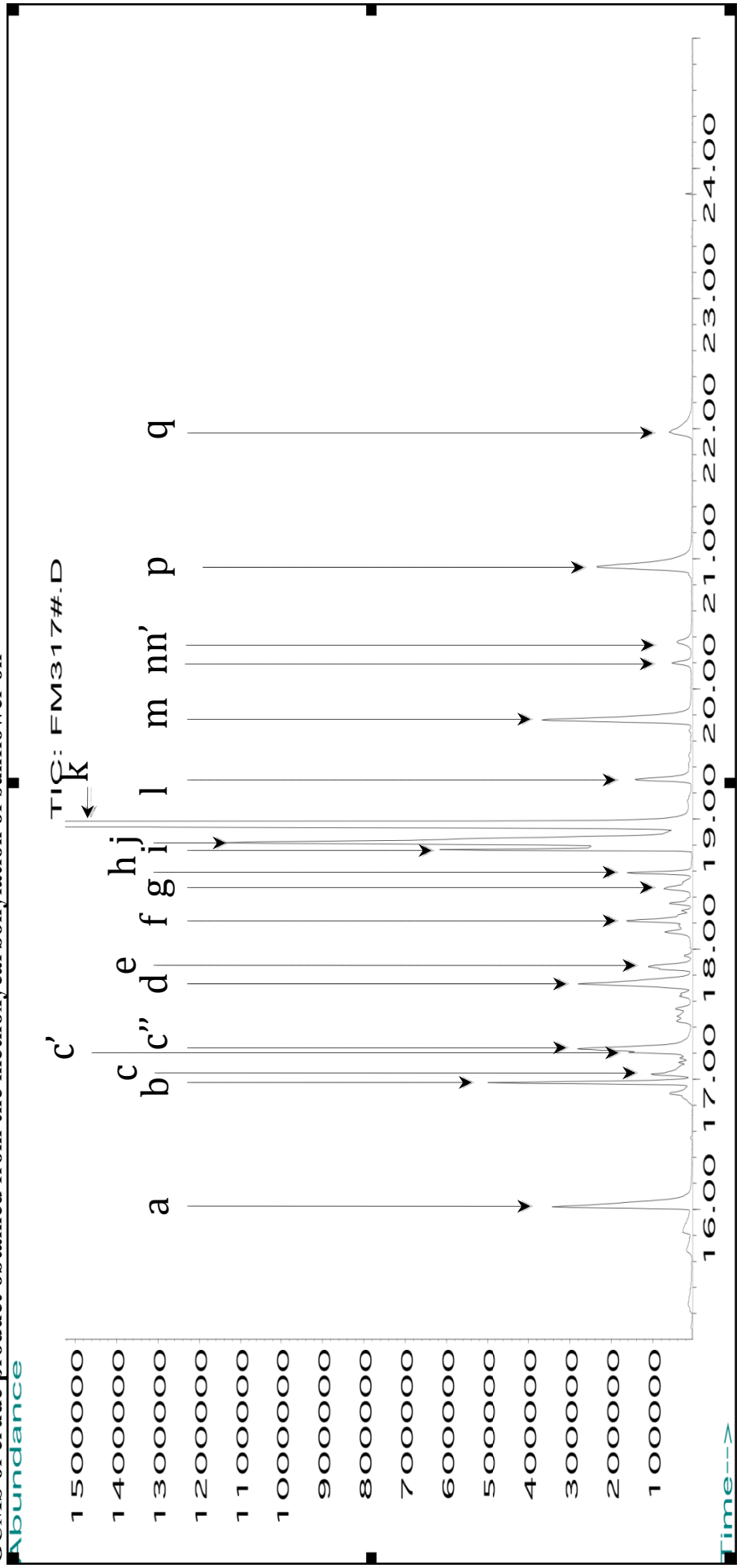



[1]H-NMR from dimethyl nonadecanedioate obtained from rapeseed oil




[1]H-NMR from dimethyl nonadecanedioate obtained from sunflower oil

**GCMS of crude product obtained from the methoxycarbonylation of sunflower oil**



**GCMS of crude product obtained from the methoxycarbonylation of olive oil**

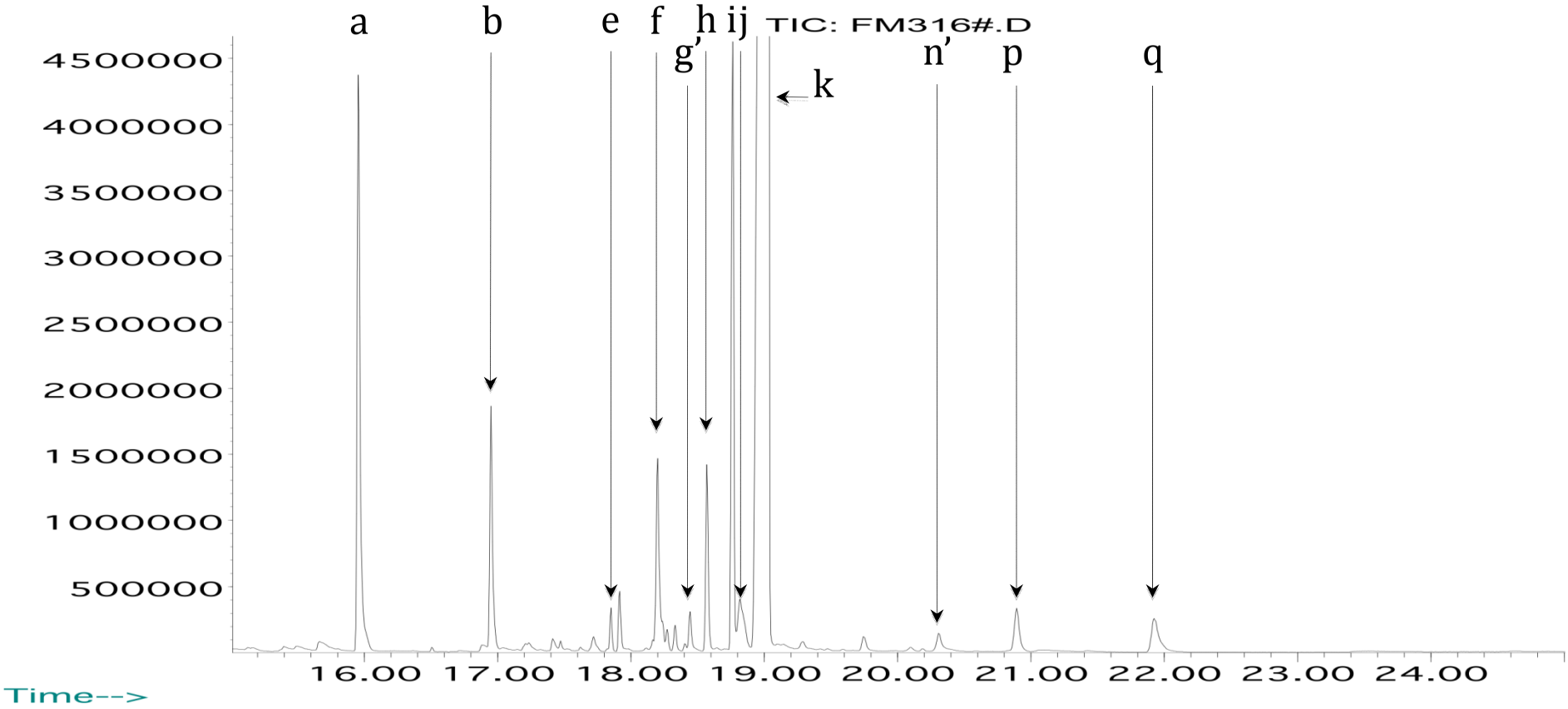
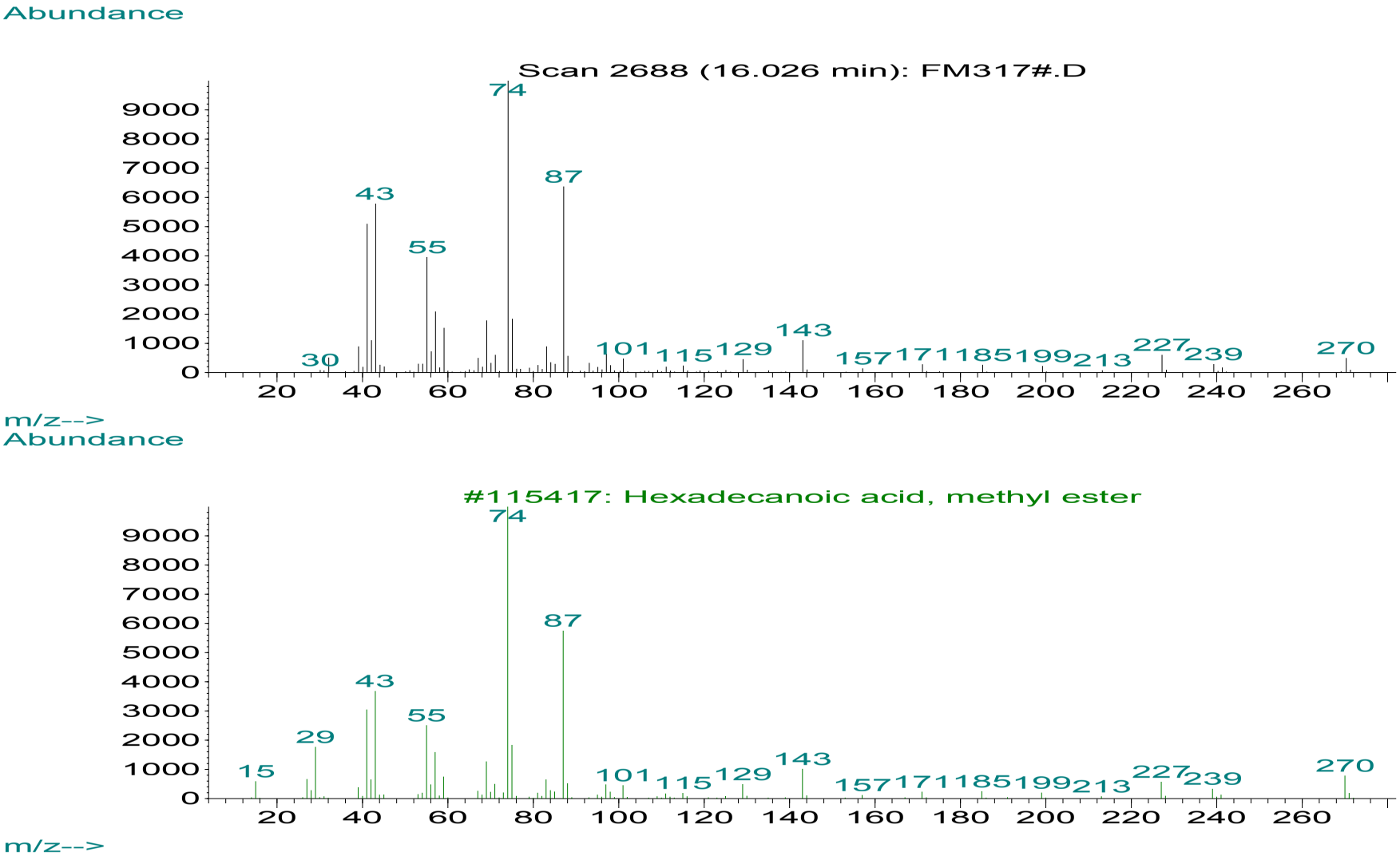


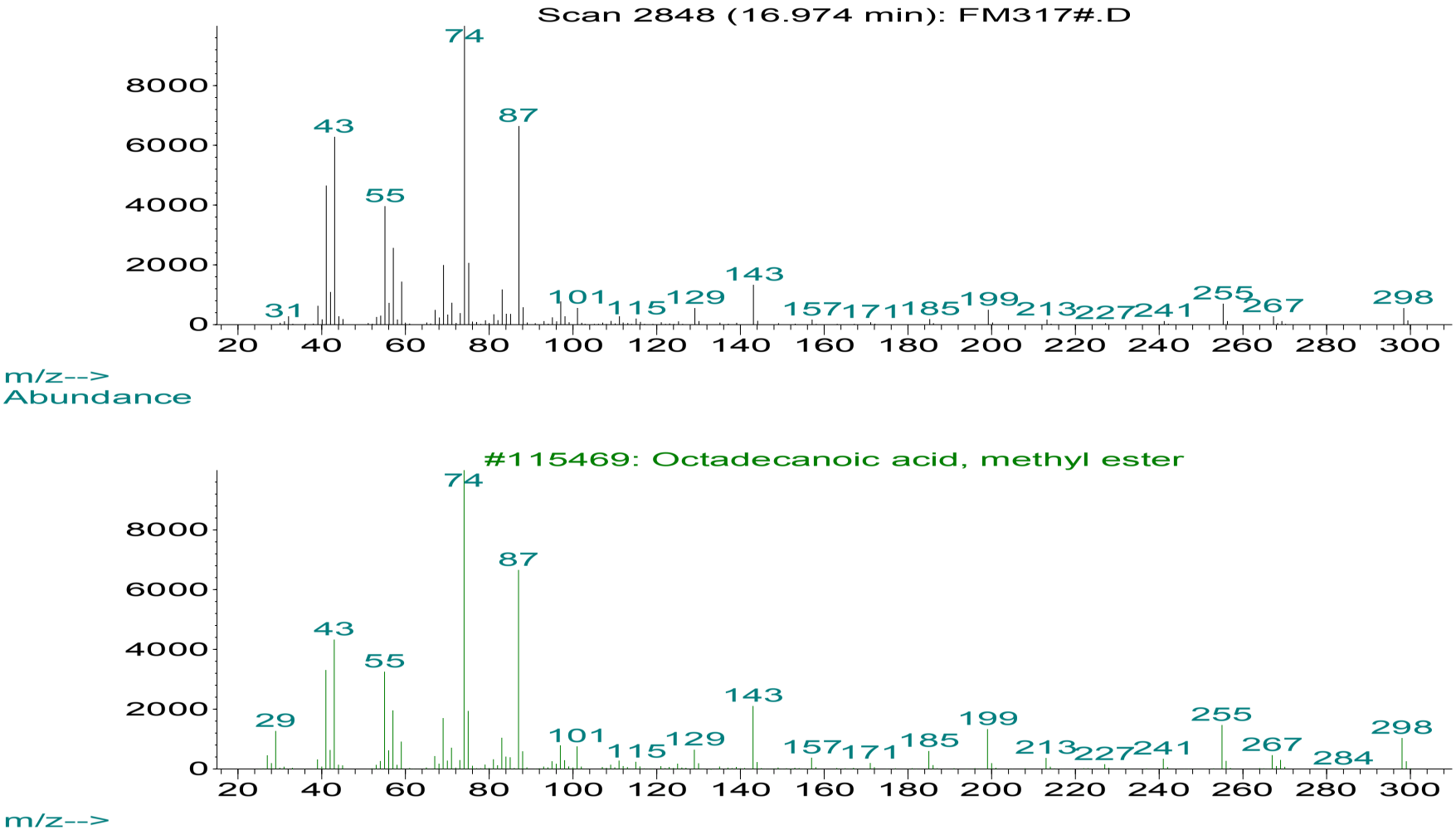
**Table 1 Tentative assignment of GCMS peaks based on observed highest mass peaks and comparisons with library spectra where possible.**

| | Highest mass peak | Assignment | % Fit |
|---|---|---|---|
| a: methyl hexadecanoate | 270 | $[M]^+$ | 97 |
| b: methyl octadecanoate | 298 | $[M]^+$ | 98 |
| c, c',c'': | 294 | | |
| d: | 281 | | |
| e: | 326 | | |
| f: | 324* | | |
| g: | 322 | | |
| g': | 324* | | |
| h: | 324* | | |
| i: 1,2-bis((di-*tert*-butylphosphino)methyl)benzene | 337 | $[M - Bu^t]^+$ | |
| j: isomer of dimethyl nonadecenedioate | 354 | $[M]^+$ | |
| k: dimethyl nonadecanedioate | 356 | $[M]^+$ | 91 |
| l: | 323 | | |
| m: | 371 | | |
| n: | 382 | | |
| n' | 354 | | |
| p: | 356 | | |
| q: 1,2-bis((di-*tert*-butylphosphoryl)methyl)benzene | 426 | $[M]^+$ | |

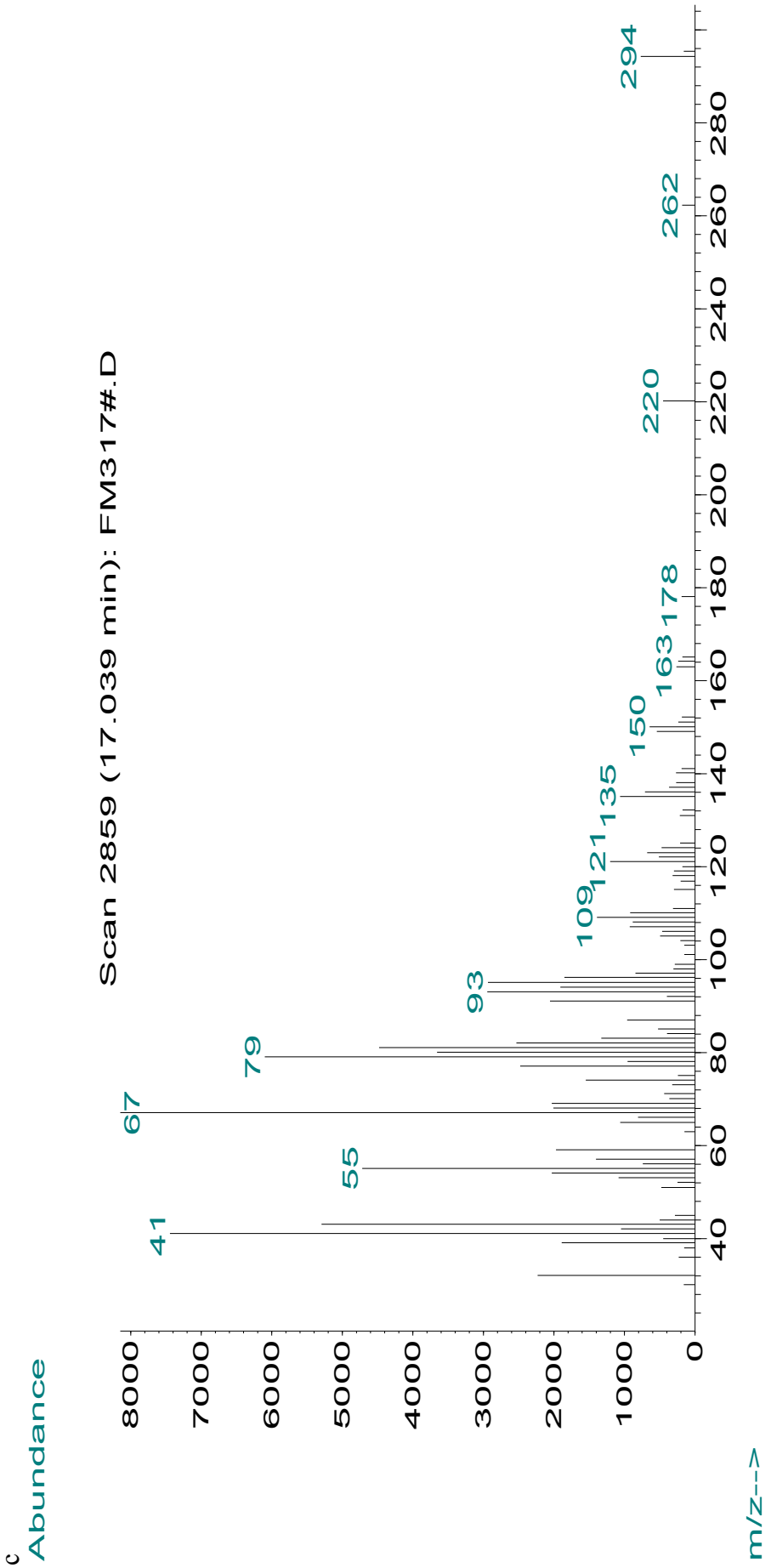
Peaks with mass 324 are probably from branched isomers of C19 dimethyl esters, but the spectra for different isomers are so we have not provided assignments.

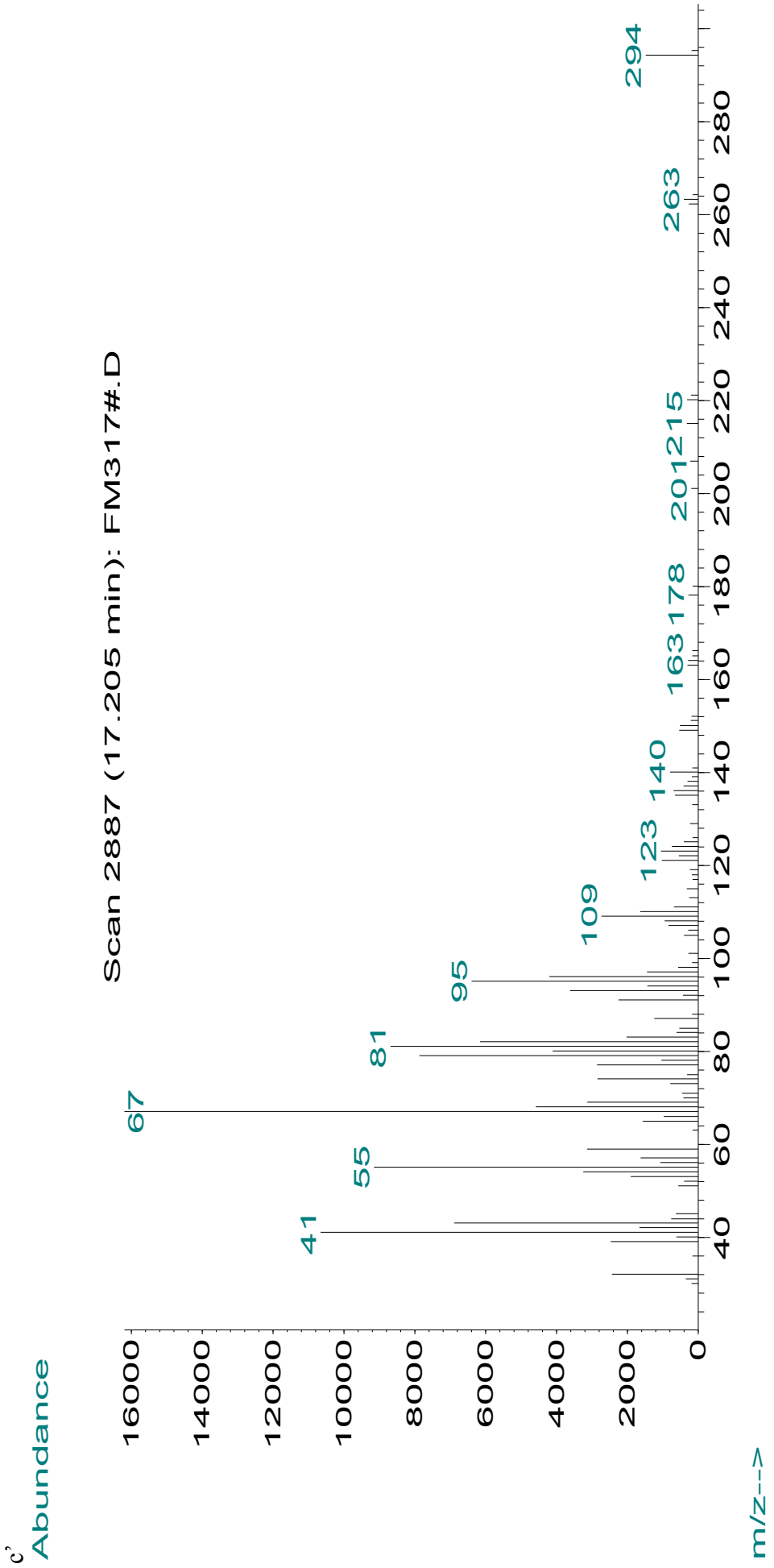


b

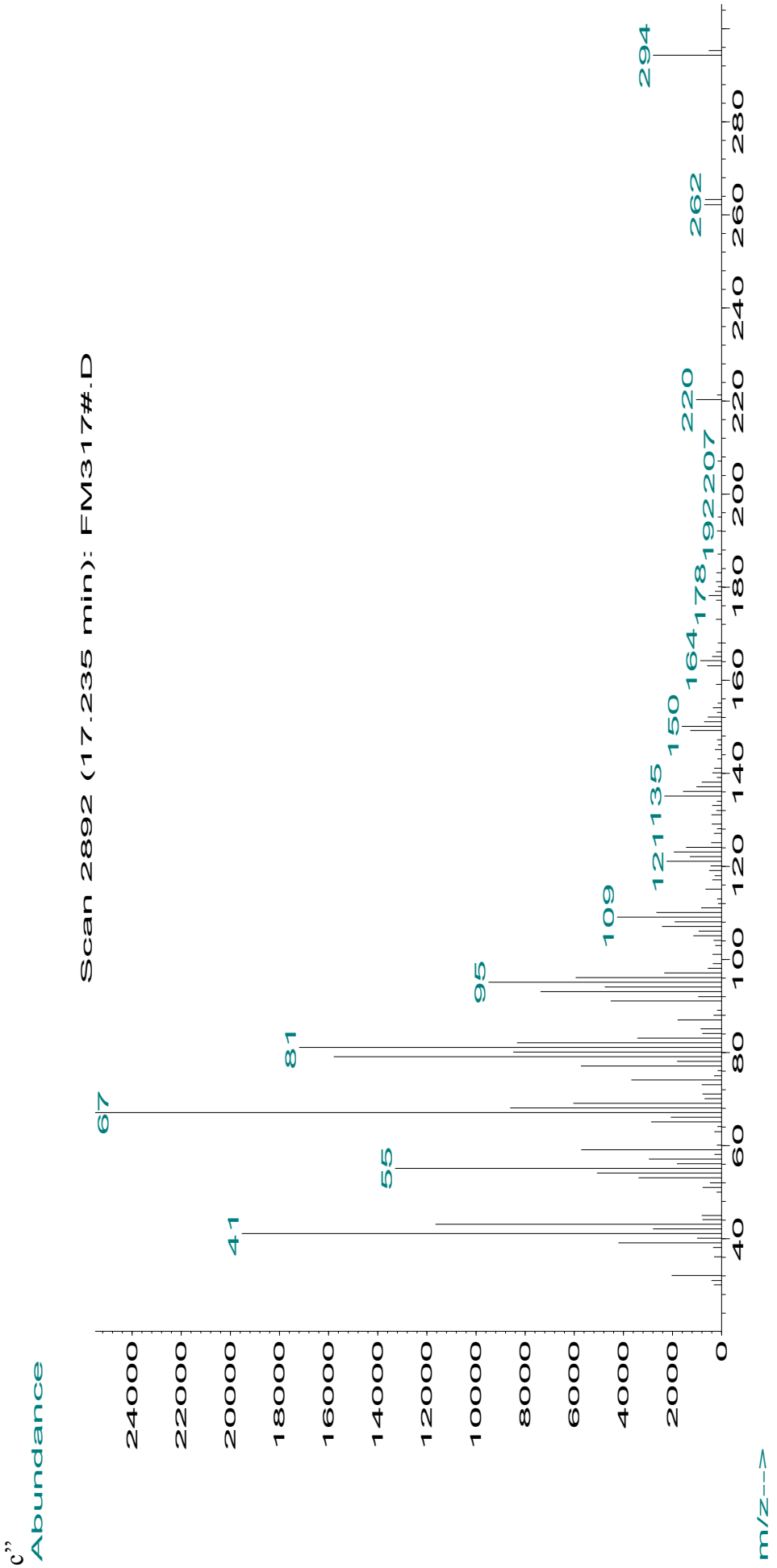


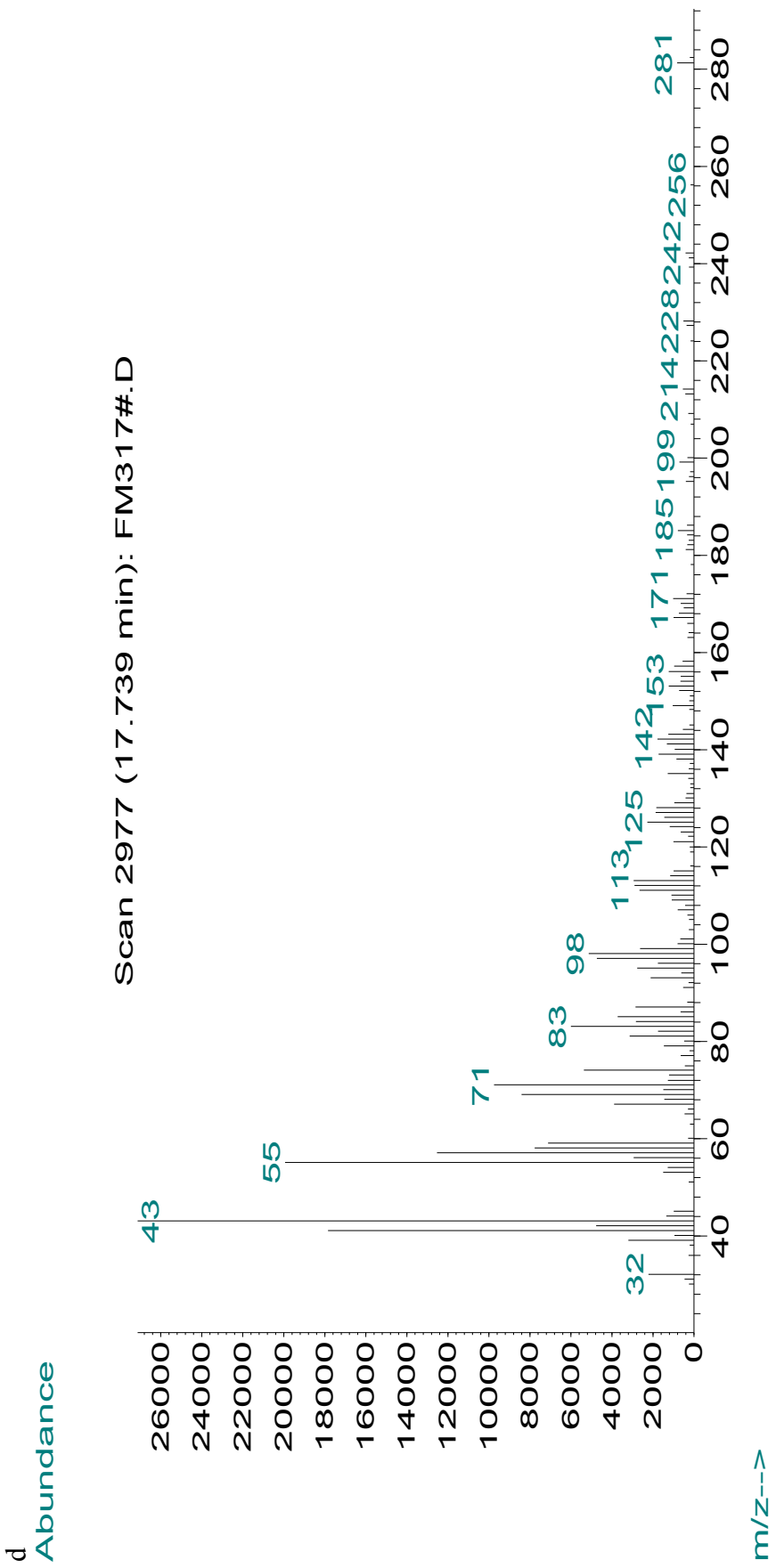
c

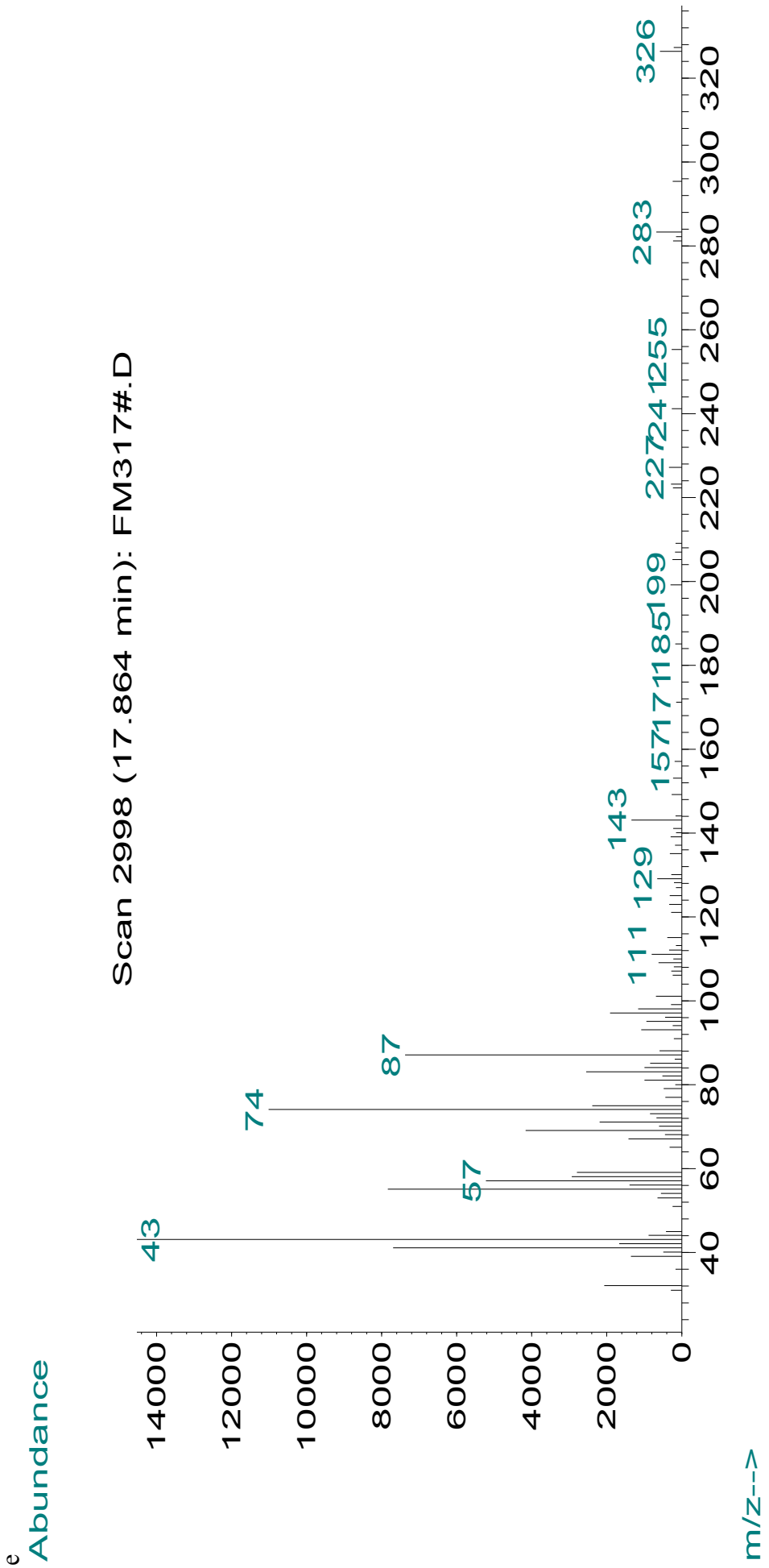




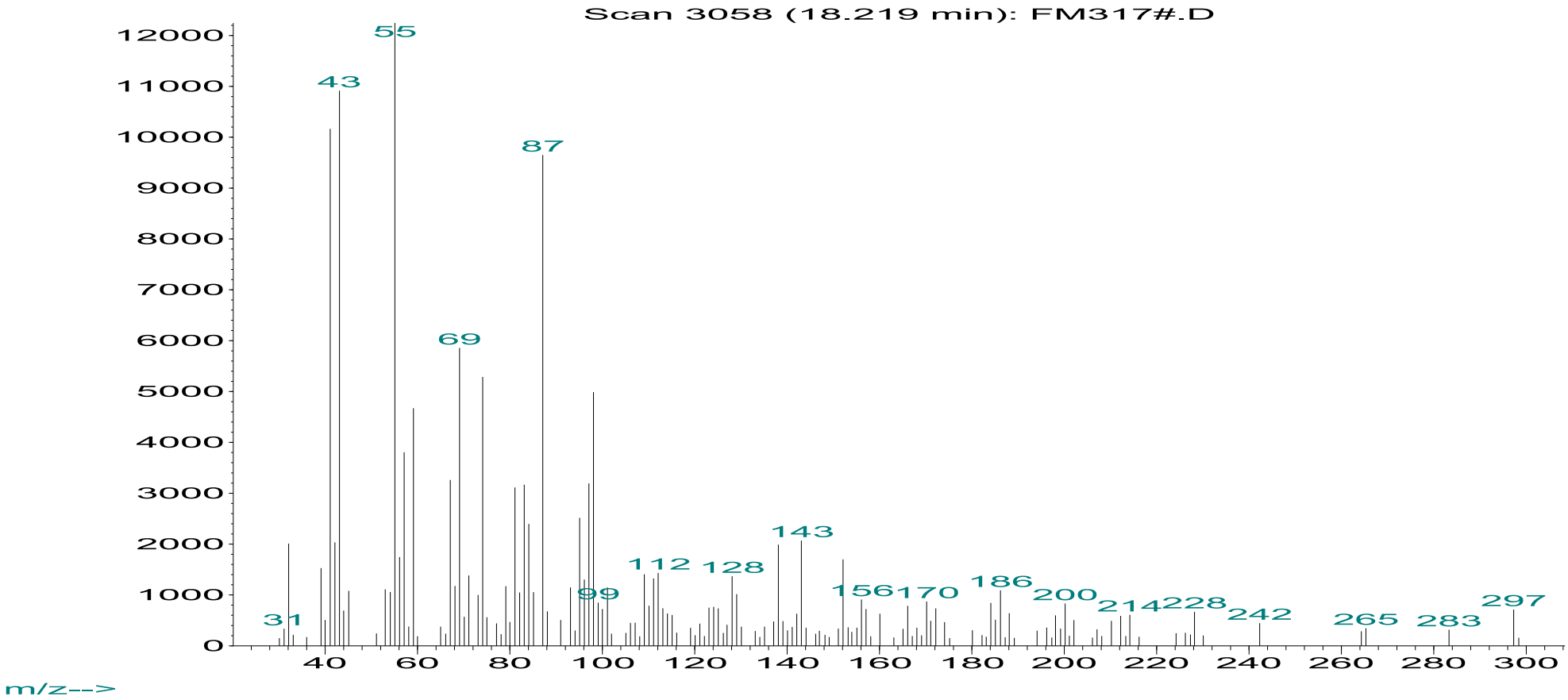
c”



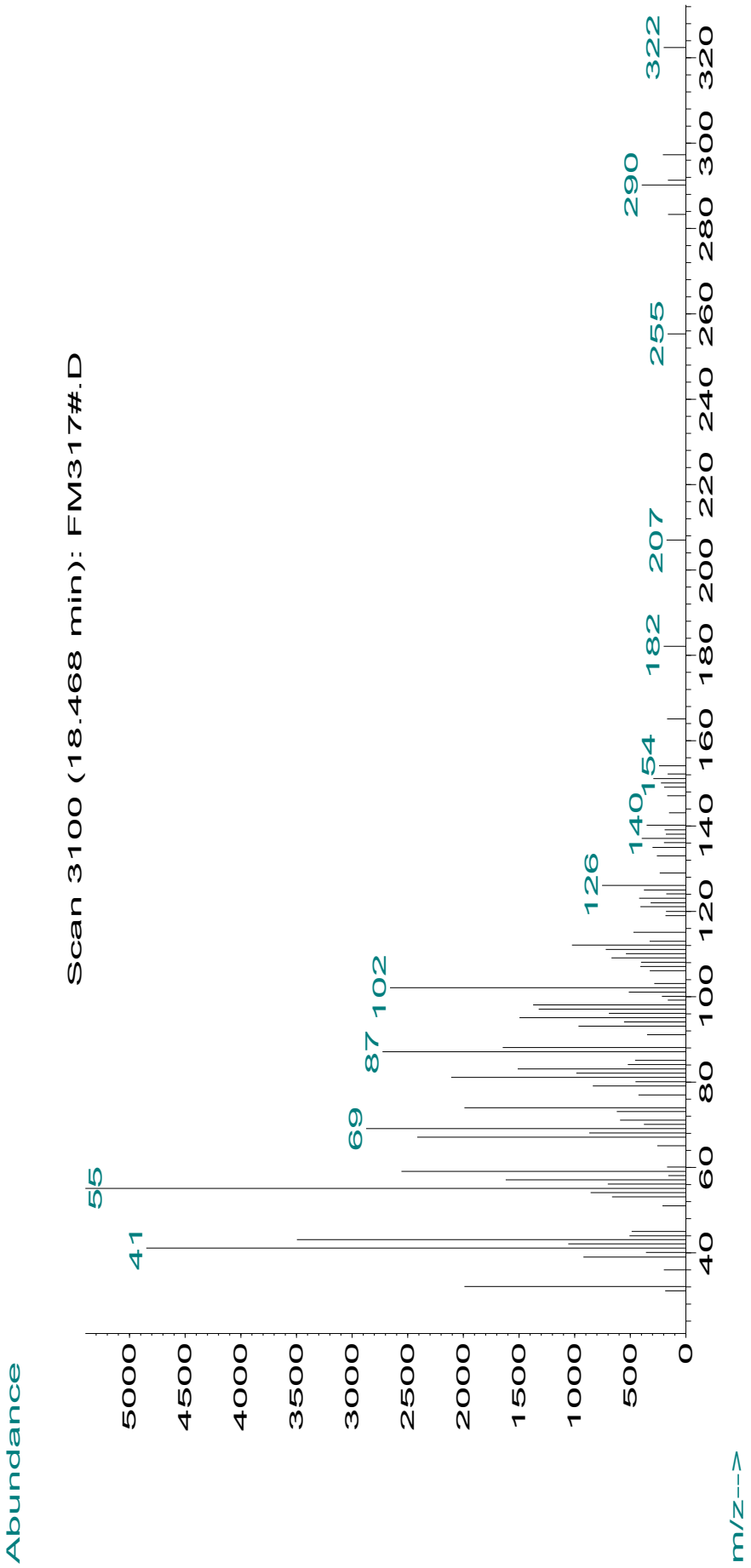




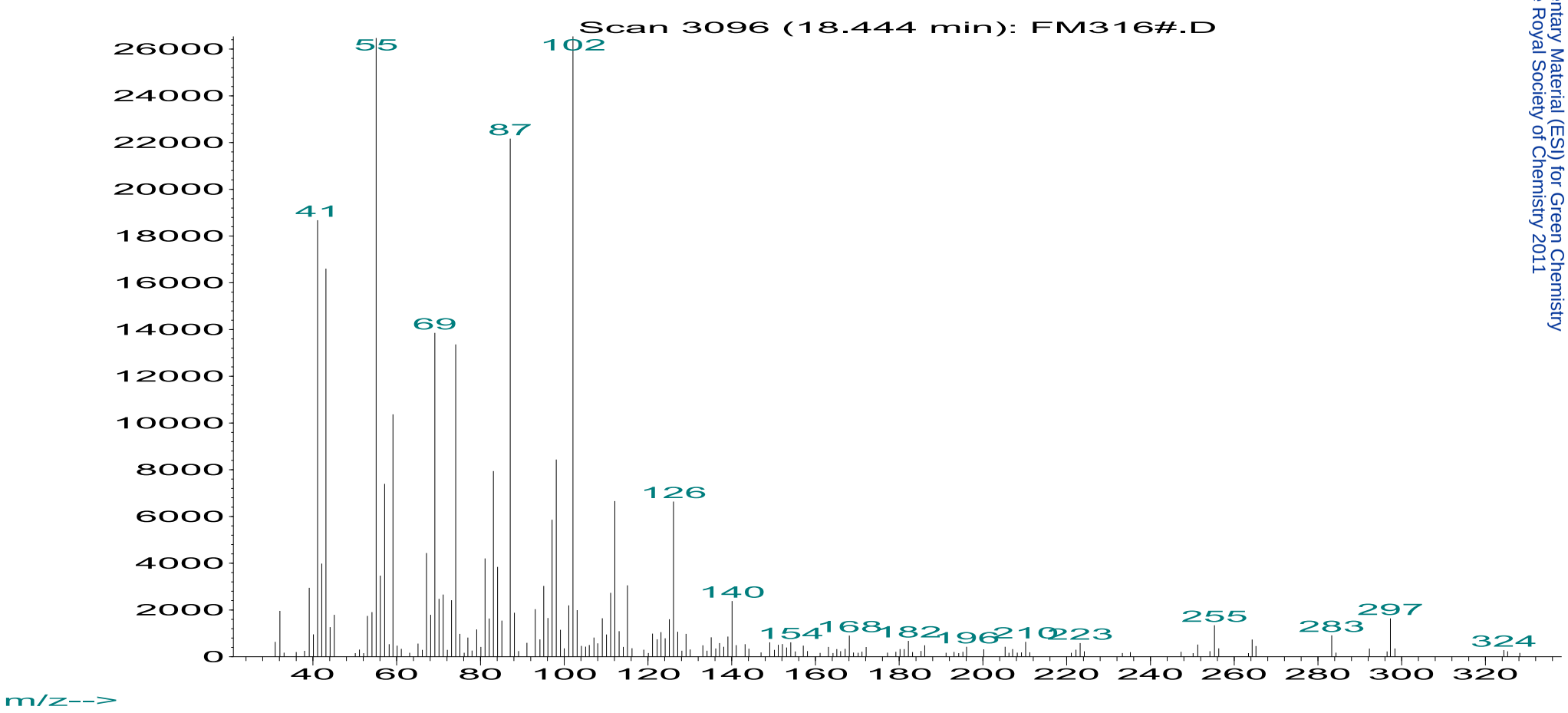
f




g




g’ (from olive oil)

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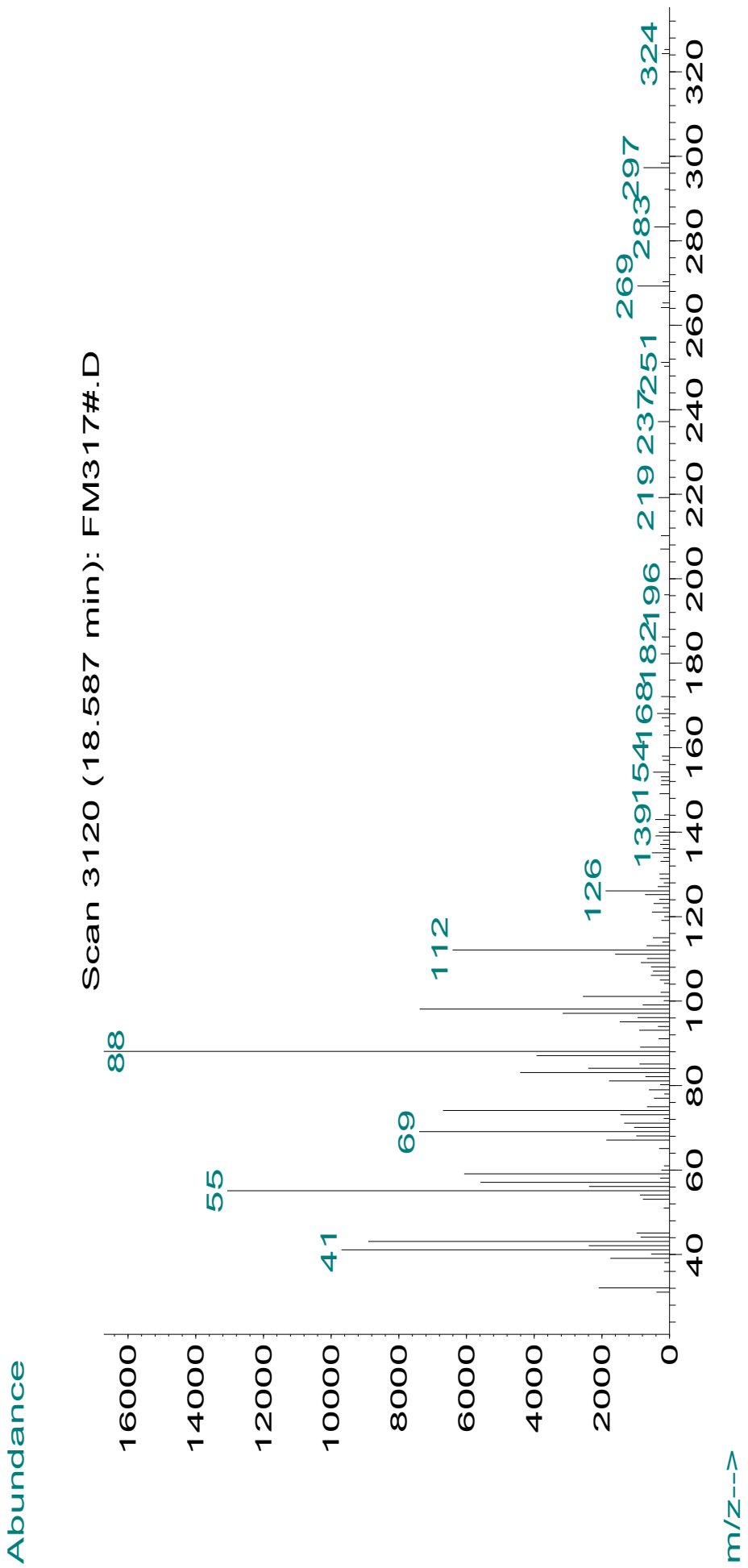
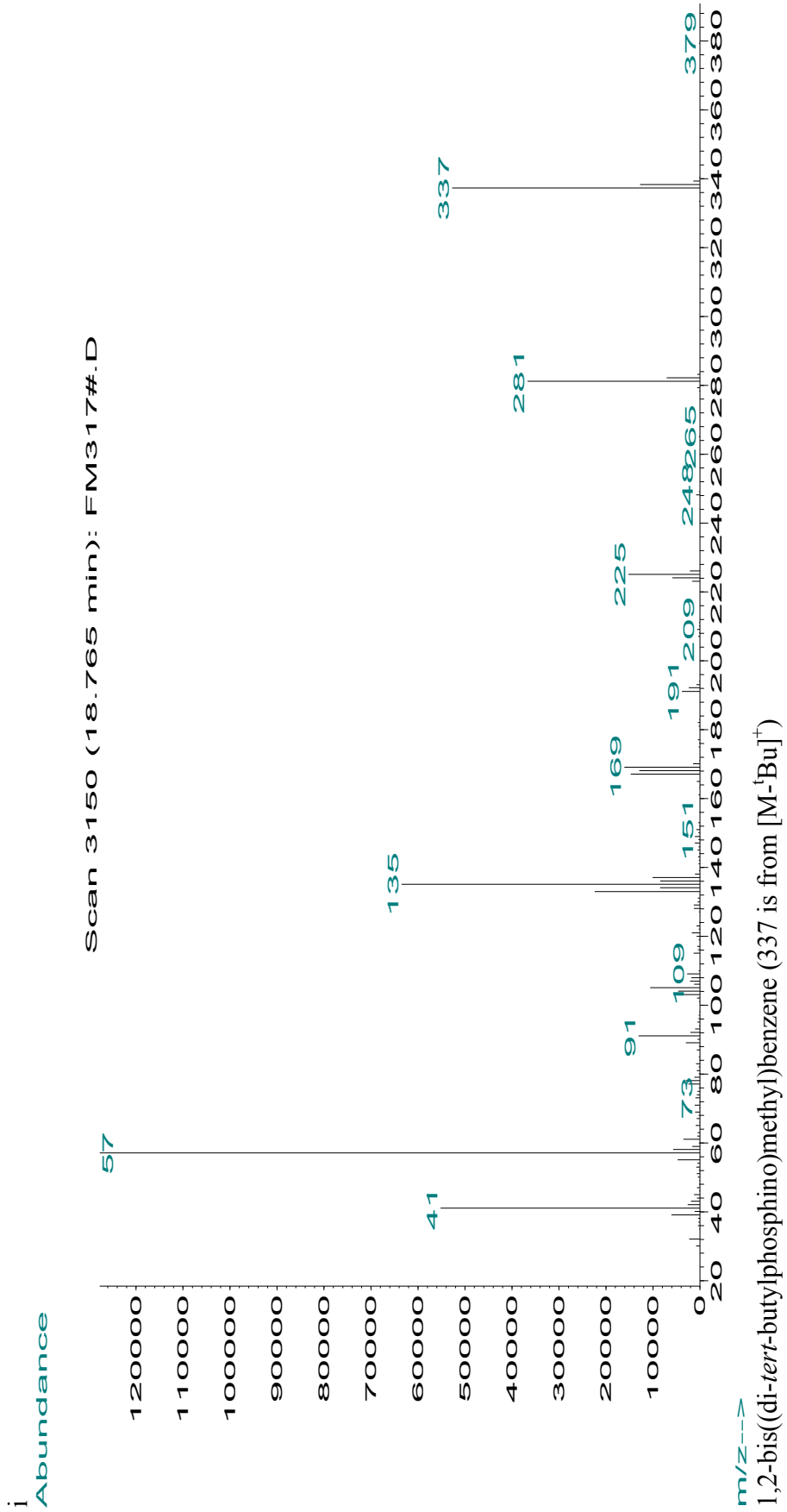
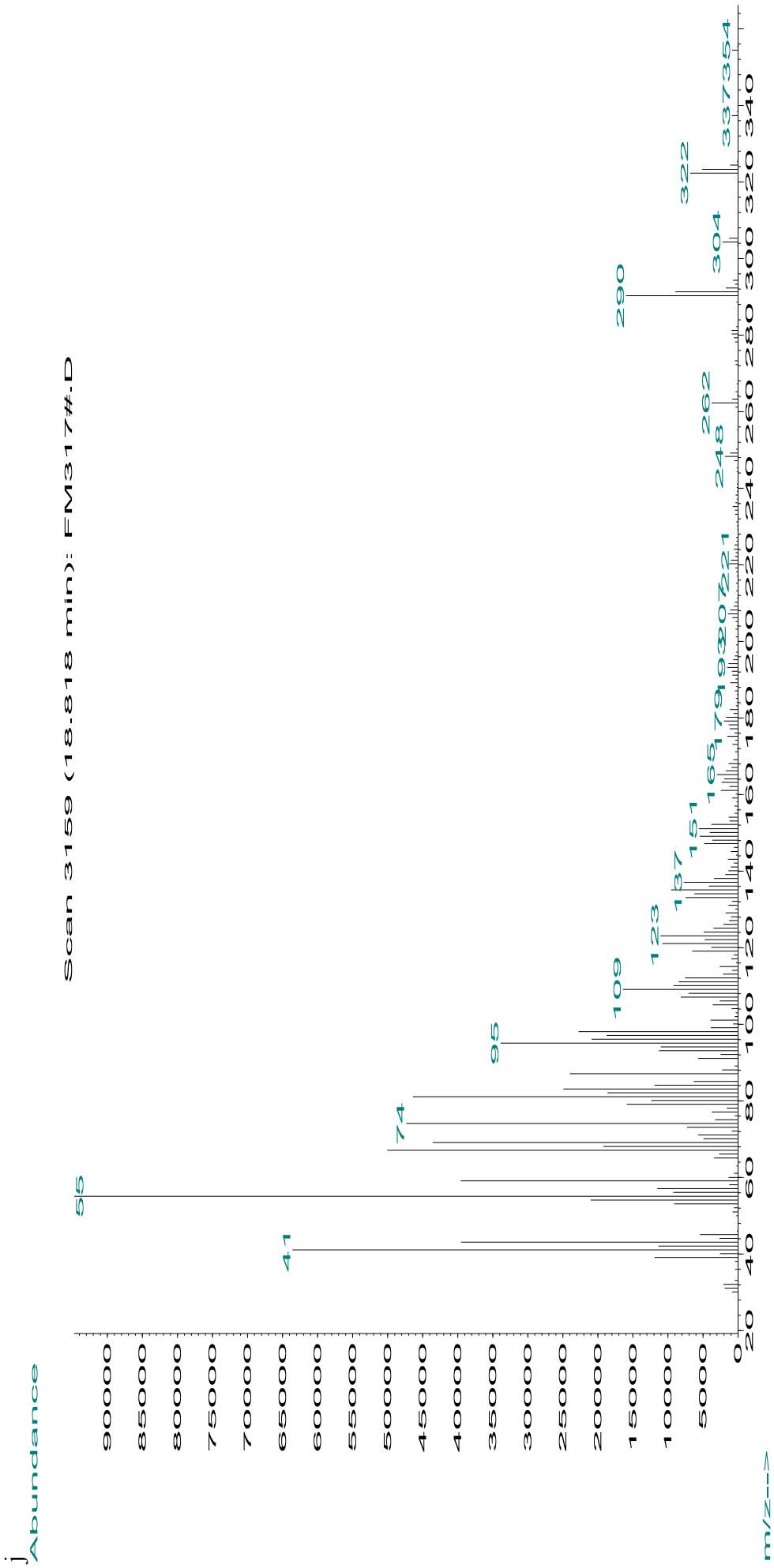
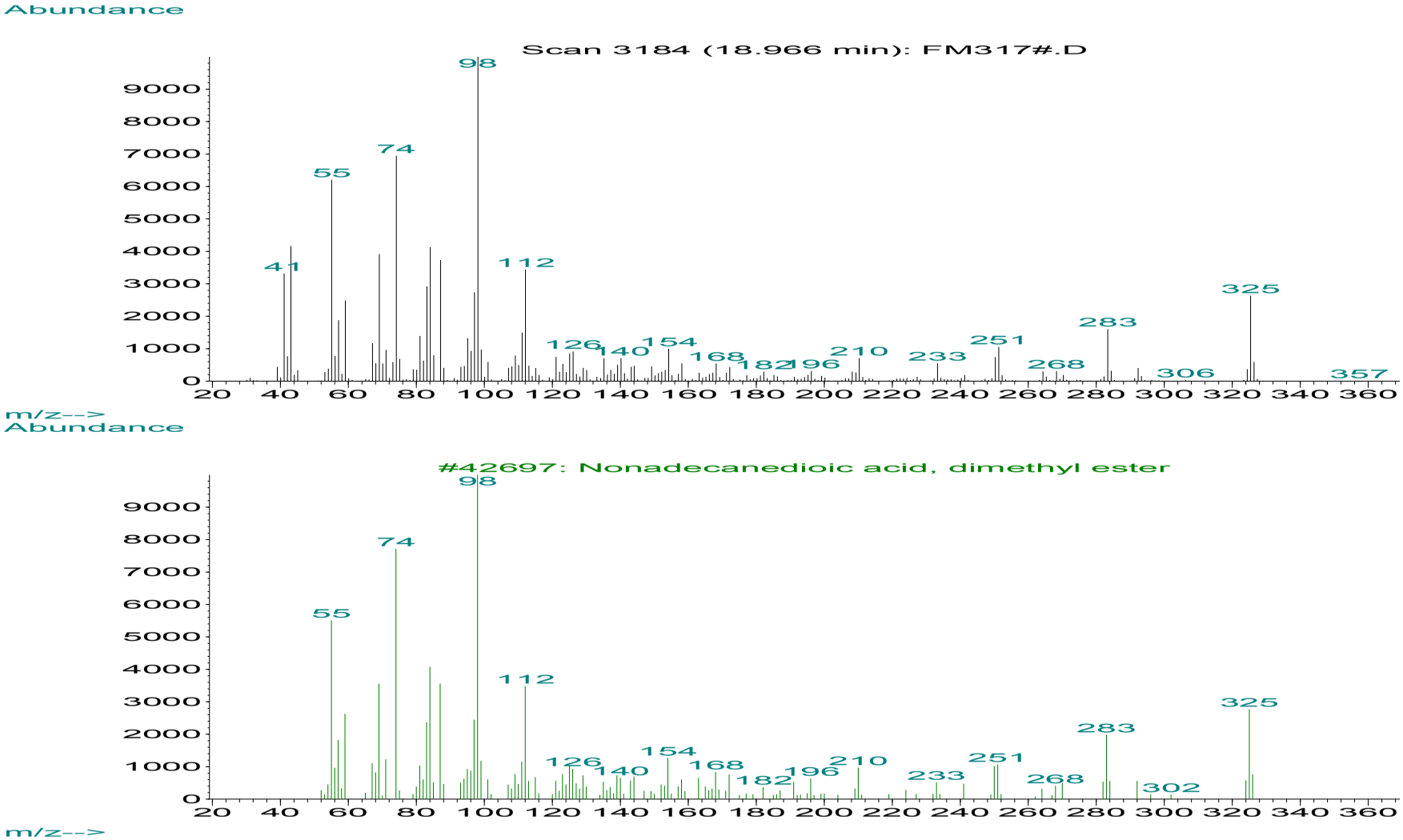




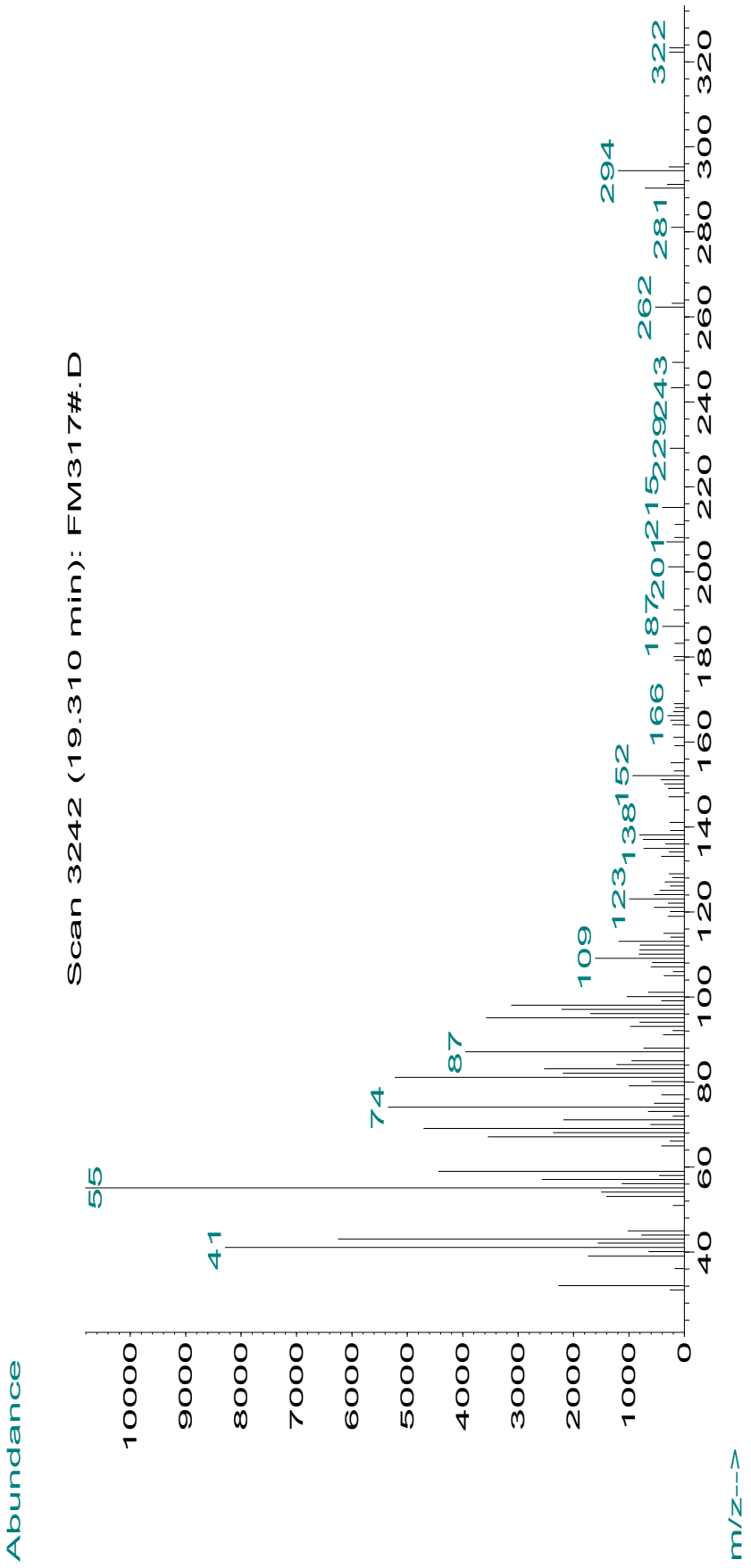

1,2-bis((di-*tert*-butylphosphino)methyl)benzene (337 is from $[M\text{-}^{t}Bu]^{+}$)

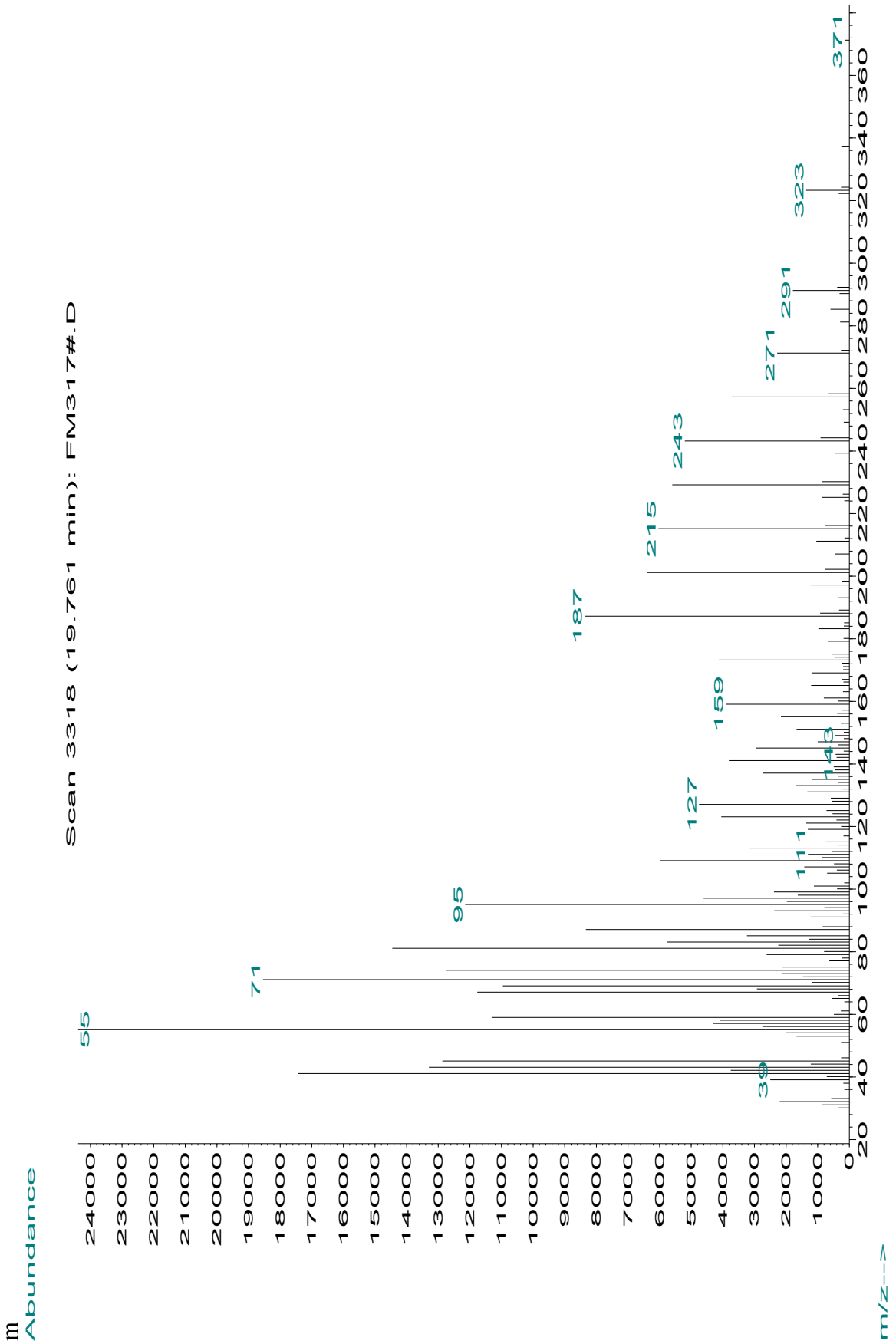



k

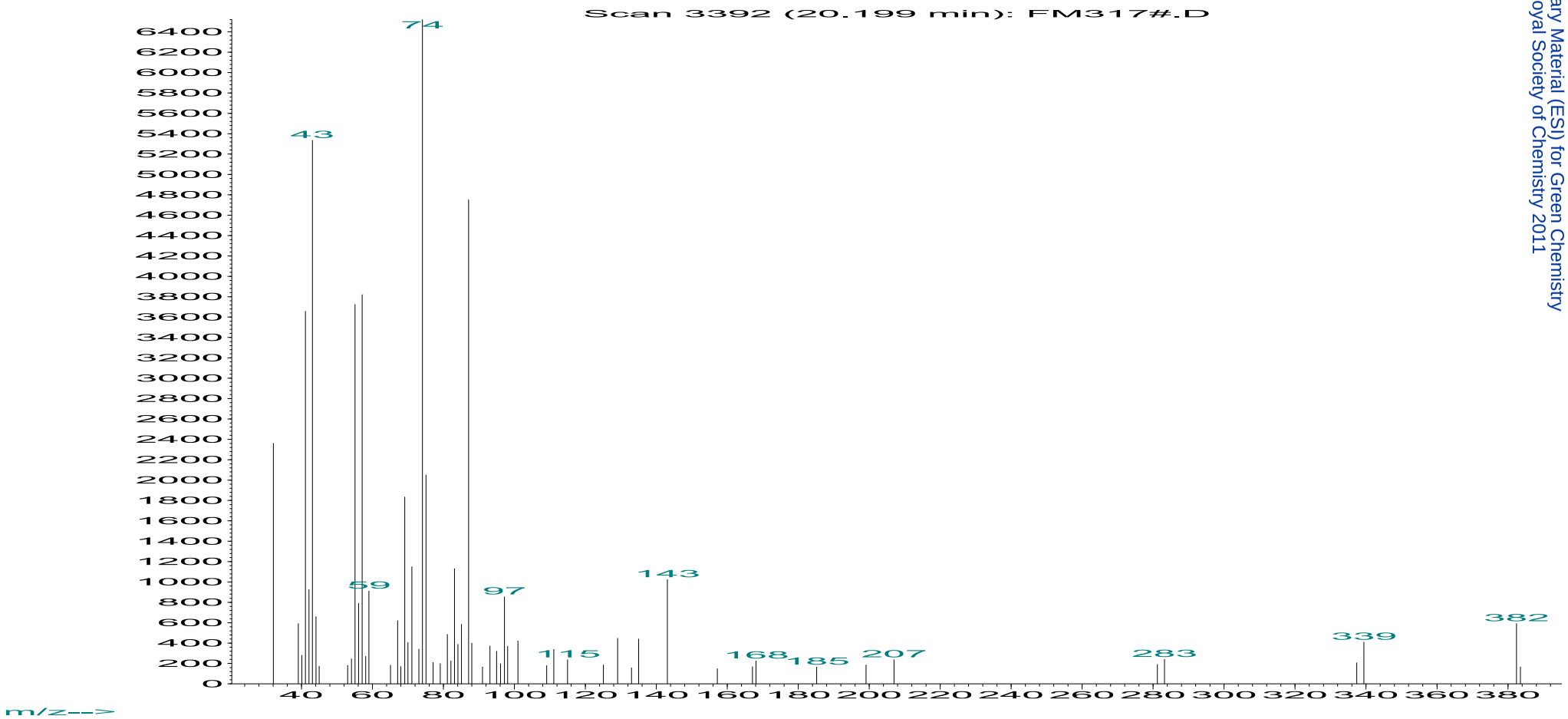



1

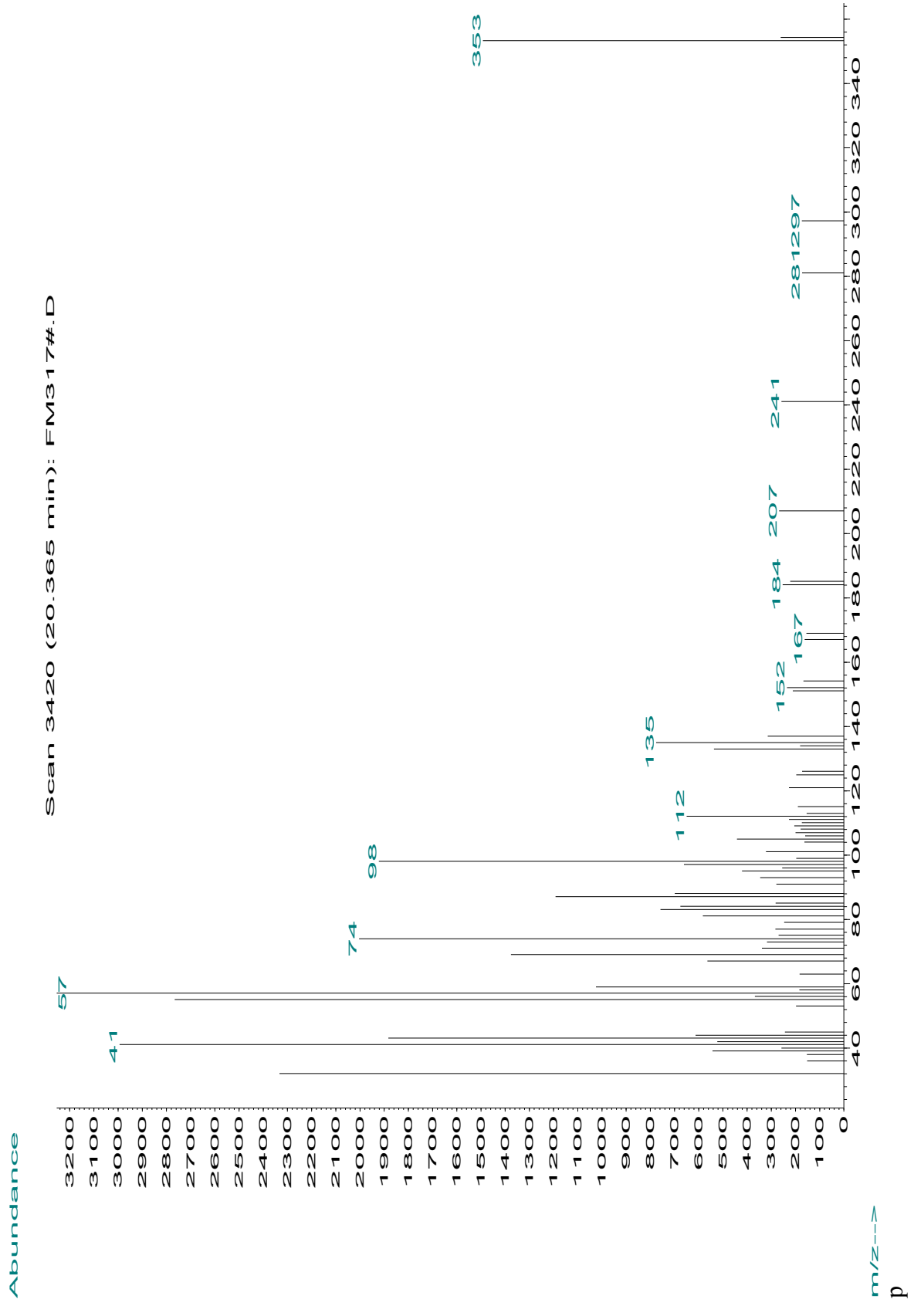




n




n`

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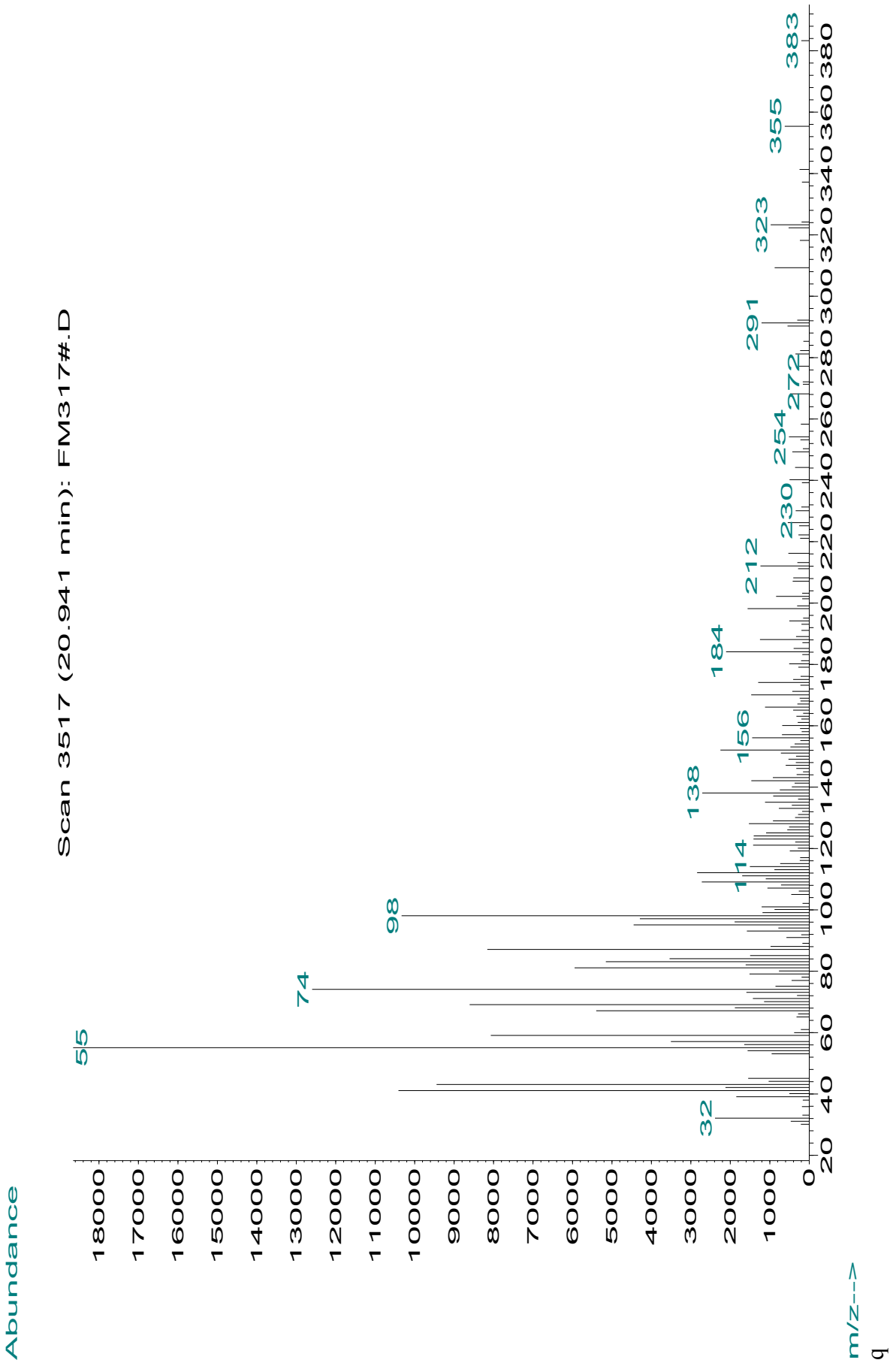
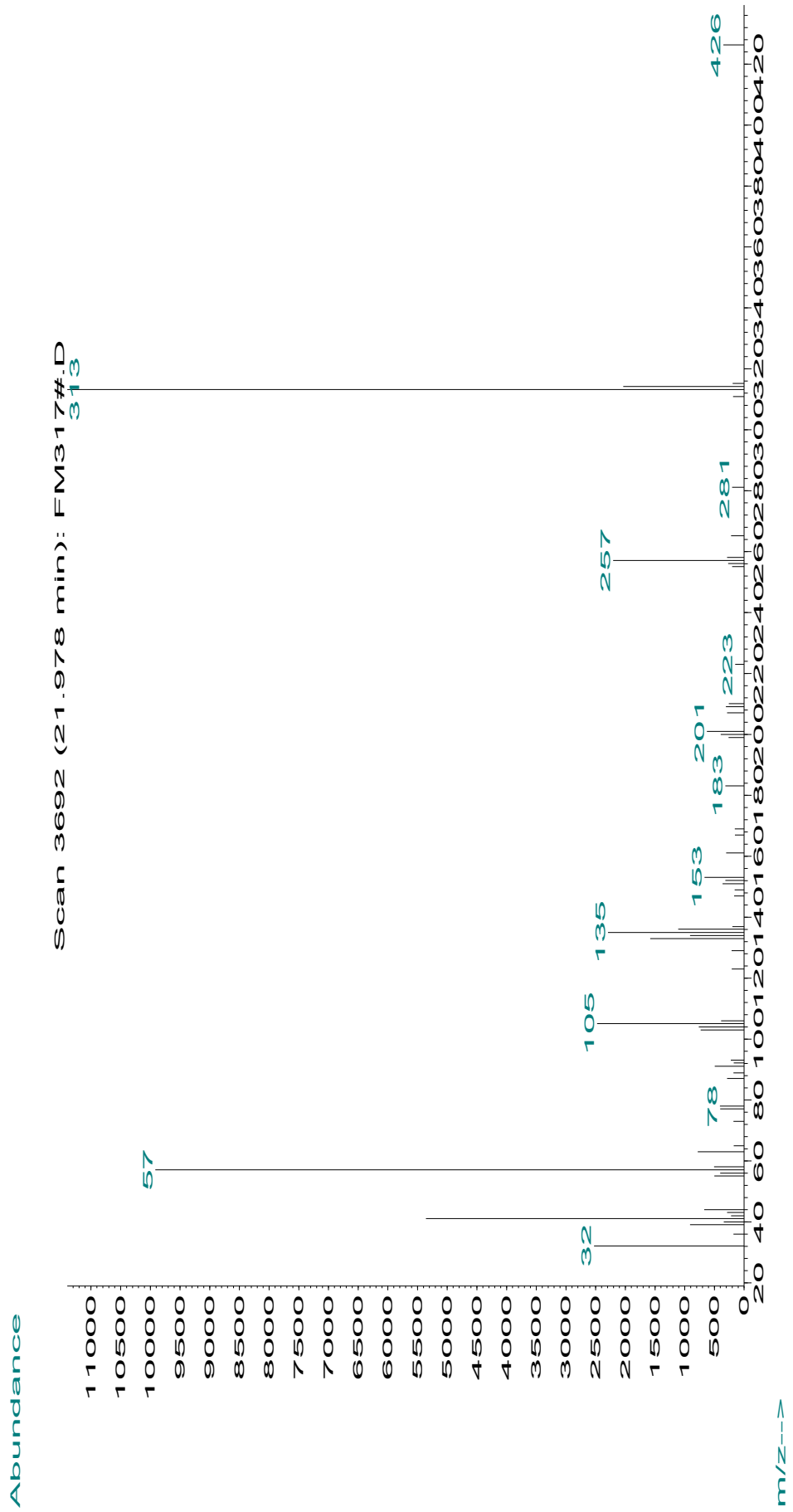
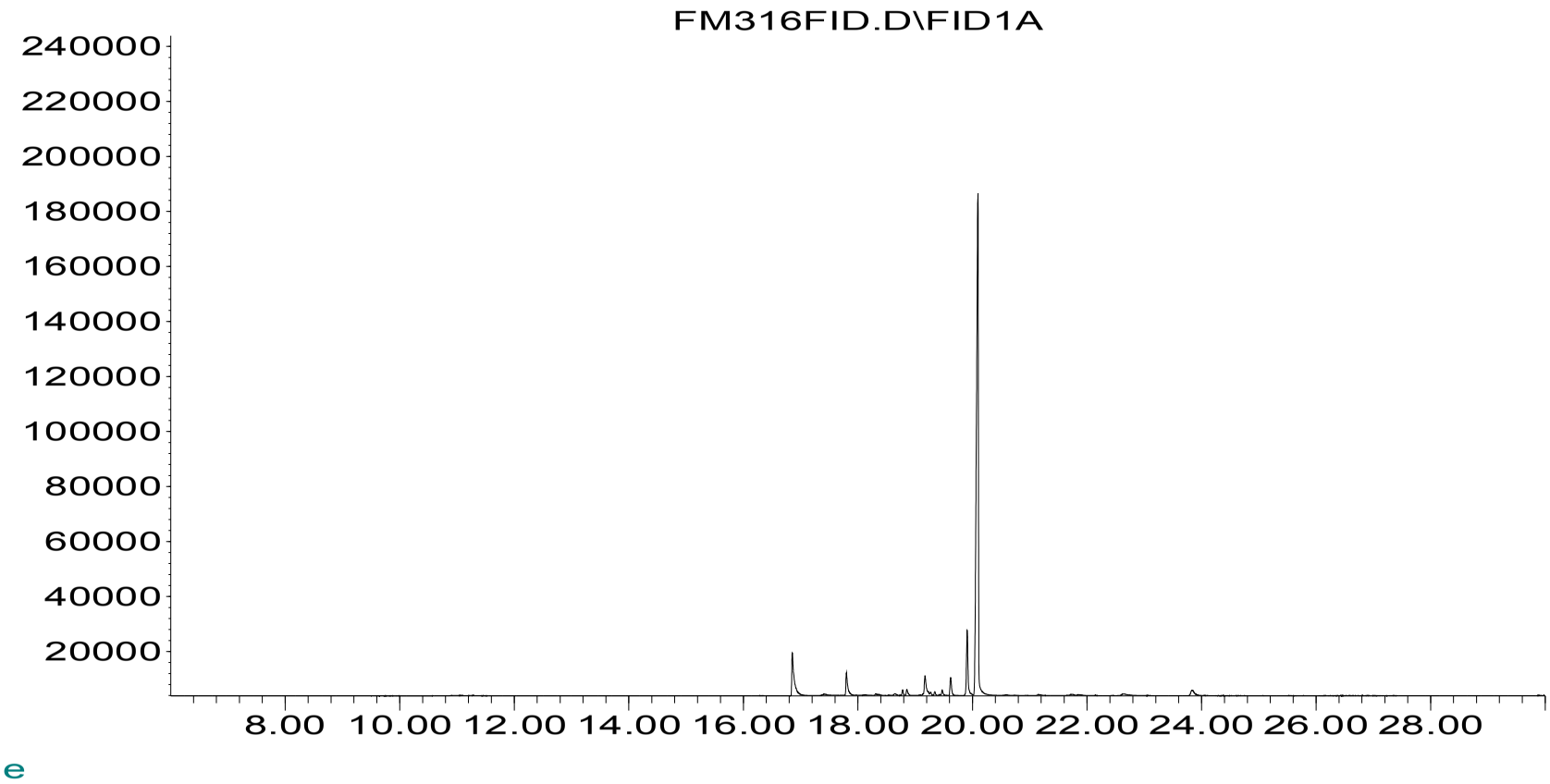



q

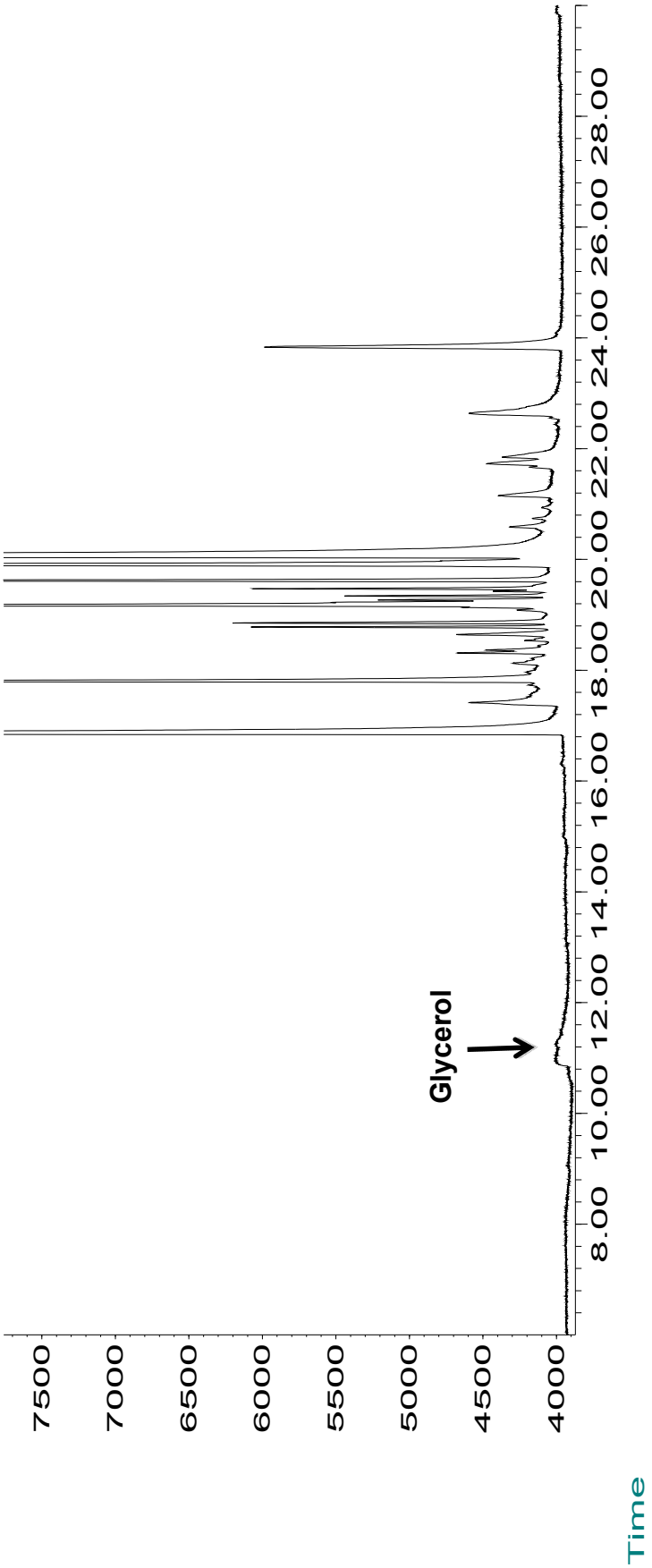



1,2-bis((di-*tert*-butylphosphoryl)methyl)benzene

**FID of crude product from the methoxycarbonylation of olive oil**



**Zoom FID for crude product from methoxycarbonylation of olive oil**

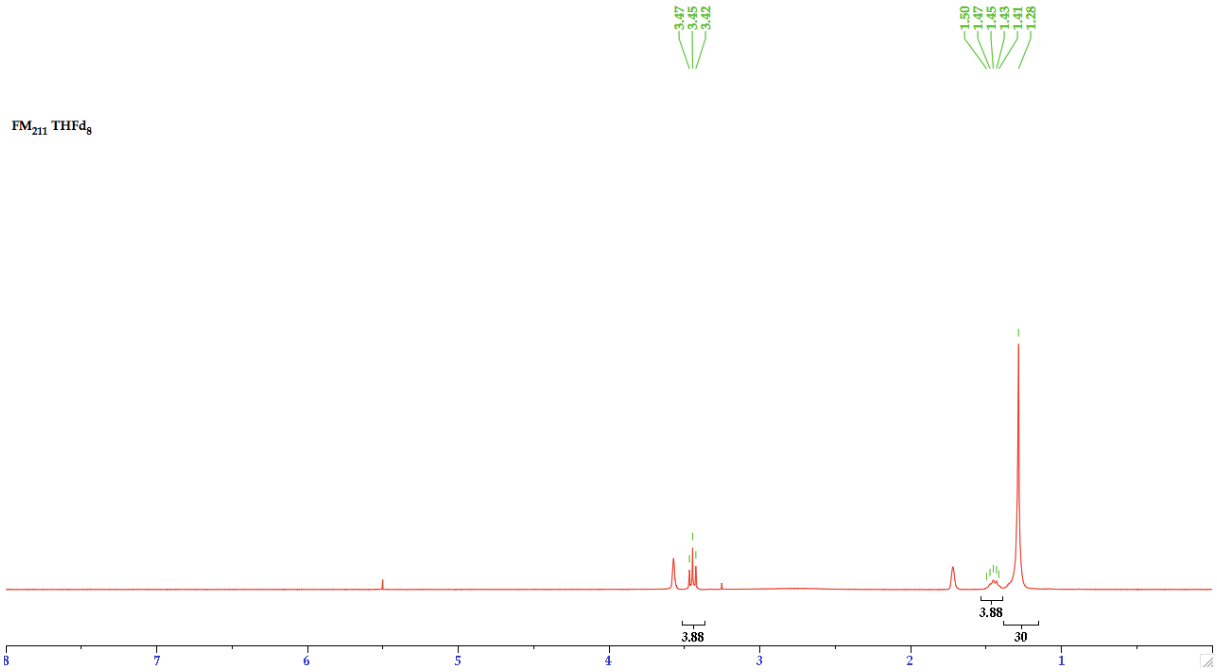


## Characterisation of reduction products

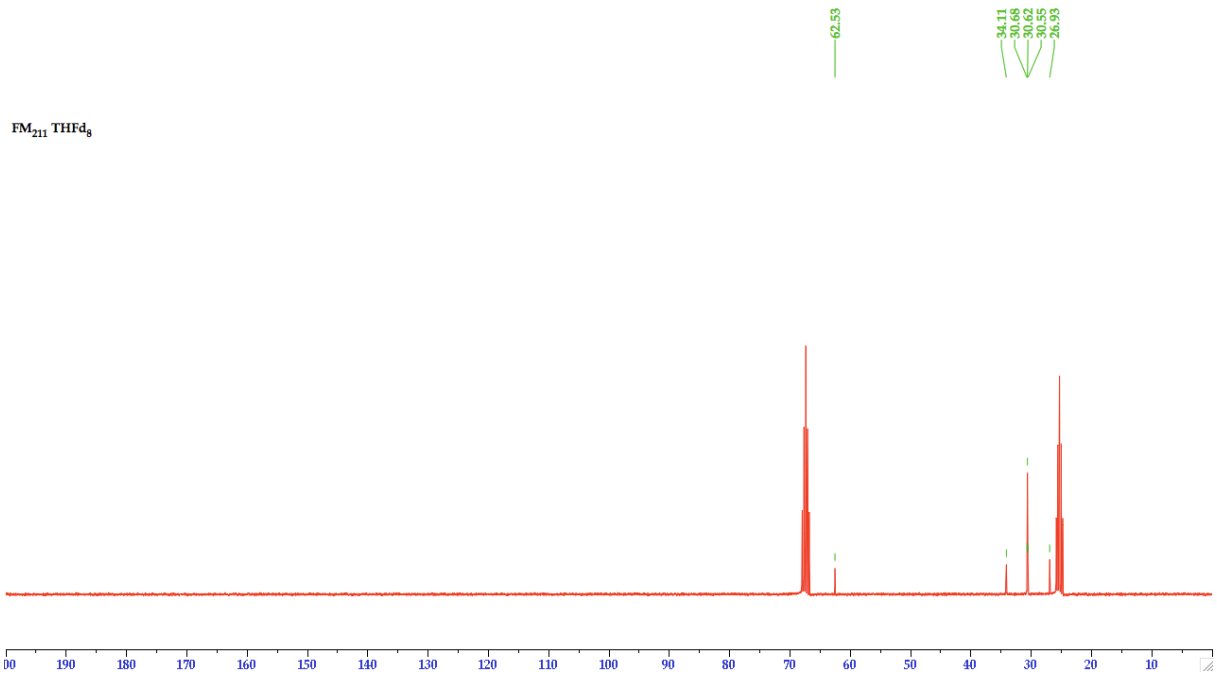
## 1,19-nonadecanediol:

## First method:

### $^{1}$H NMR spectrum

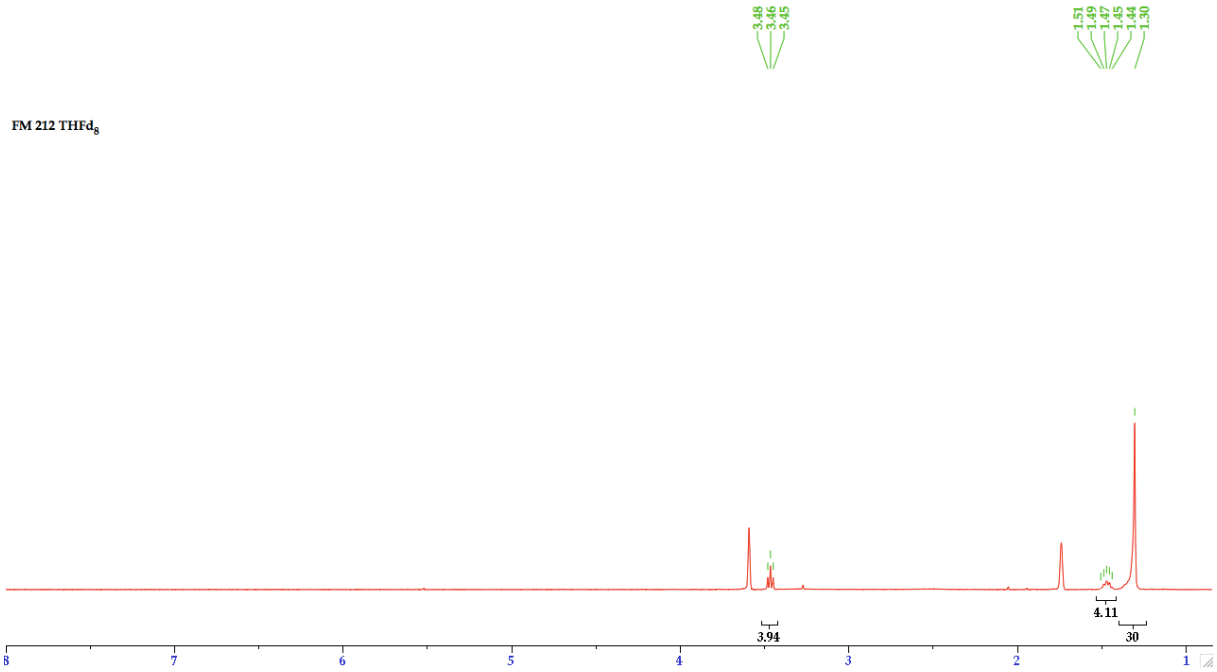



### $^{13}$C NMR spectrum

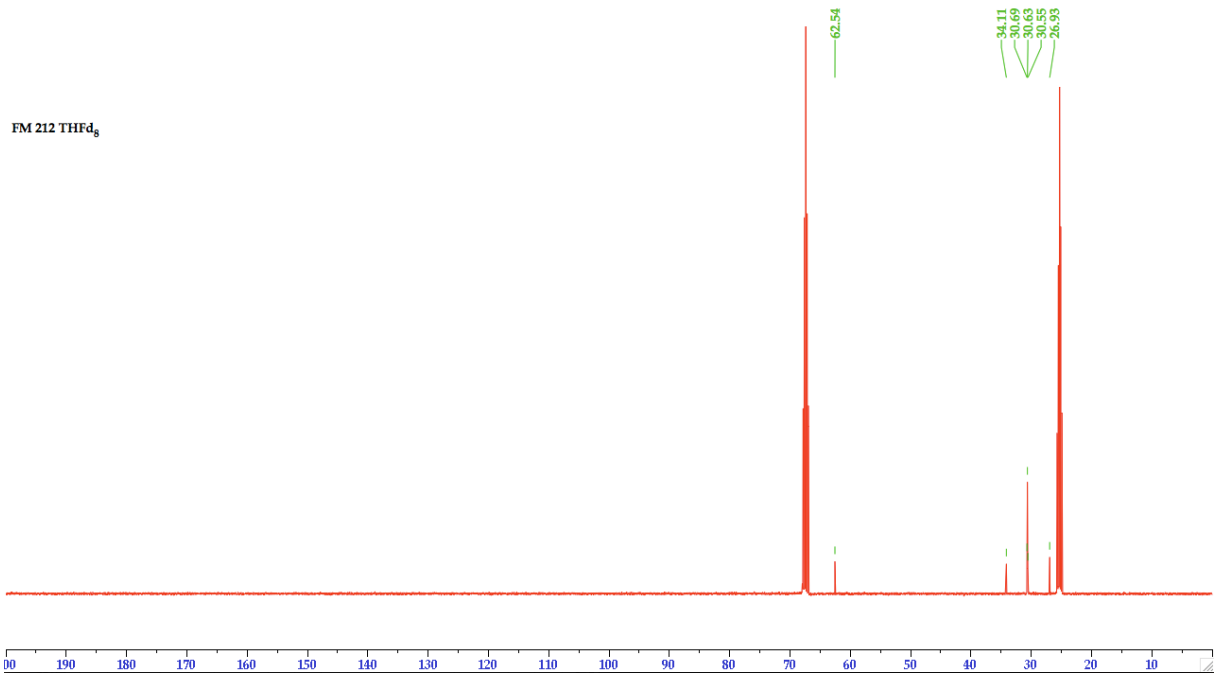


## Second method:

## $^{1}$H NMR spectrum

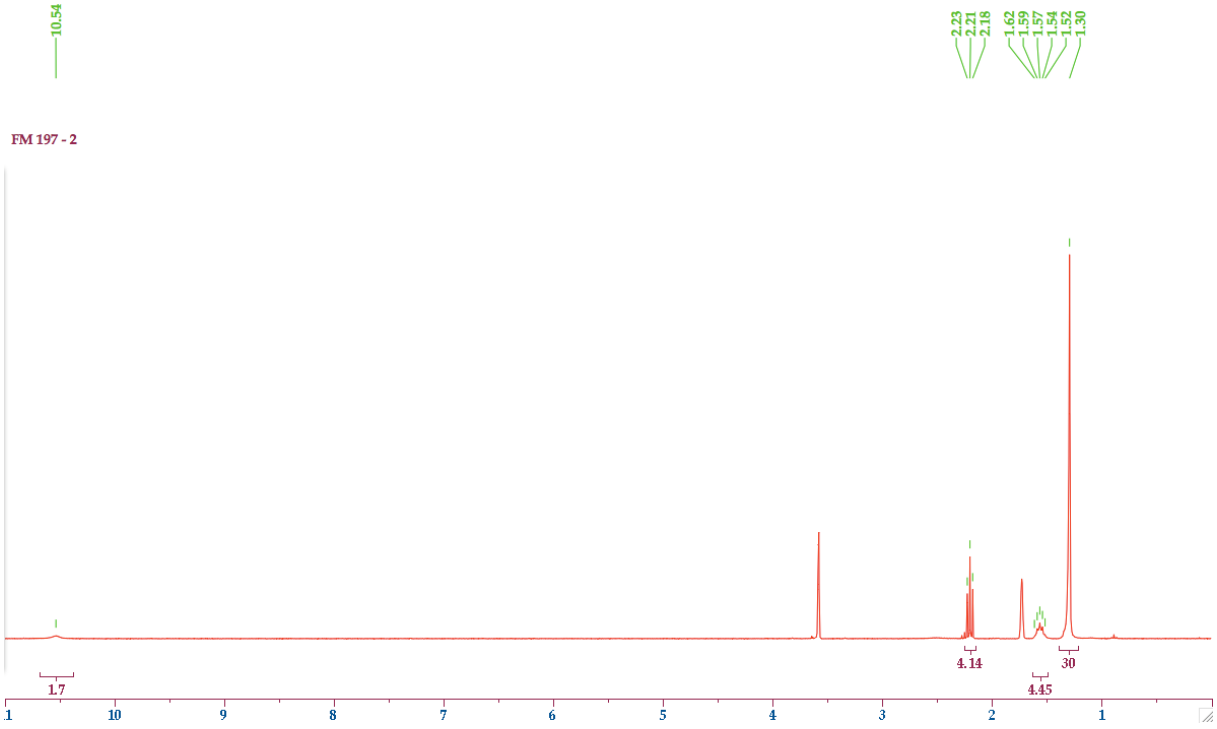



## $^{13}$C NMR spectrum

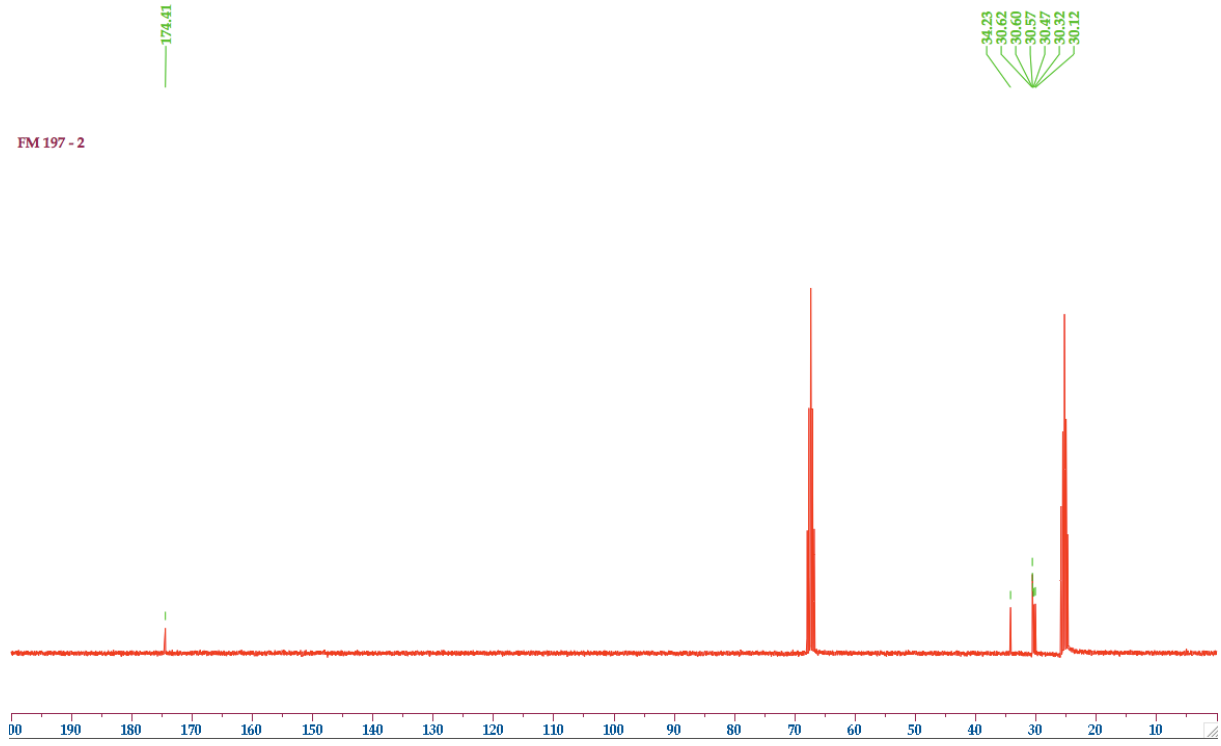


*1, 19-Nonadecanedioic acid:*

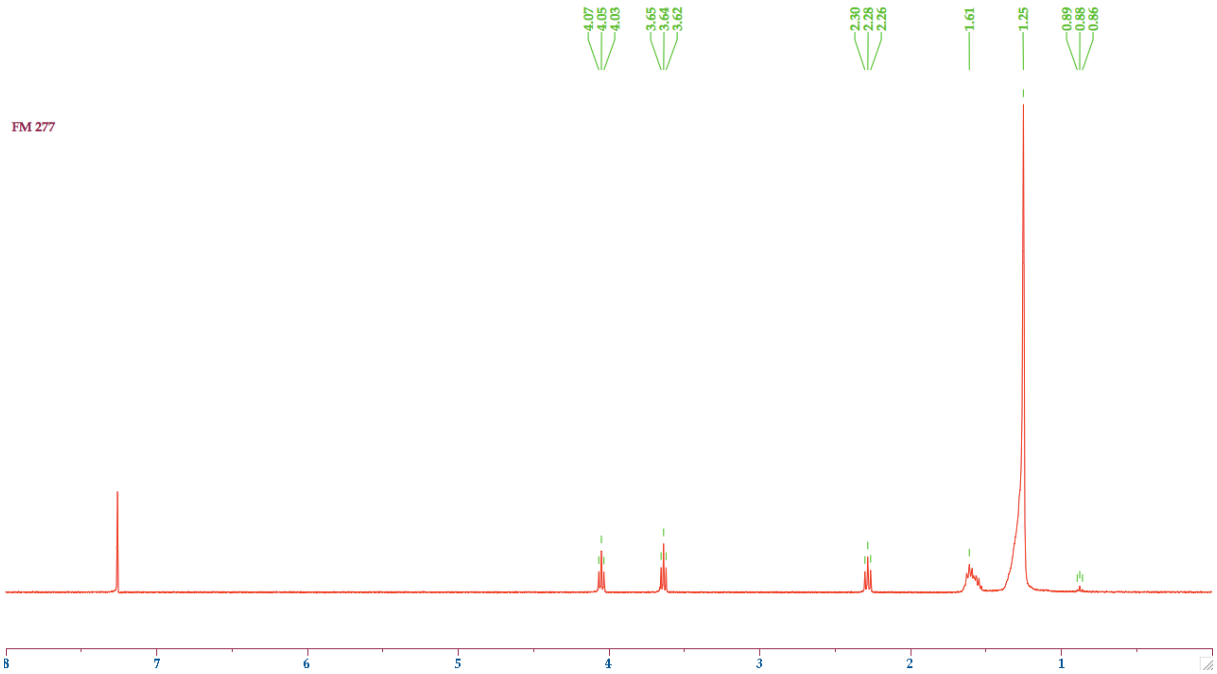
**$^{1}$H NMR spectrum**




**$^{13}$C NMR spectrum**

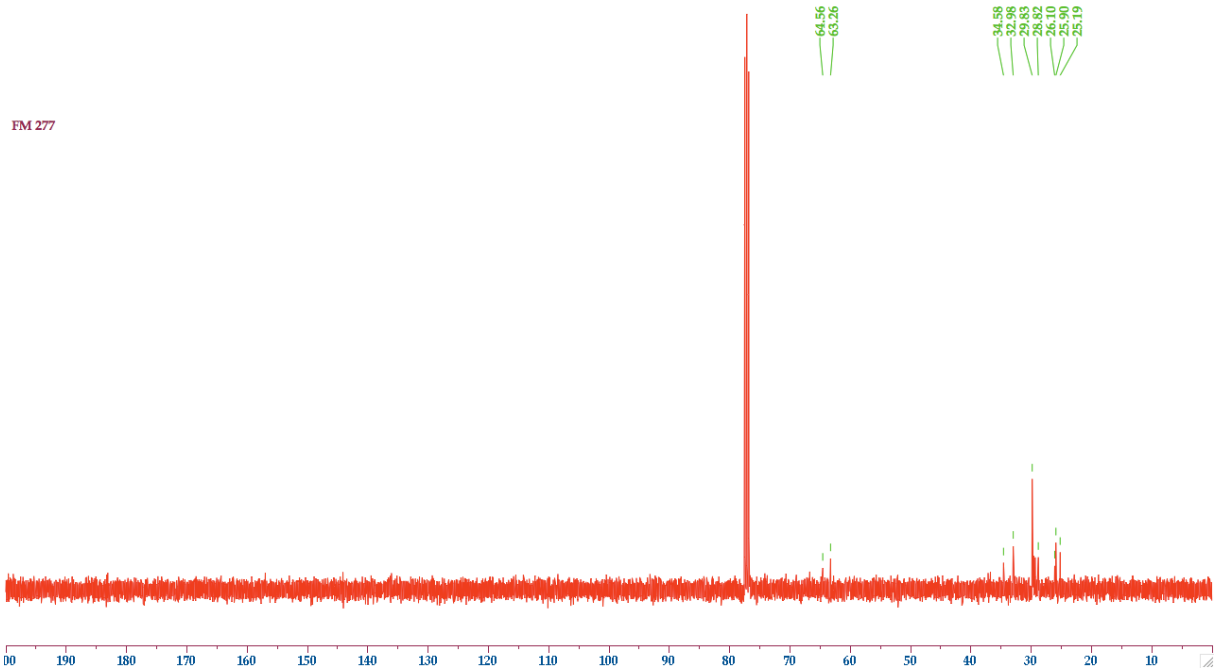


**Oligoesters prepared from the hydrogenation of 1,19-nonadecadianoic acid**
**$^{1}$H NMR spectrum of purified product** (the crude product also contained diol)

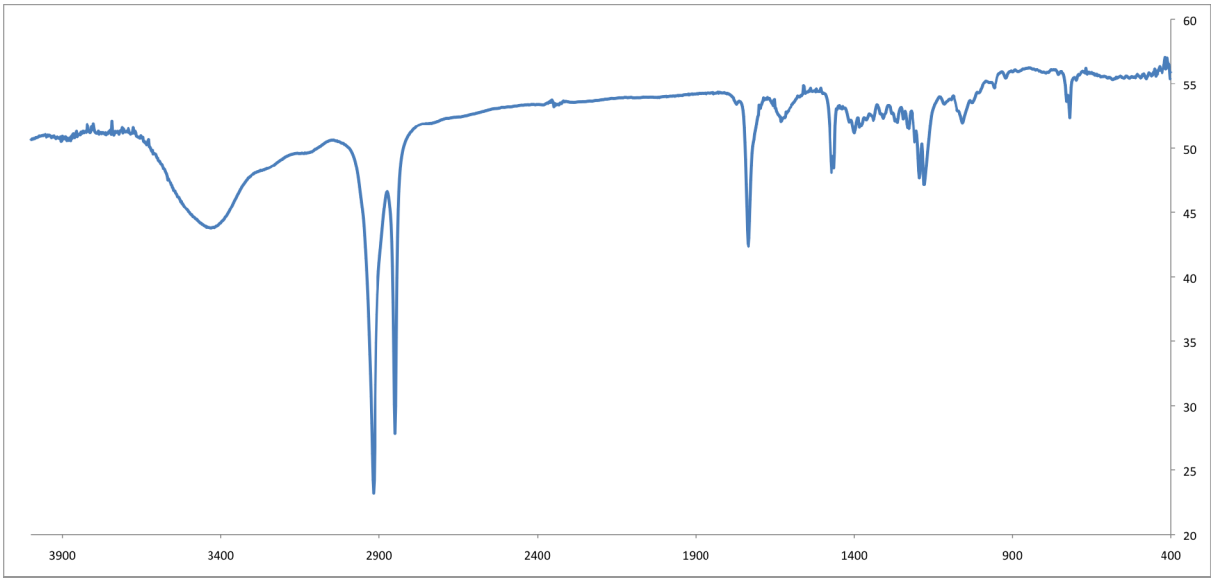



Integration of the resonances between □□2 and 4.5 ppm gives an average chain length of 3 monomer units terminated mainly by -$CH_2OH$ groups. The small resonance at □□0.8 ppm is from methyl endgroups which can arise from decarbonylation as shown in Scheme 2 of the main paper and/or from dehydration of an alcohol end group followed by hydrogenation of the terminal alkene.

**$^{13}$C NMR Spectrum**



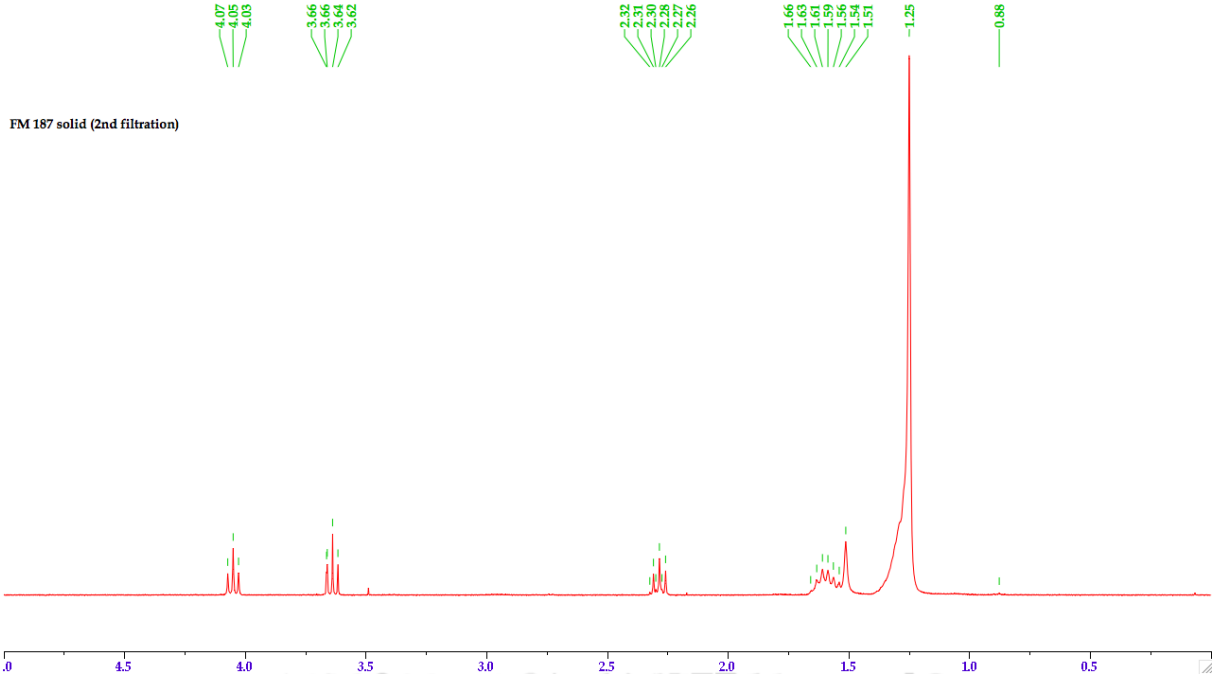
IR Spectrum




**Oligoesters used for hydrogenation in the presence of water**

A sample of oligoesterwas prepared by the first method described for the hydrogenation of dimethyl 1,19-nonadecanedioate in the presence of 10 % water, but using an impure sample of triphos. This preparation led to oligoesters, but was not reproducible when using other batches of triphos.

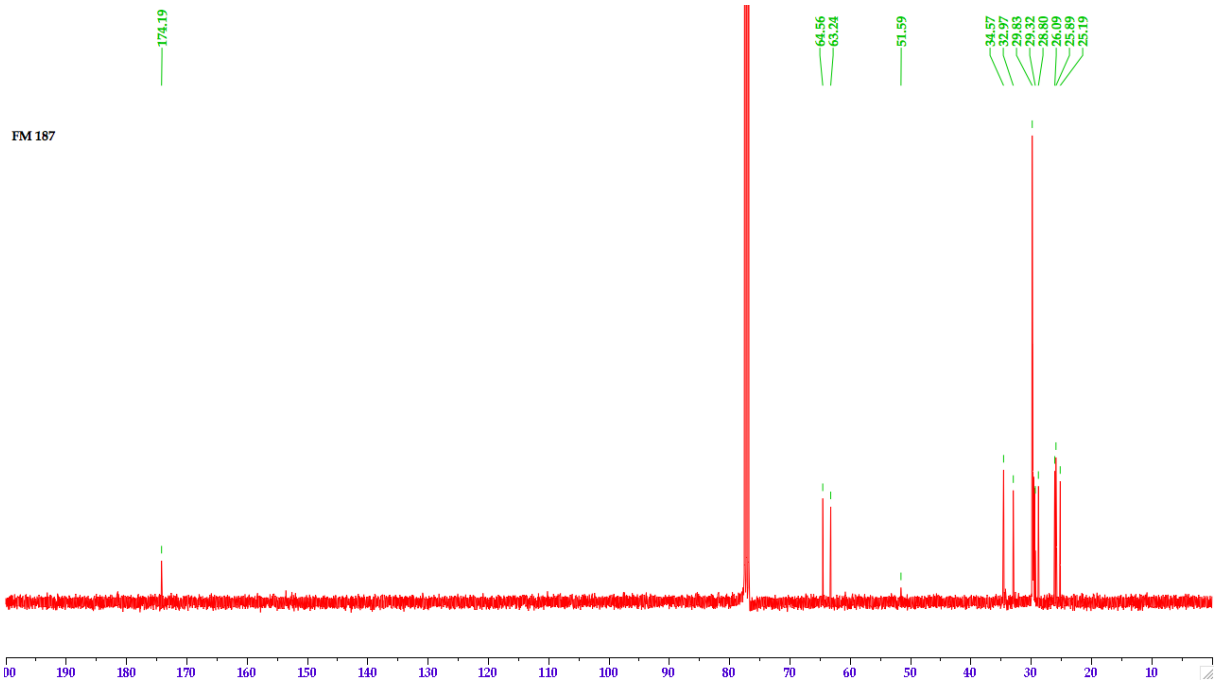
**$^{1}$H NMR spectrum**



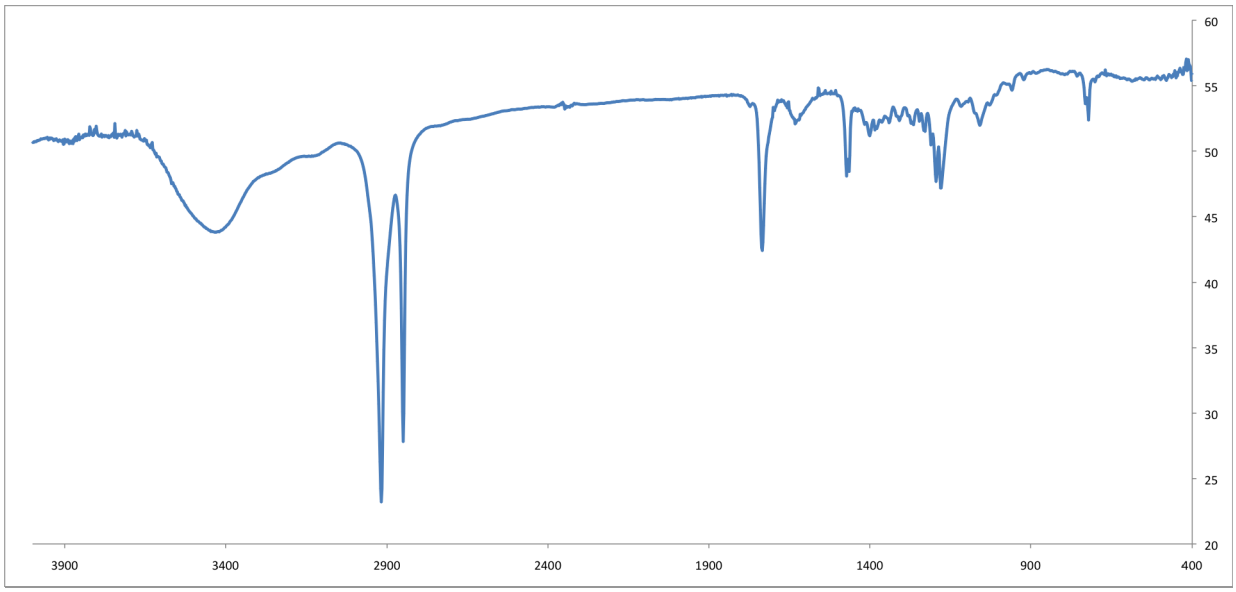

The average chain length is calculated as 3 units and the main end groups are –$CH_2OH$ (signal

at □ 3.64 ppm. Some -$CO_2$Me end groups are also observed (small signals □ 3.5 (*Me*O) and at □ 2.3 (C$H_2$$CO_2$Me) ppm next to the in chain C$H_2$C(O)- signal at □ 2.28 ppm. The signal at □ 4.05 ppm is from the in chain C$H_2$O

**$^{13}$C NMR spectrum**




**IR spectrum**



**MALDI-TOF MS**