

g-C₃N₄/Metal Halide Perovskite Composites as Photocatalysts for Singlet Oxygen Generation Processes for the Preparation of Variable Oxidized Synthons

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1. Experimental method

Pag. S2

2. LC-MS spectra

Pag. S3

Catalysts legend:

Entry	Catalyst	Formula
1	C1	g-C ₃ N ₄ /PEA ₂ PbCl ₄ 5%
2	C2	g-C ₃ N ₄ /PEA ₂ SnBr ₄ 5%
3	C3	g-C ₃ N ₄ /PEA ₂ PbBr ₄ 5%
7	C4	g-C ₃ N ₄ /DMASnBr ₃ 5%

1. Experimental method

For all the DA and ene reactions the following experimental procedure was used:

1.4 mmol of diene or alkene substrates were dissolved in 20 mL pure acetonitrile in the presence of 15 mg of the catalyst (typically 13% w/w) in a 35 mL cylindrical pyrex reaction vessel and the mixture was saturated with oxygen gas by bubbling for 15 minutes. The sealed vessel was then irradiated under vigorous stirring in a Solar Box Co.Fo.Me.Gra. 1500e (500 W/m²) for 24 hours (unless specified). Further saturations with oxygen (a couple) were done during the reaction time. After this period of time, the suspension was filtered off to obtain a clear solution that was evaporated at moderate reduced pressure heating with a water bath at 30 °C. The residues were submitted to GC-MS analyses to determine the structures of the products and the corresponding yields.

2. LC-MS spectra

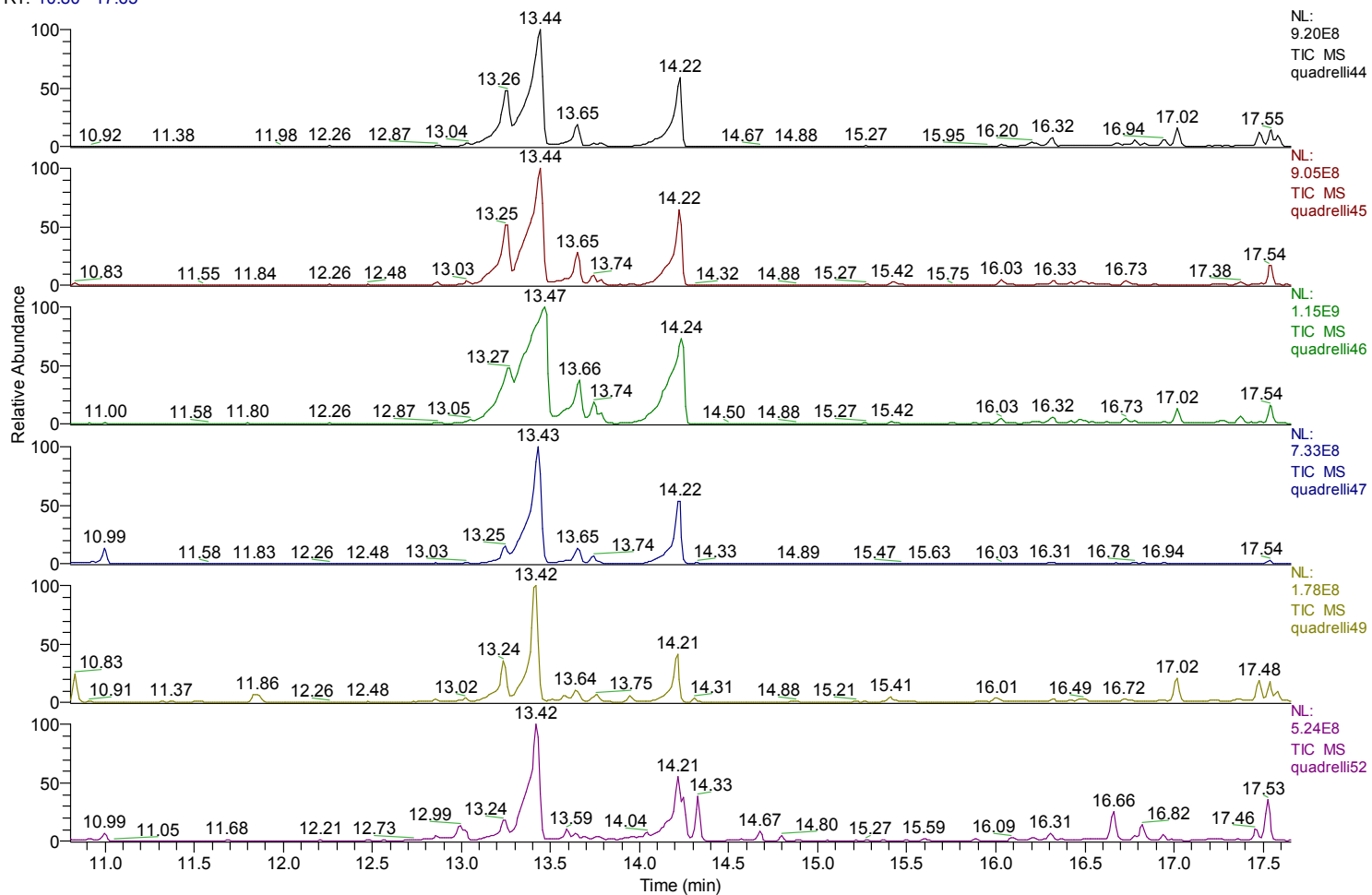
Blank experiments

d:\lavoricgs_2020\...\quadrelli45

2/13/2020 5:04:47 PM

bianco_catB CH

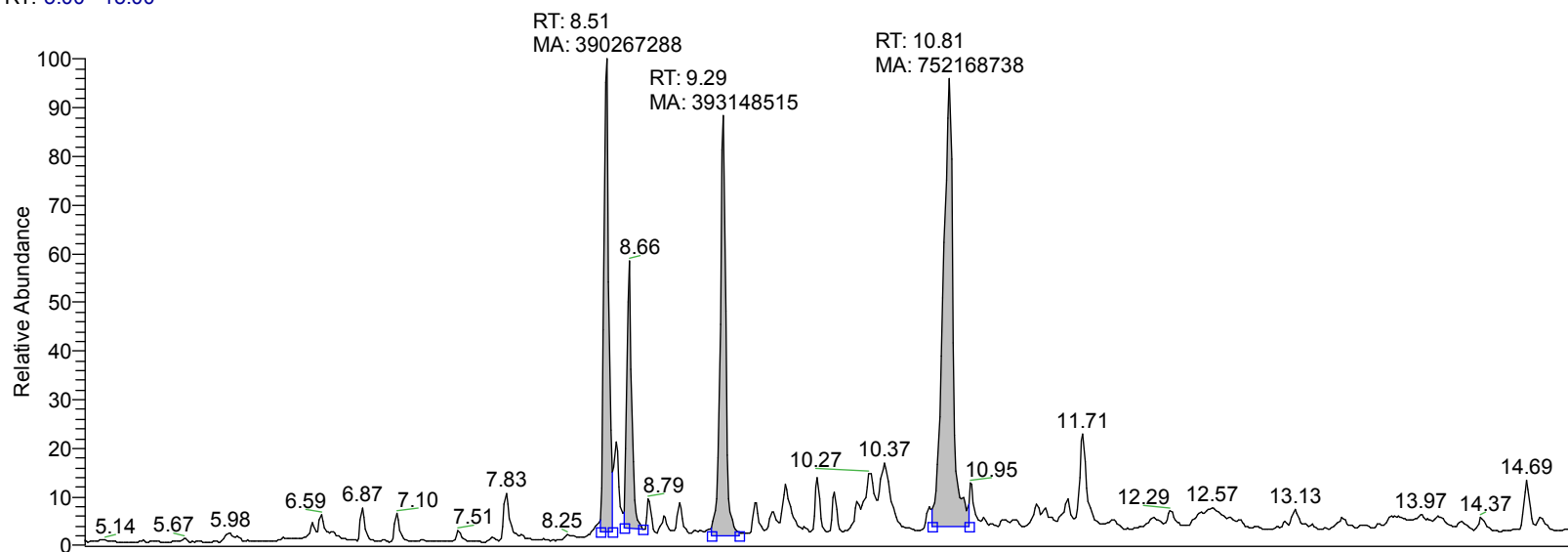
RT: 10.80 - 17.65



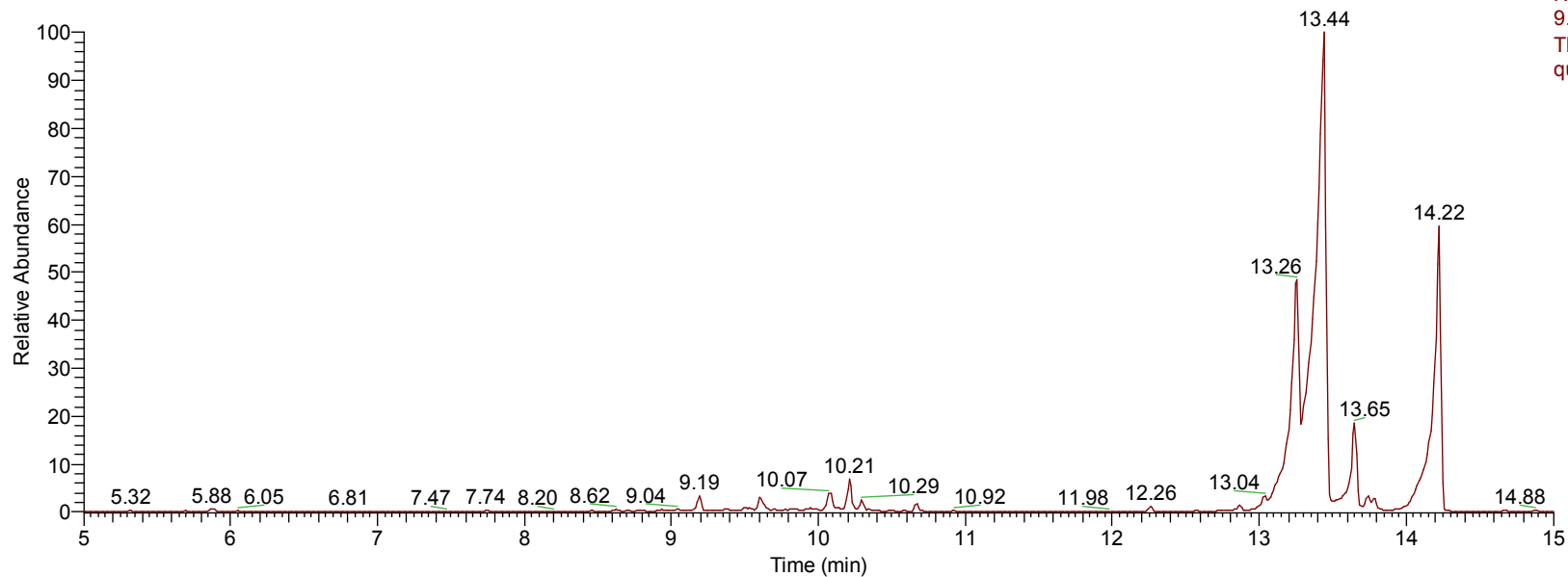
C1, Reaction with 1,3-cyclohexadiene

RT: 5.00 - 15.00

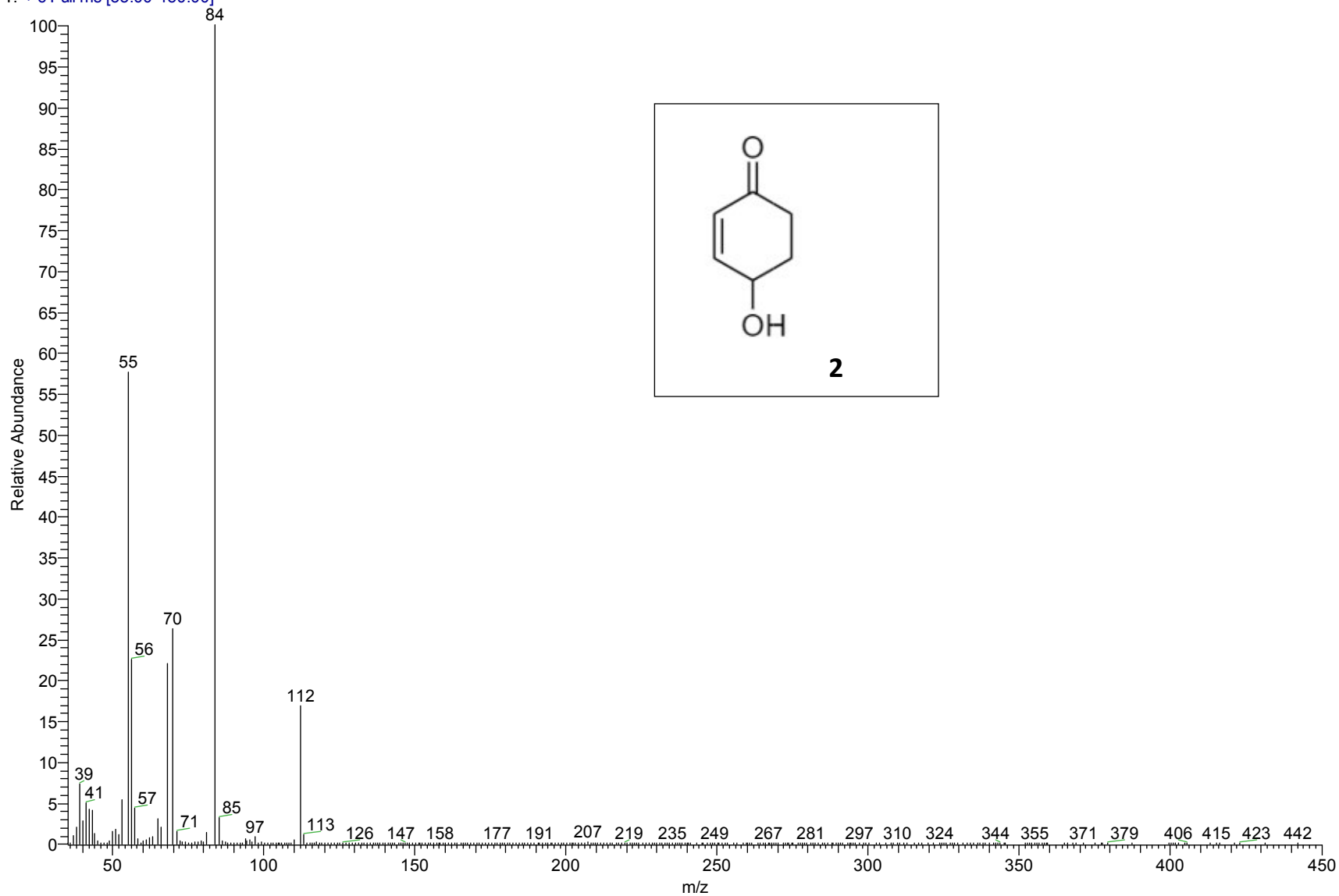
NL:
1.77E8
TIC MS
quadrelli25



NL:
9.20E8
TIC MS
quadrelli44

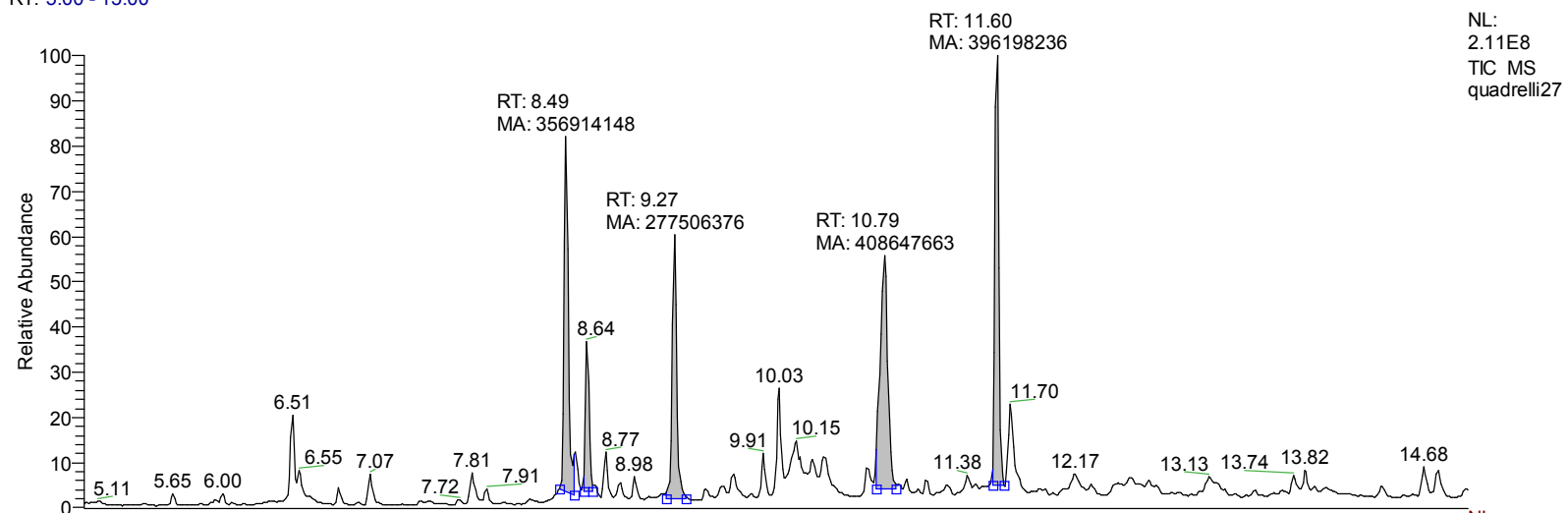


quadrelli25 #680 RT: 10.81 AV: 1 NL: 5.46E7
T: + c Full ms [35.00-450.00]

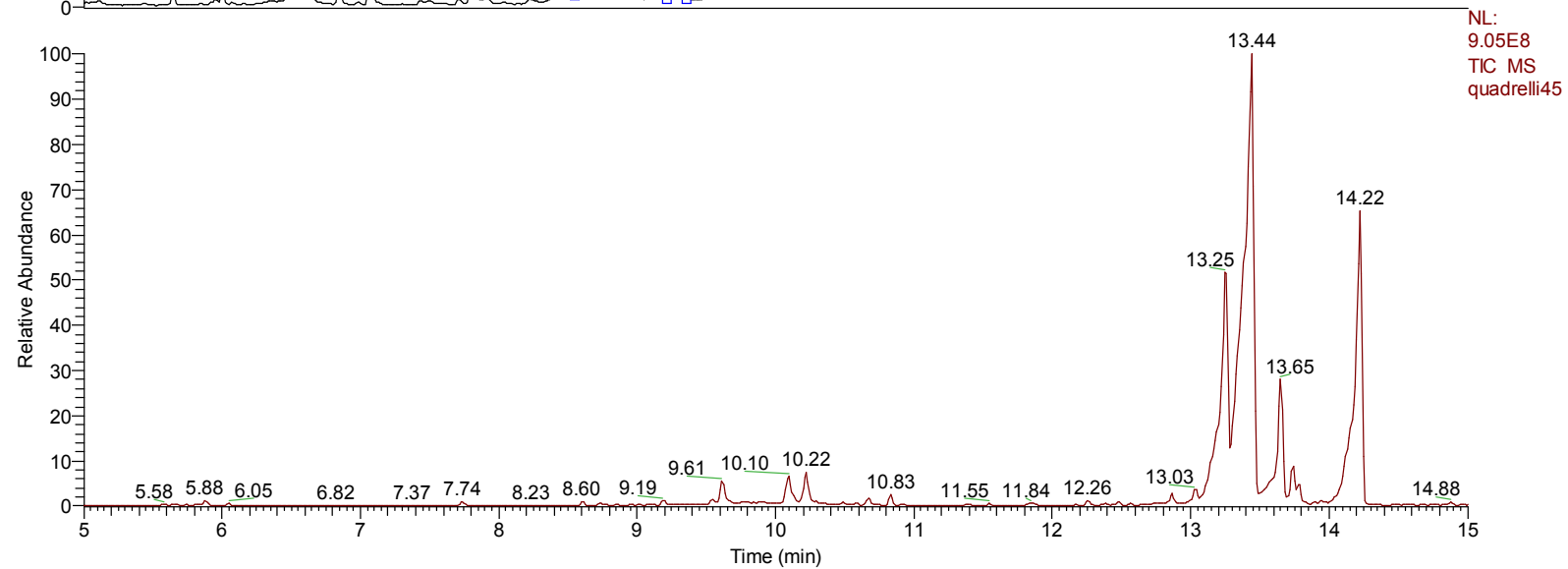


C2, Reaction with 1,3-cyclohexadiene

RT: 5.00 - 15.00

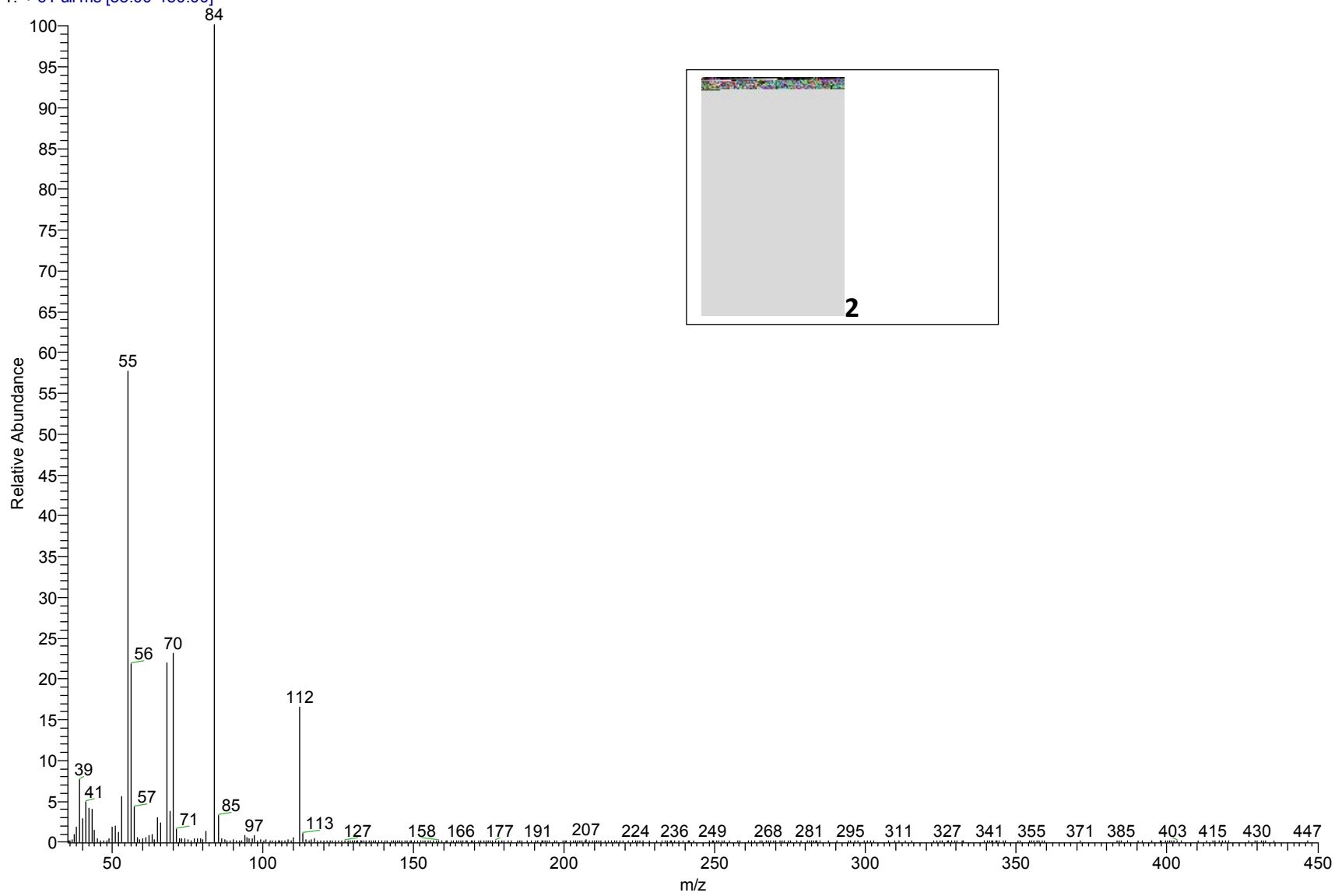


NL:
2.11E8
TIC MS
quadrelli27



NL:
9.05E8
TIC MS
quadrelli45

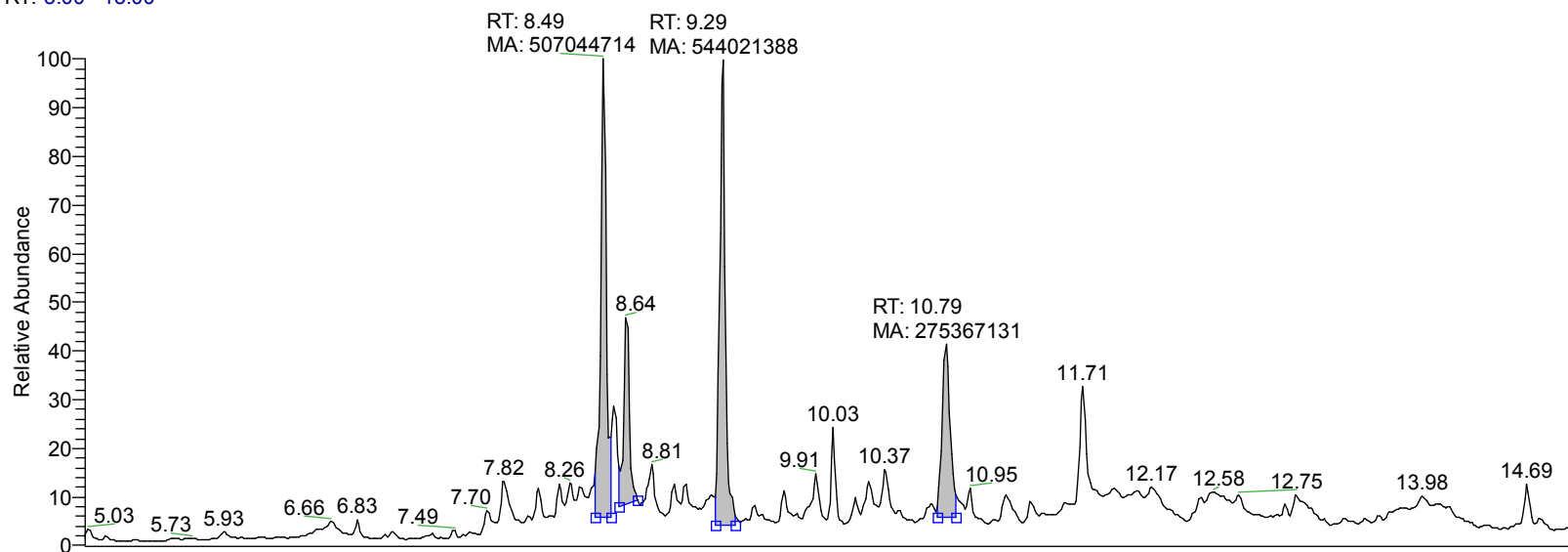
quadrelli27 #678 RT: 10.79 AV: 1 NL: 3.79E7
T: + c Full ms [35.00-450.00]



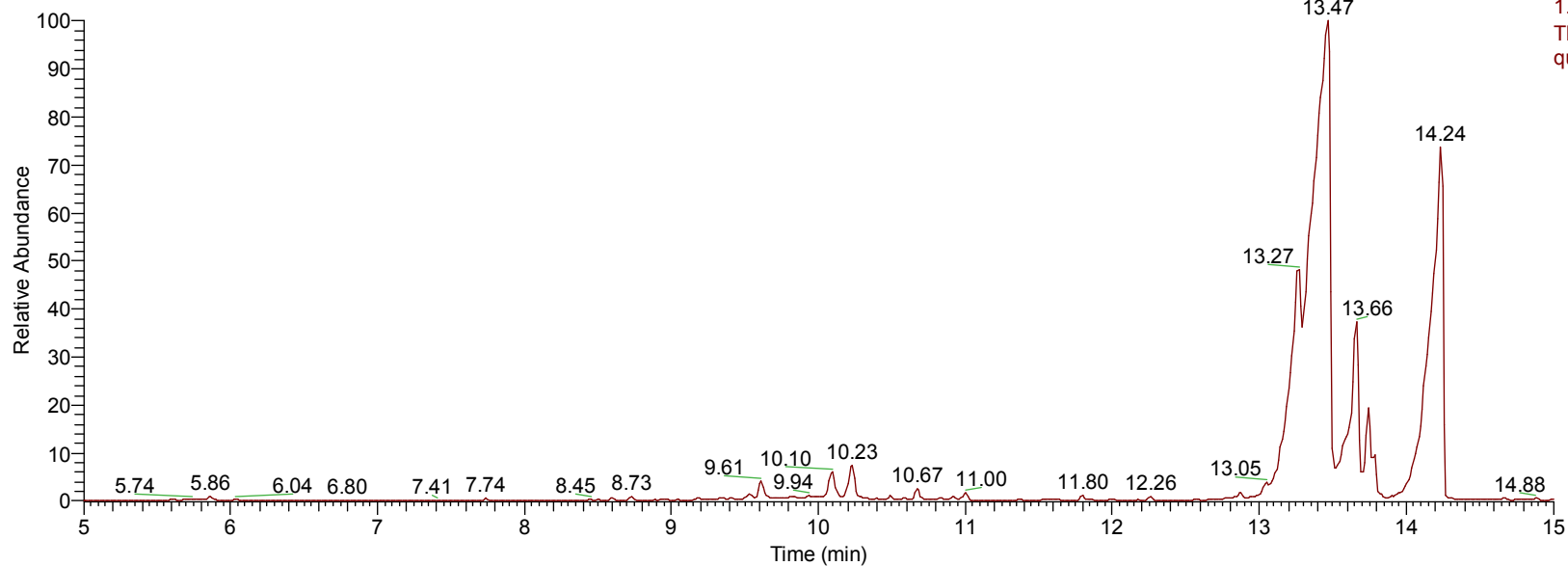
C3, Reaction with 1,3-cyclohexadiene

RT: 5.00 - 15.00

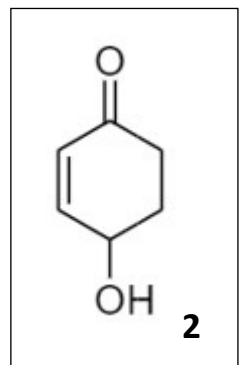
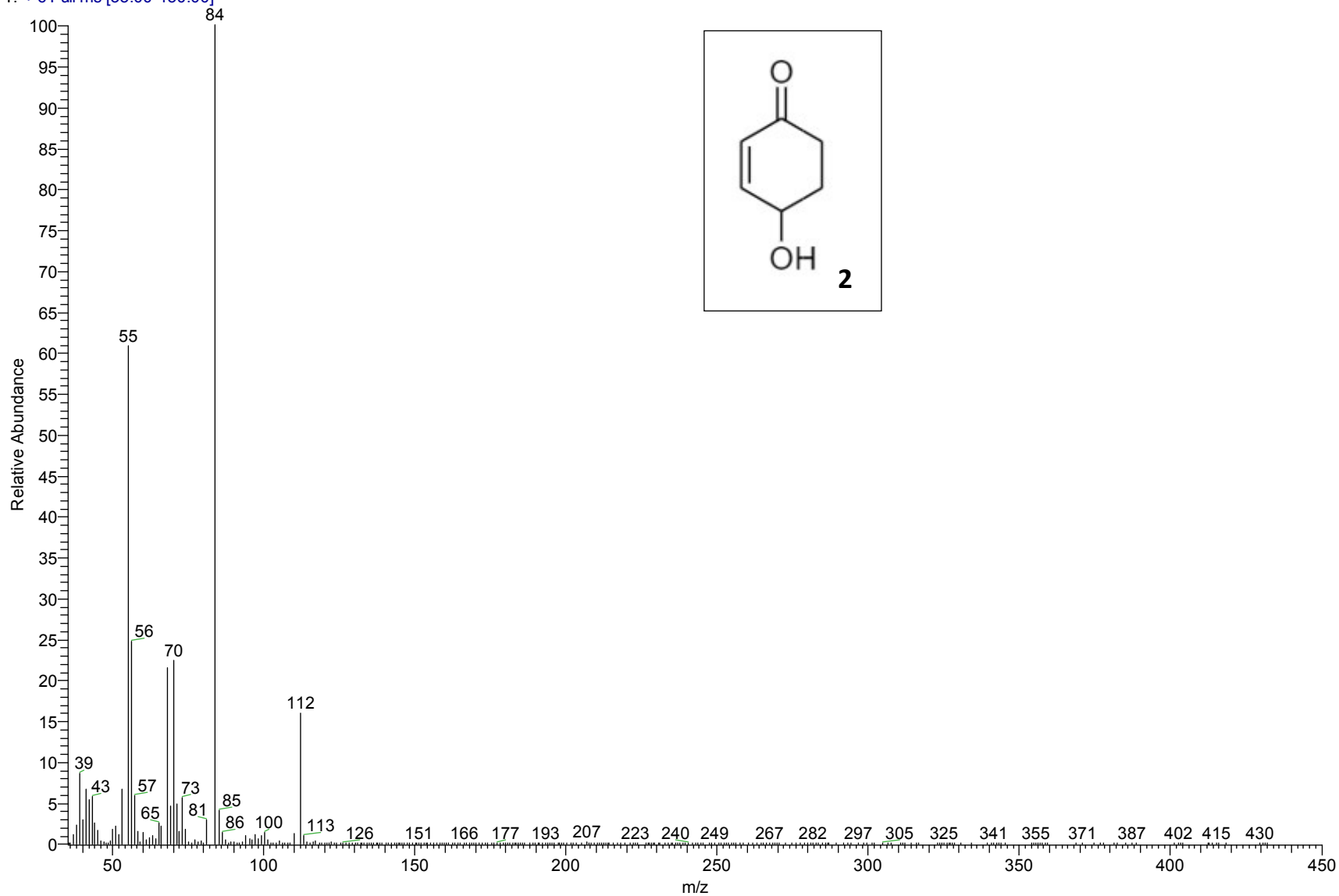
NL:
2.05E8
TIC MS
quadrelli30



NL:
1.15E9
TIC MS
quadrelli46



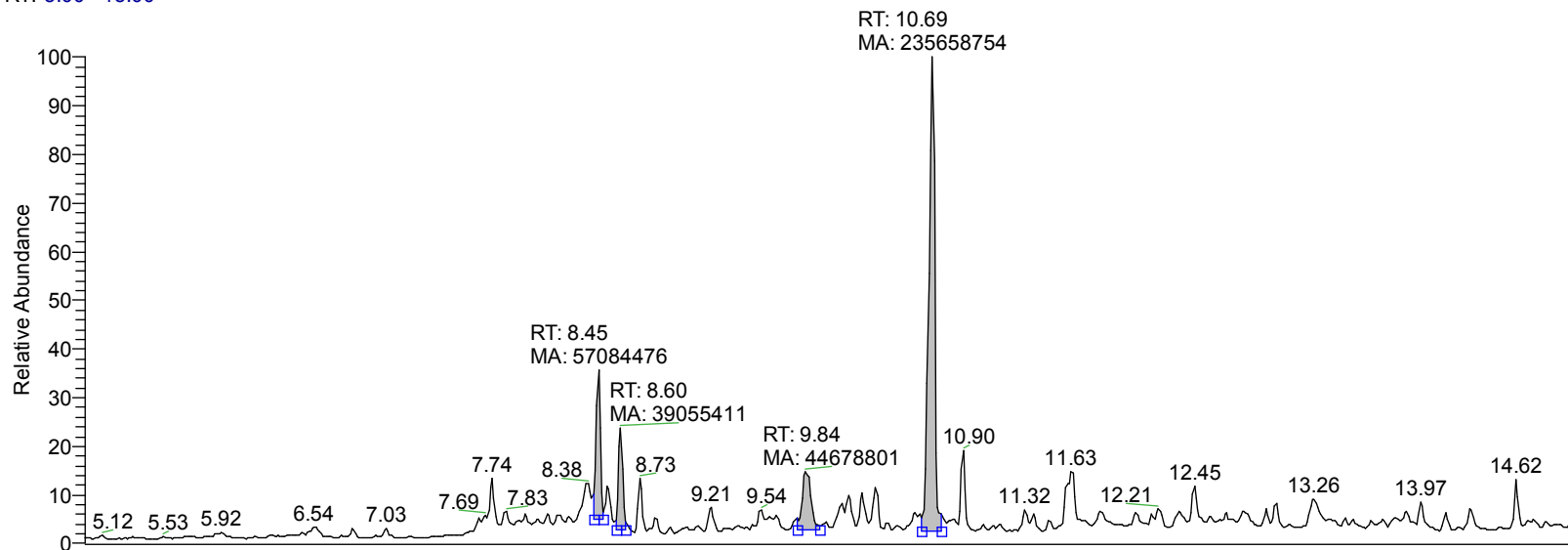
quadrelli30 #678 RT: 10.79 AV: 1 NL: 2.41E7
T: + c Full ms [35.00-450.00]



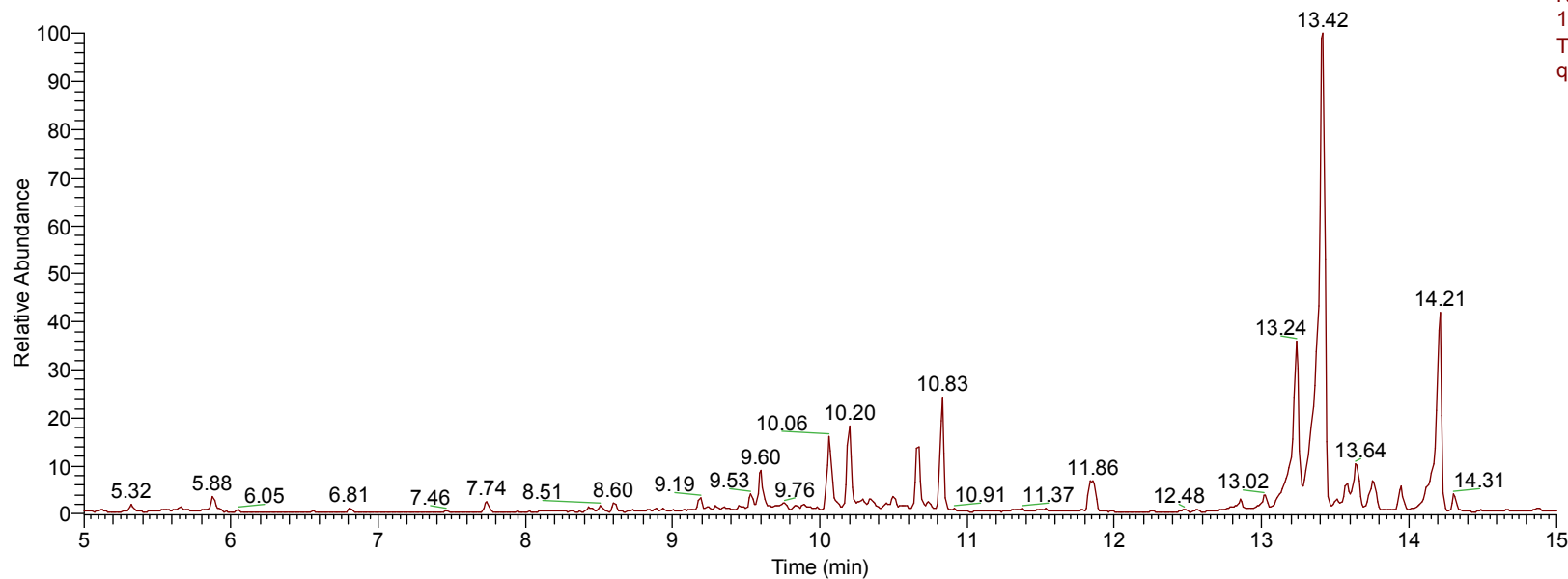
C4, Reaction with 1,3-cyclohexadiene

RT: 5.00 - 15.00

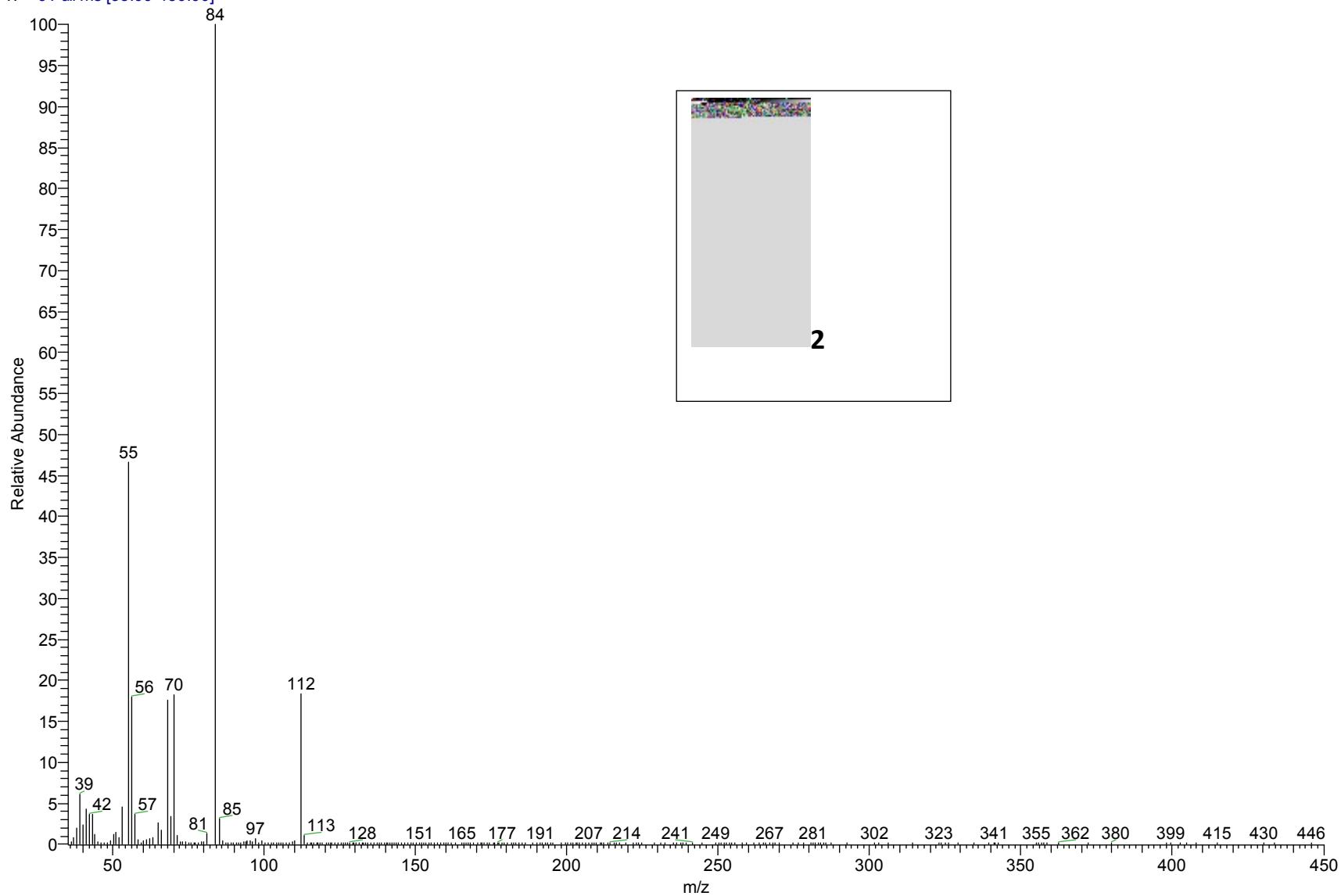
NL:
8.99E7
TIC MS
quadrelli50



NL:
1.78E8
TIC MS
quadrelli49



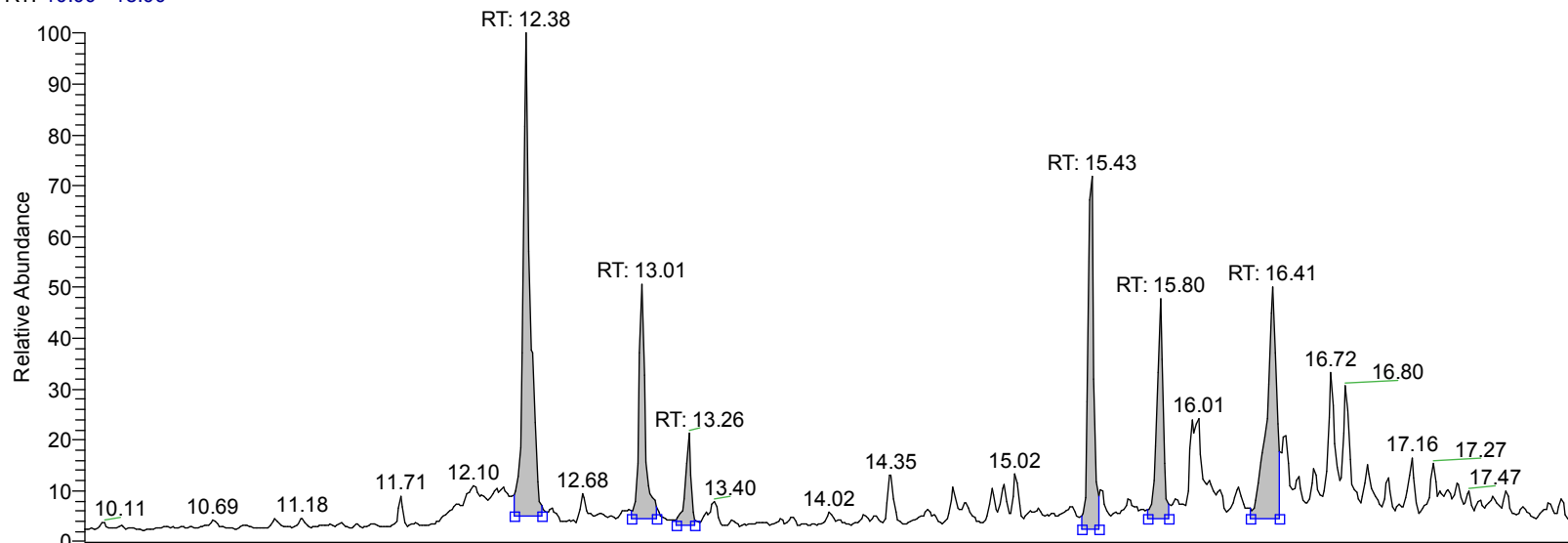
quadrelli50 #670 RT: 10.69 AV: 1 NL: 3.27E7
T: + c Full ms [35.00-450.00]



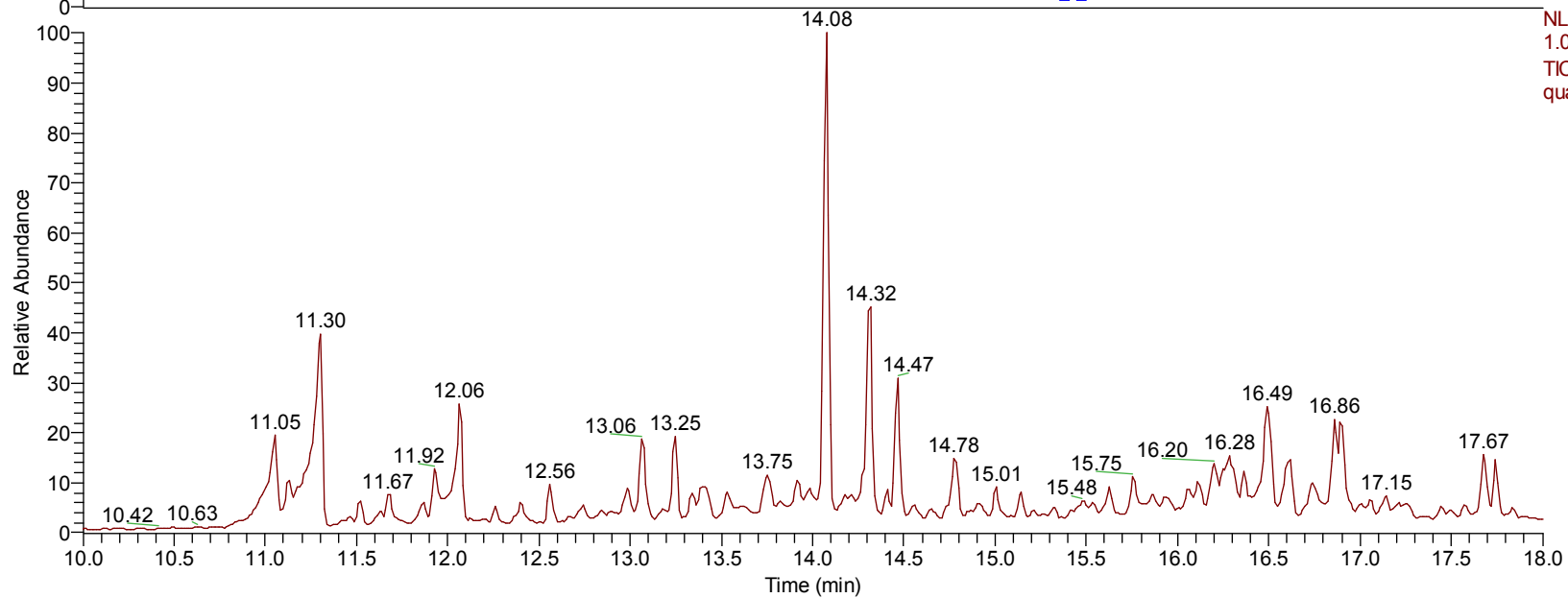
C1, Reaction with cyclopentadiene

RT: 10.00 - 18.00

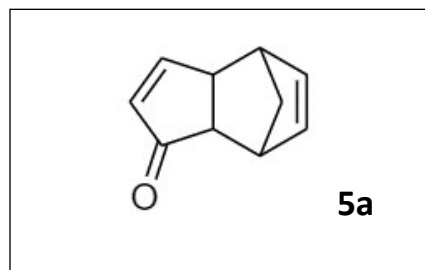
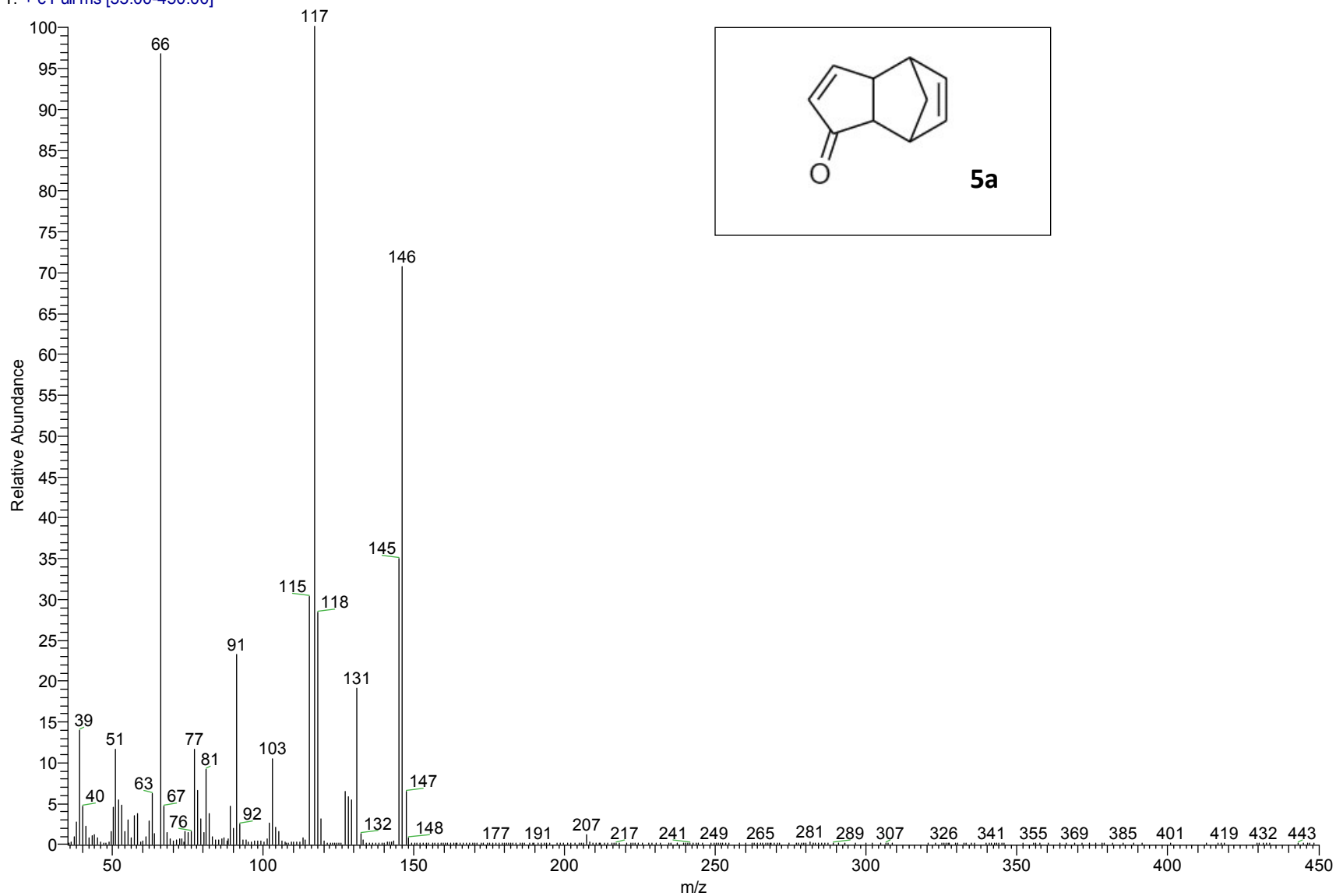
NL:
7.89E7
TIC MS
quadrelli32



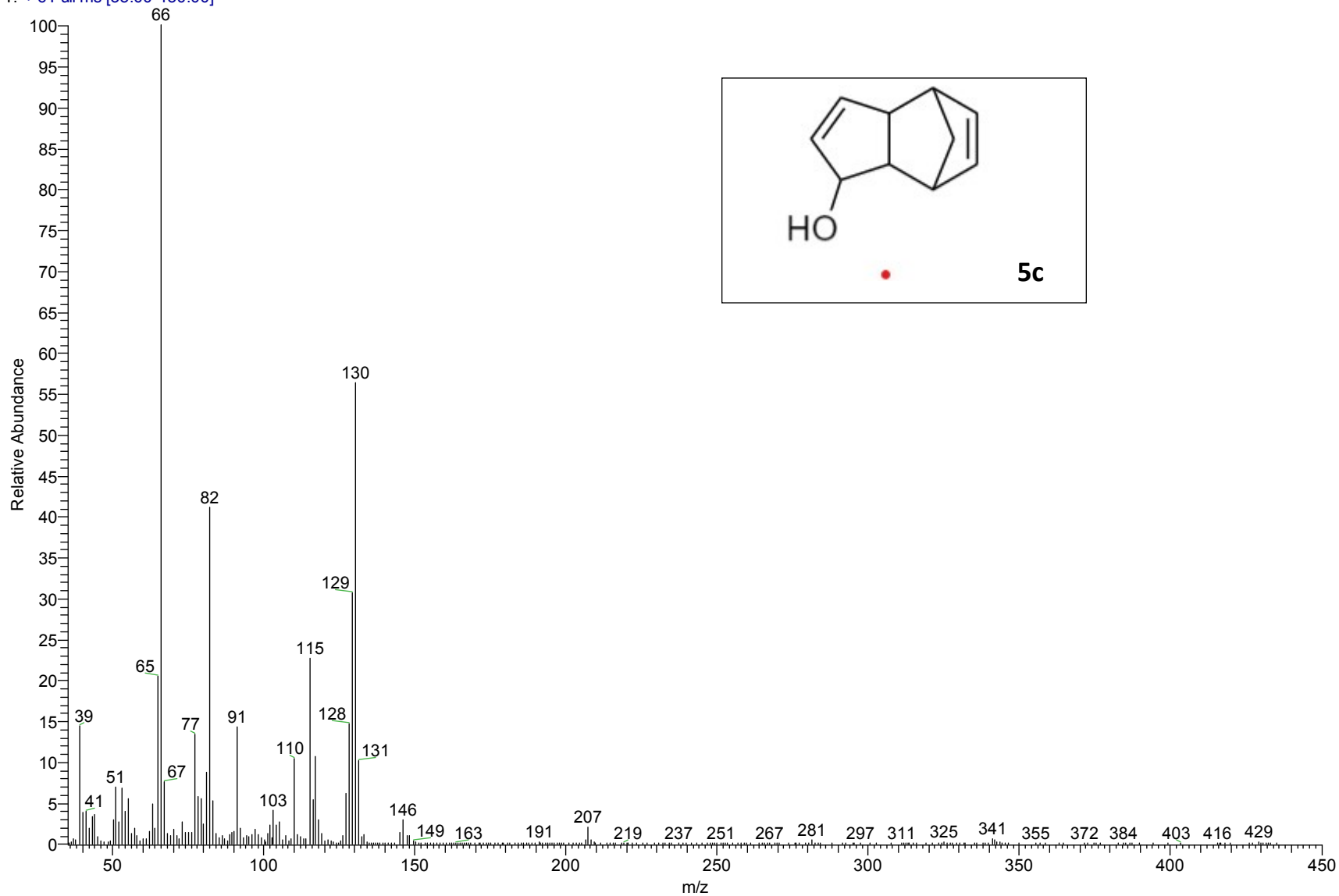
NL:
1.03E8
TIC MS
quadrelli56



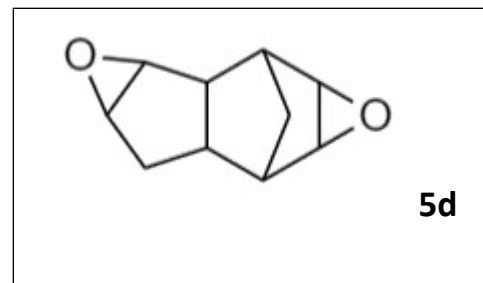
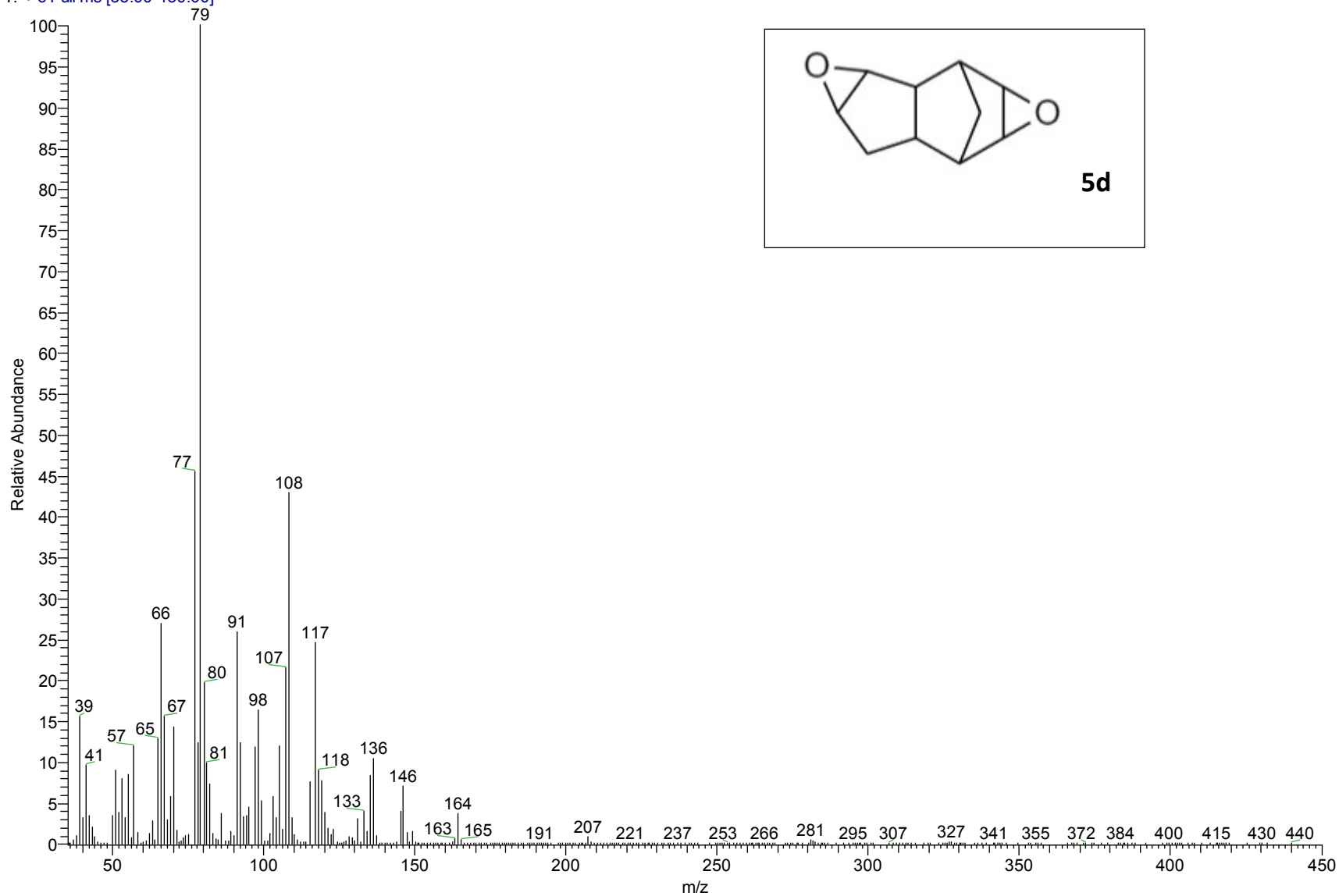
quadrelli32 #871 RT: 13.01 AV: 1 NL: 6.66E6
T: + c Full ms [35.00-450.00]



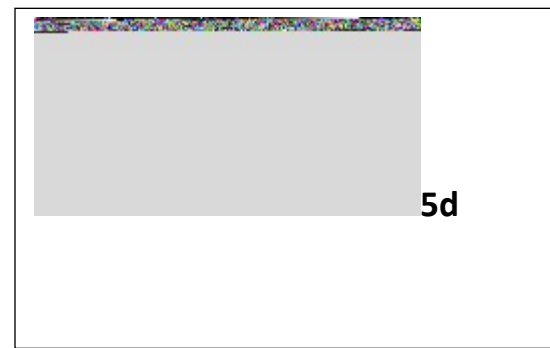
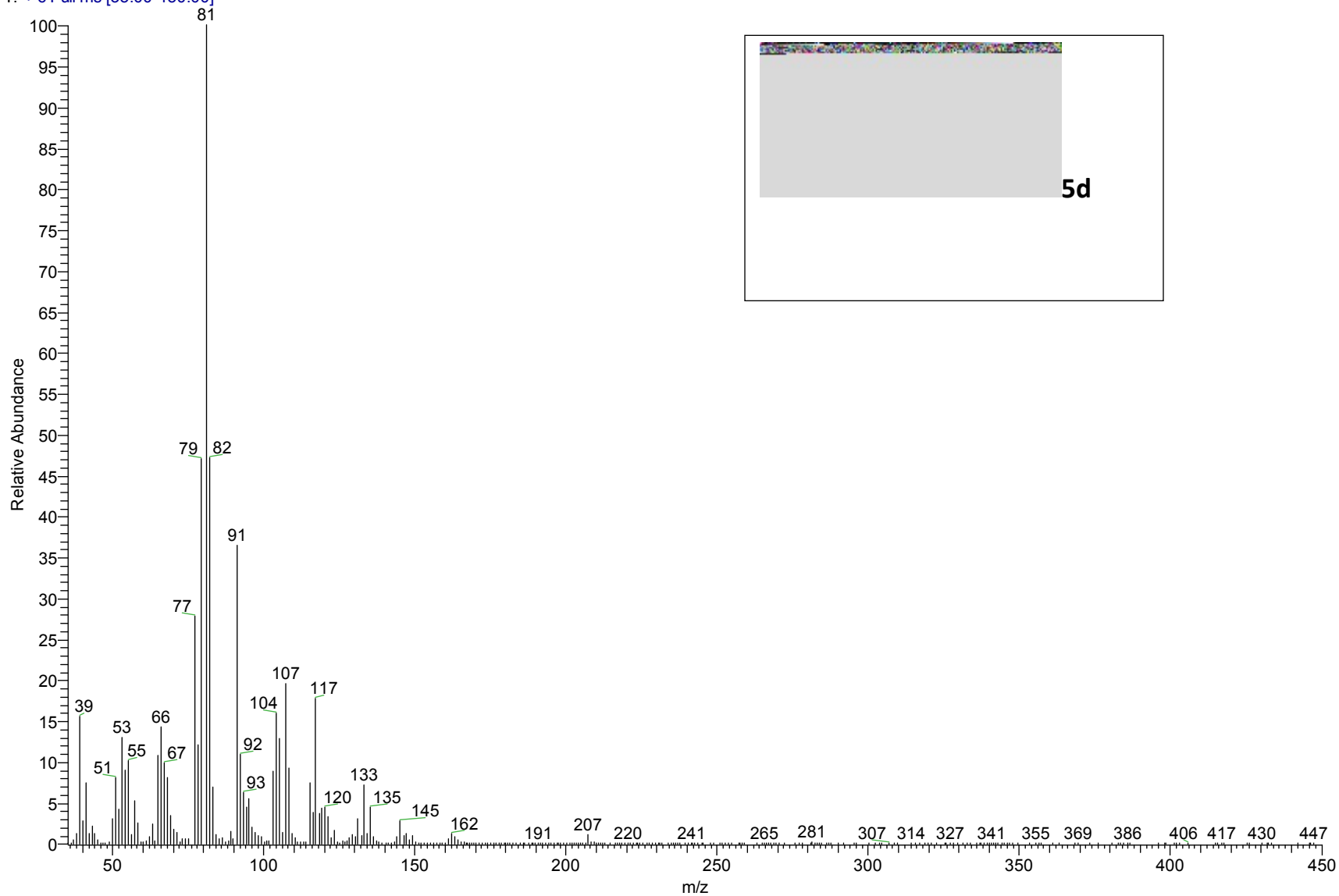
quadrelli32 #893 RT: 13.26 AV: 1 NL: 3.09E6
T: + c Full ms [35.00-450.00]



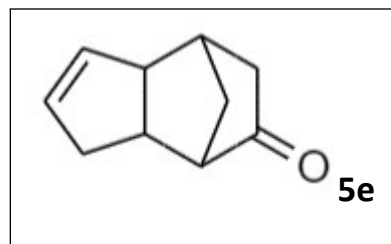
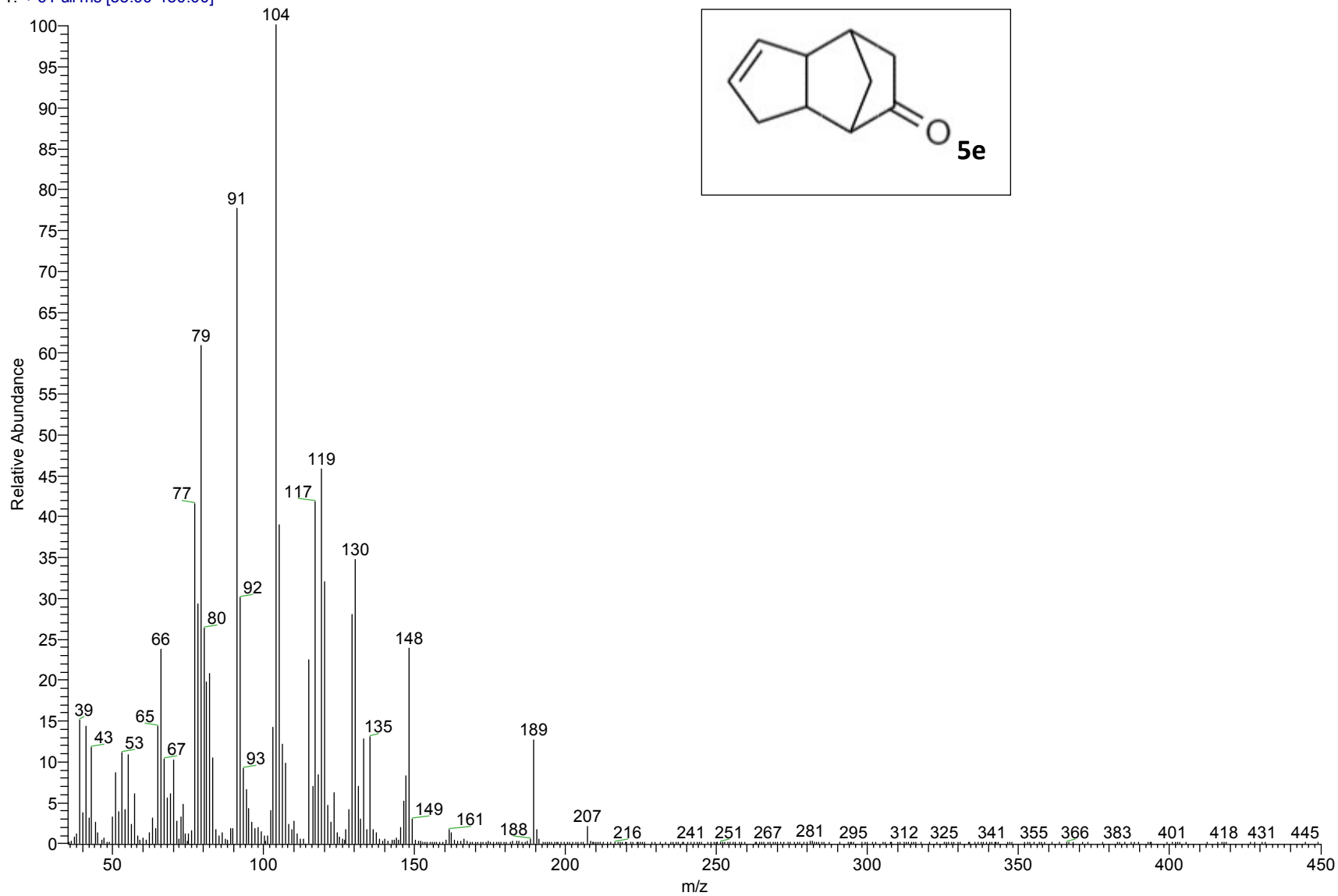
quadrelli32 #1082 RT: 15.43 AV: 1 NL: 8.51E6
T: + c Full ms [35.00-450.00]



quadrelli32 #1114 RT: 15.80 AV: 1 NL: 6.11E6
T: + c Full ms [35.00-450.00]



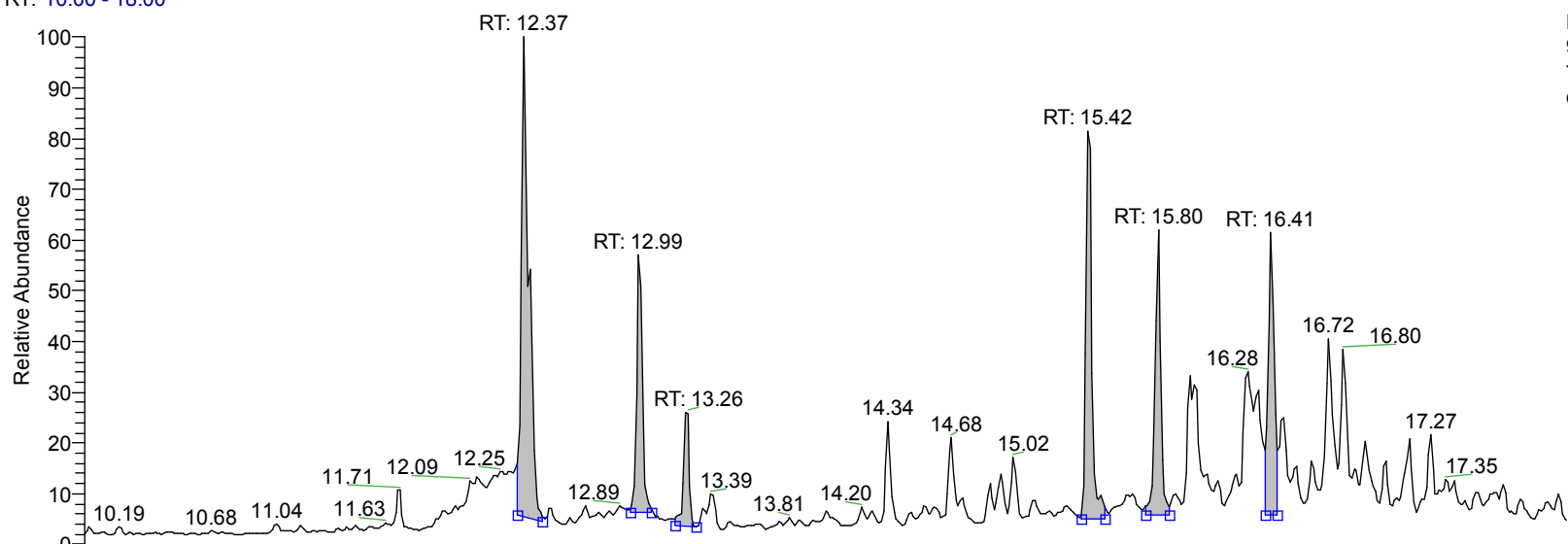
quadrelli32 #1167 RT: 16.41 AV: 1 NL: 3.62E6
T: + c Full ms [35.00-450.00]



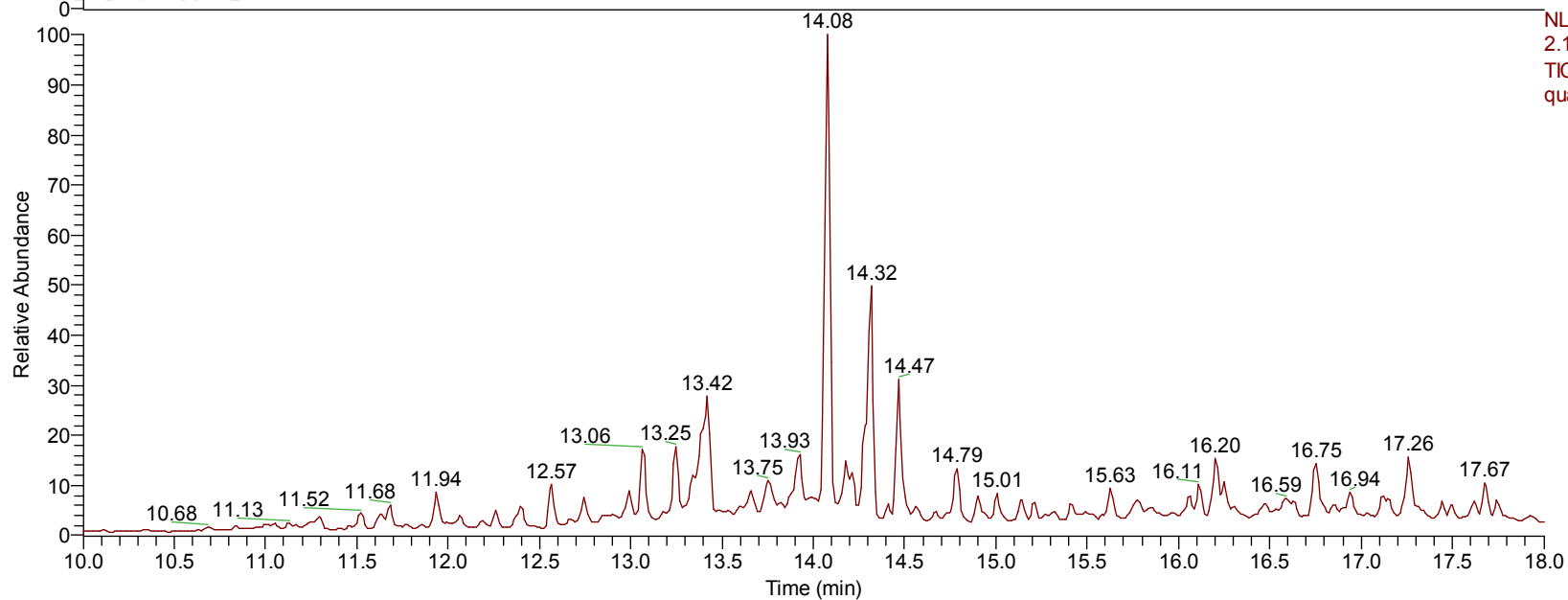
C2, Reaction with cyclopentadiene

RT: 10.00 - 18.00

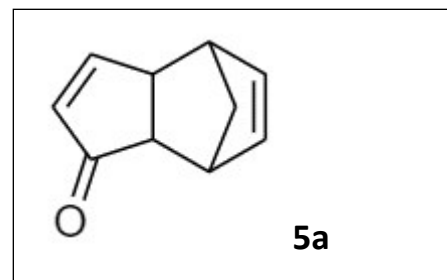
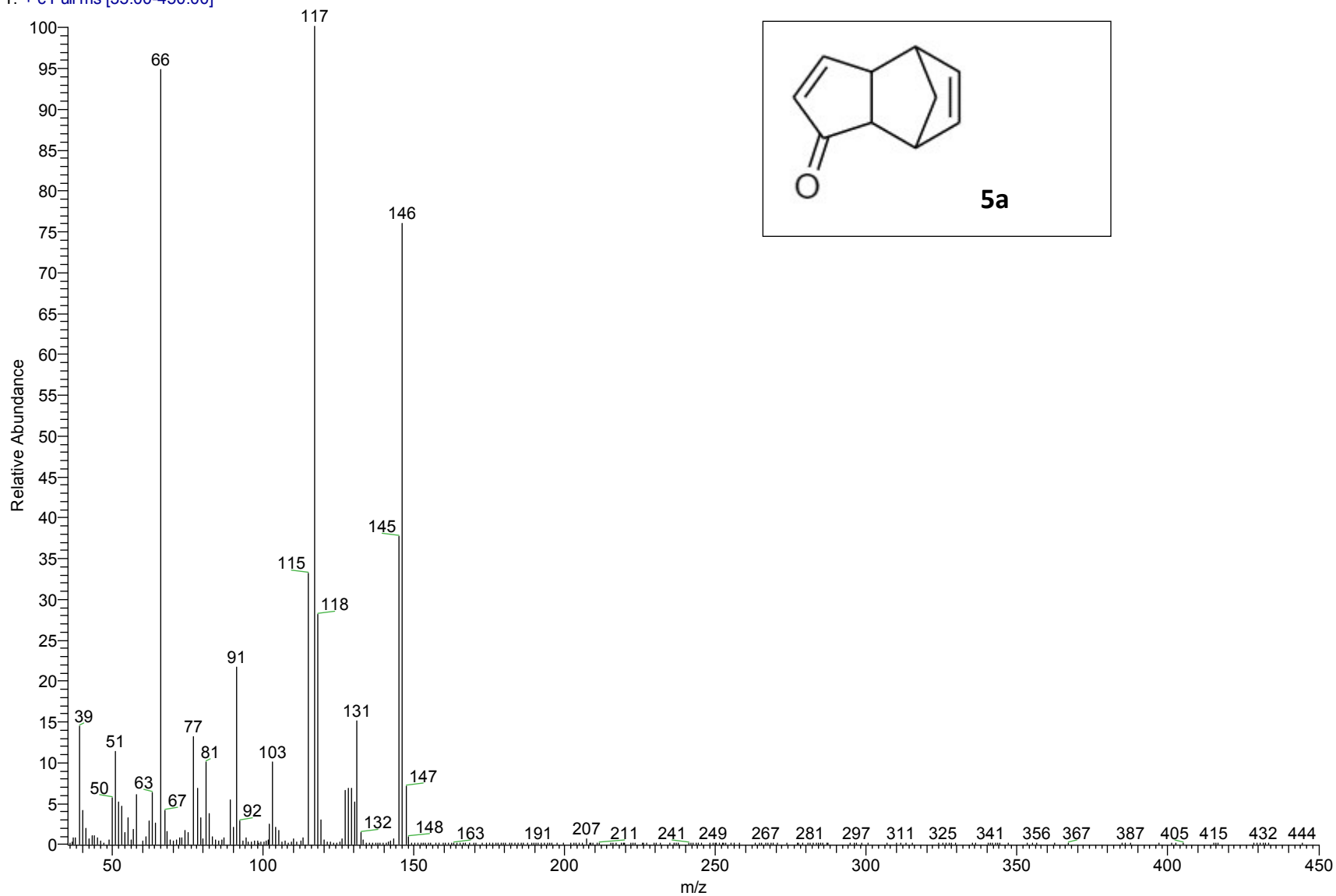
NL:
9.30E7
TIC MS
quadrelli37



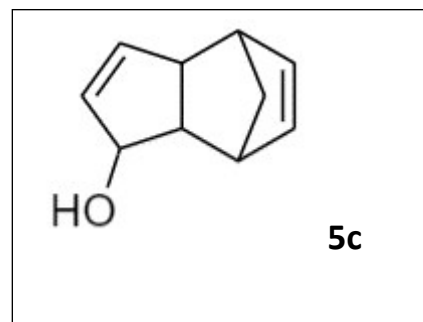
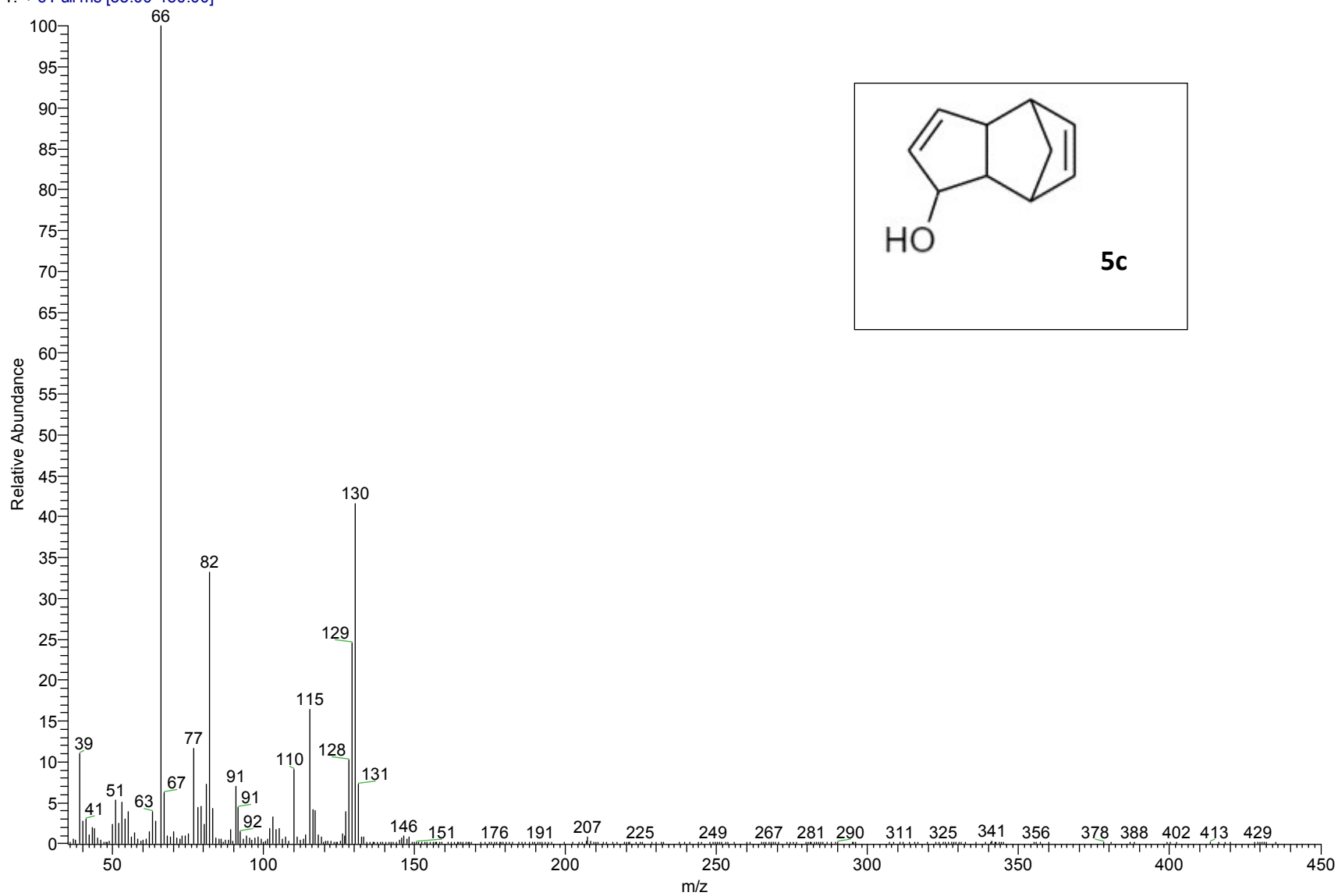
NL:
2.15E8
TIC MS
quadrelli57



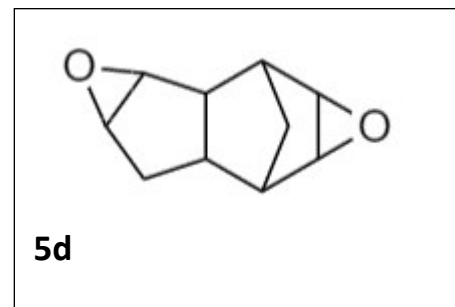
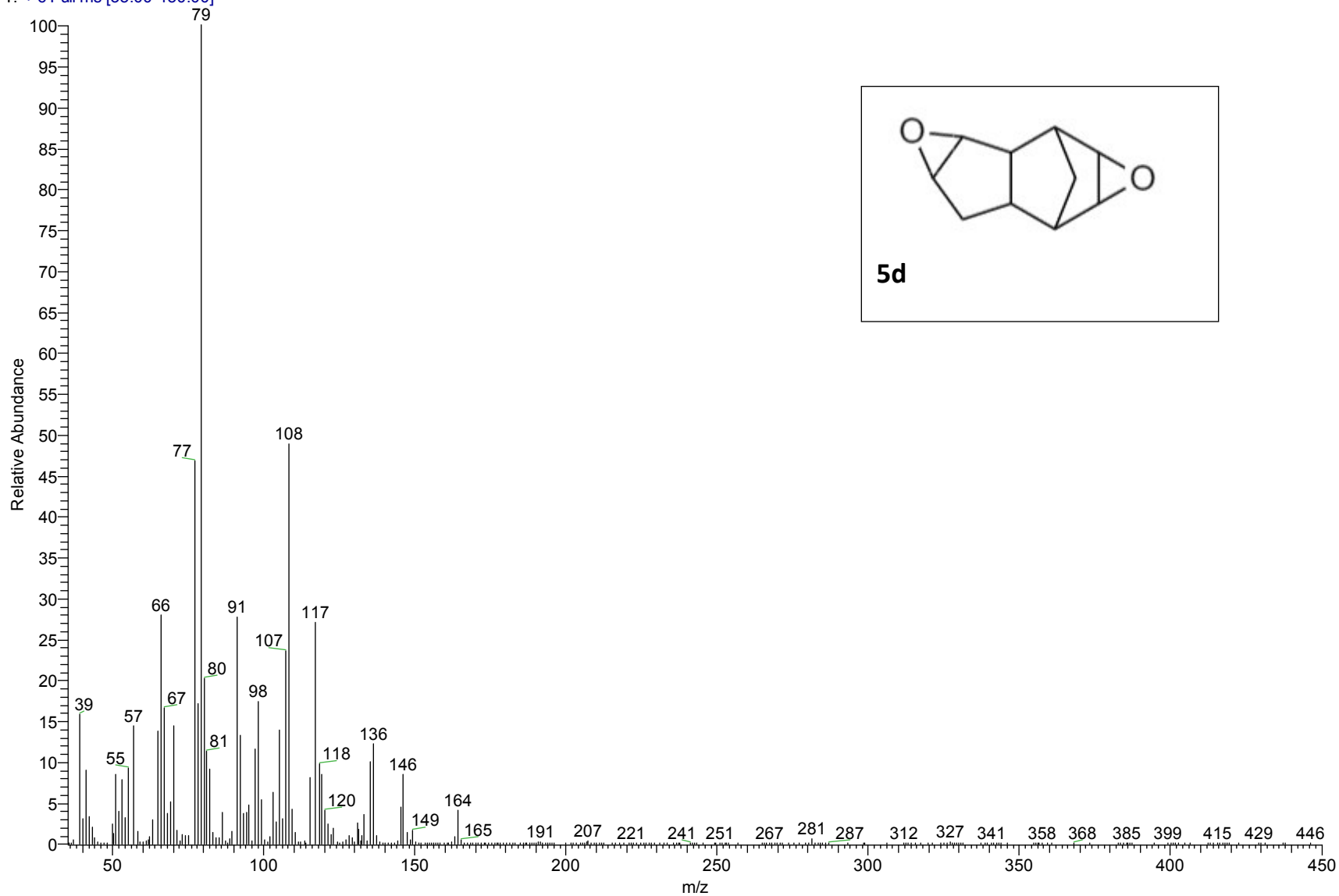
quadrelli37 #870 RT: 12.99 AV: 1 NL: 8.70E6
T: + c Full ms [35.00-450.00]



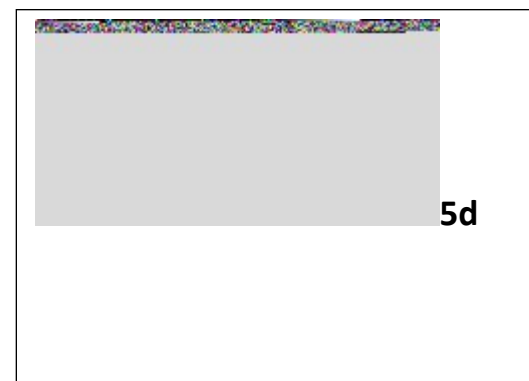
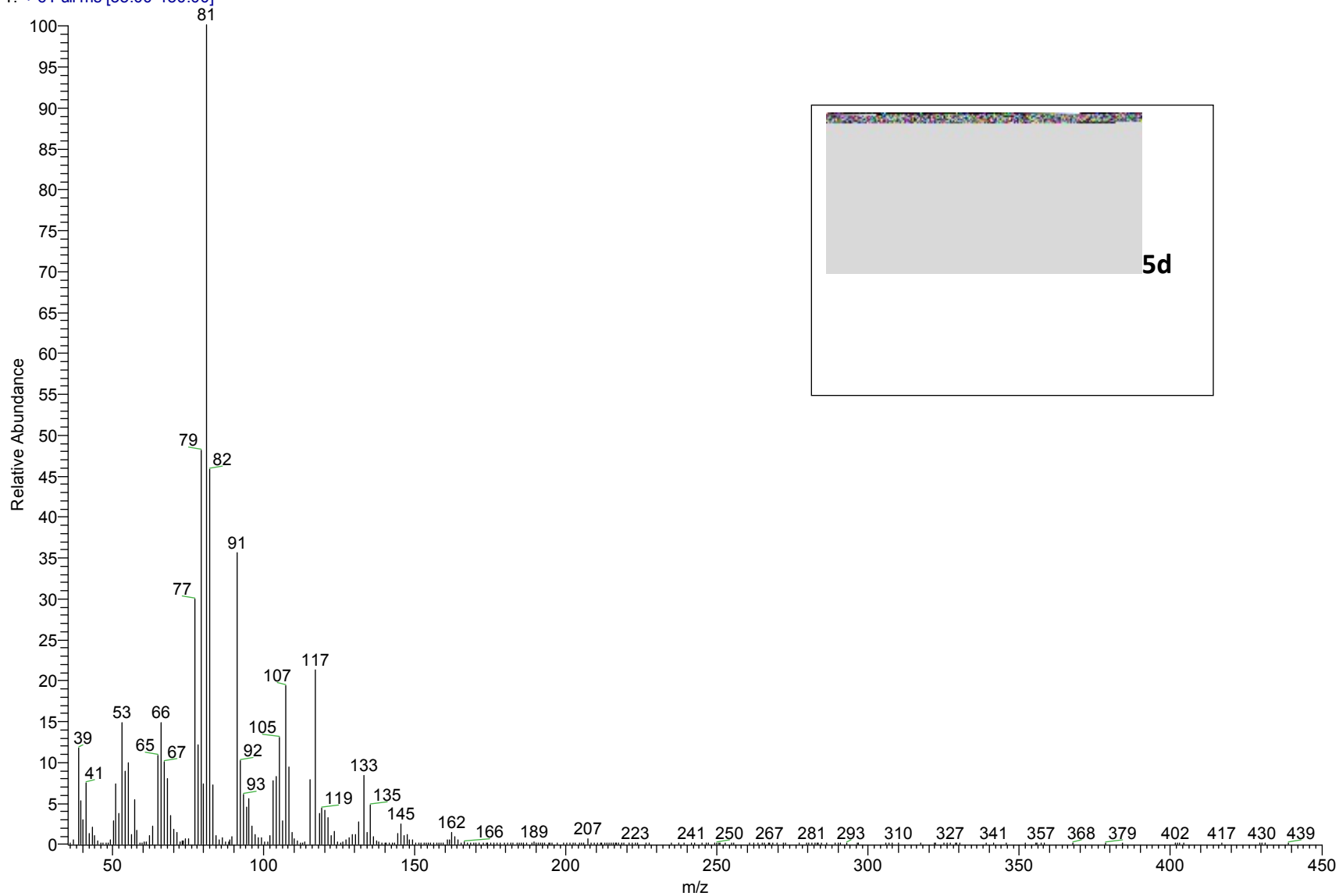
quadrelli37 #893 RT: 13.26 AV: 1 NL: 5.99E6
T: + c Full ms [35.00-450.00]



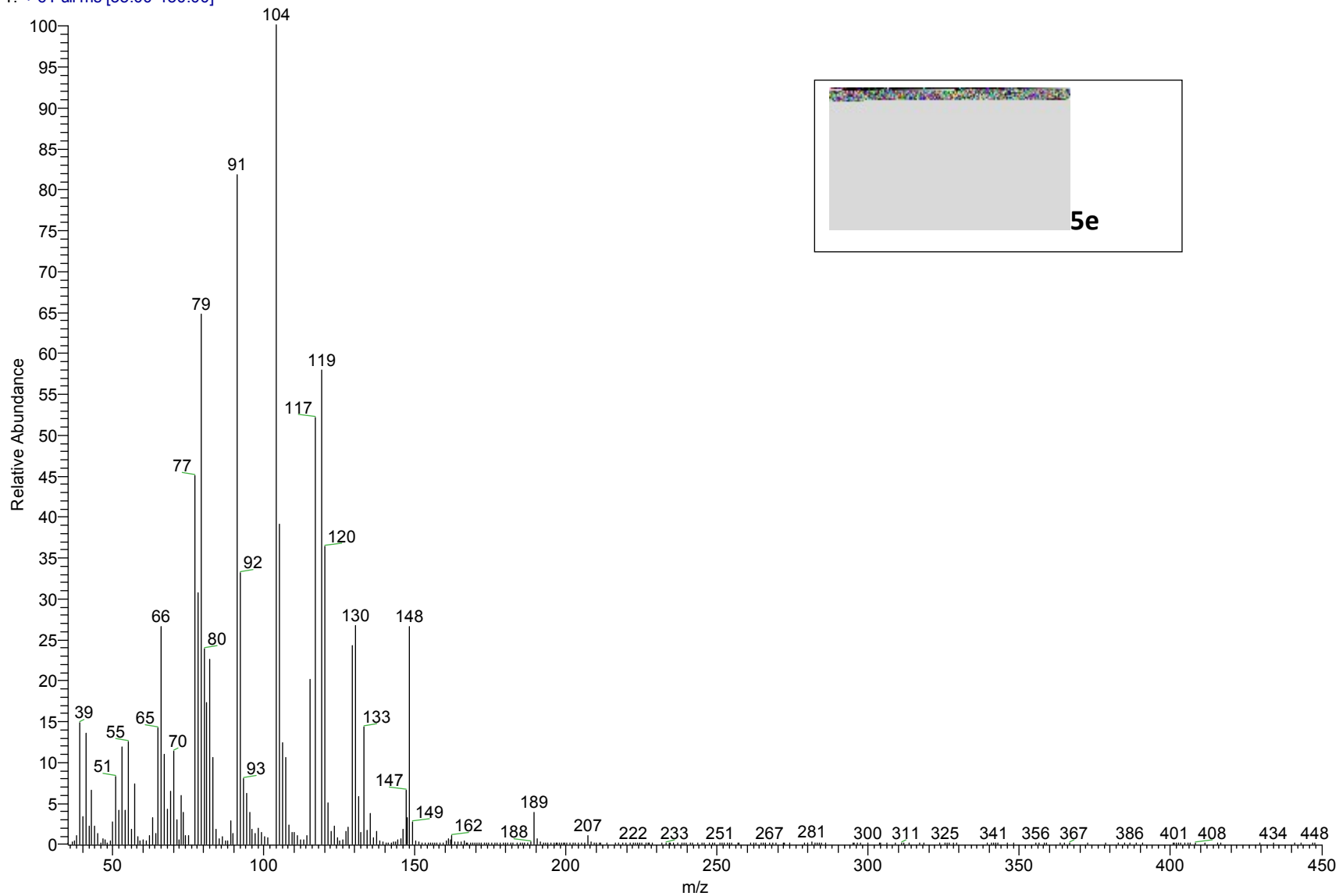
quadrelli37 #1081 RT: 15.42 AV: 1 NL: 1.07E7
T: + c Full ms [35.00-450.00]



quadrelli37 #1114 RT: 15.80 AV: 1 NL: 9.45E6
T: + c Full ms [35.00-450.00]



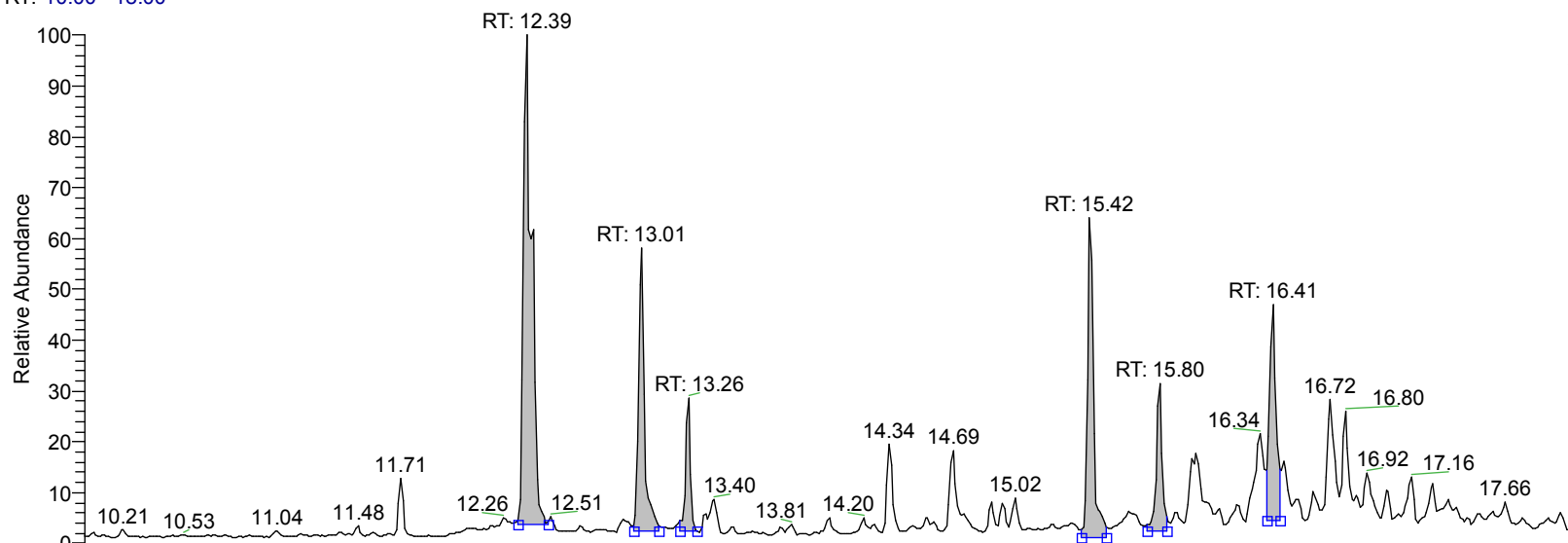
quadrelli37 #1167 RT: 16.41 AV: 1 NL: 5.50E6
T: + c Full ms [35.00-450.00]



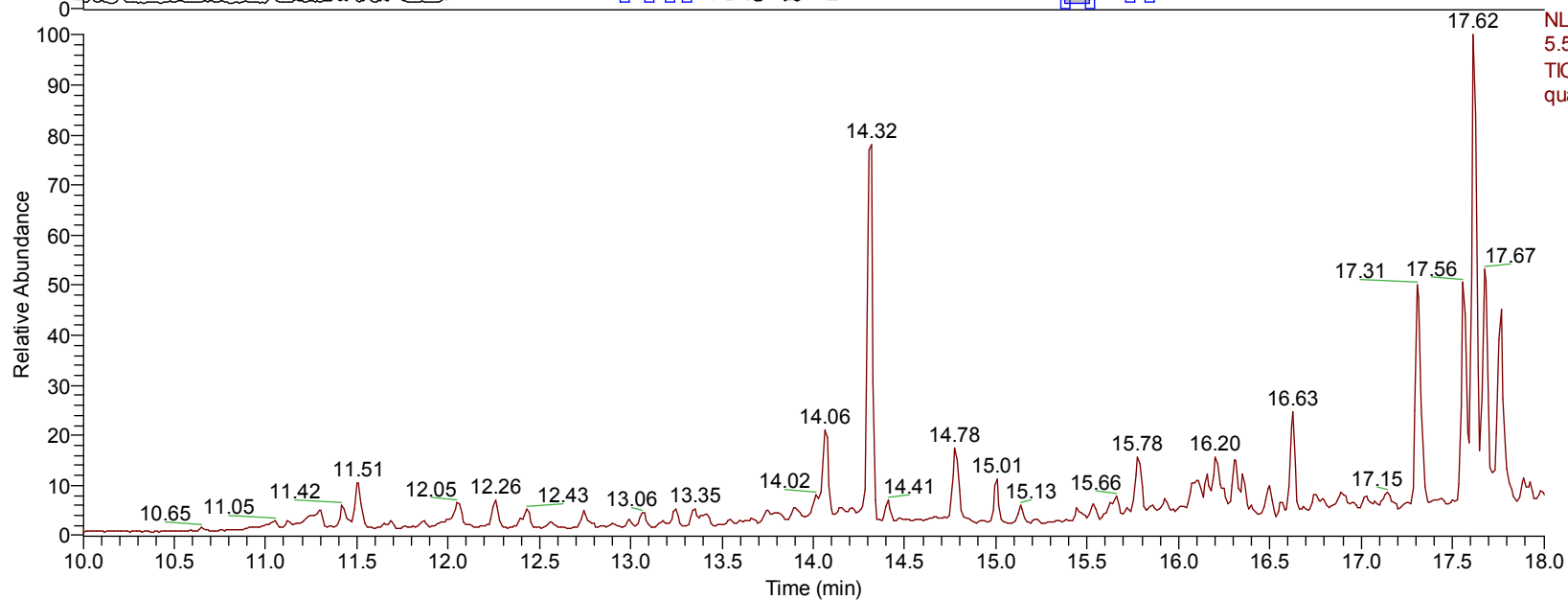
C3, reactions with cyclopentadiene

RT: 10.00 - 18.00

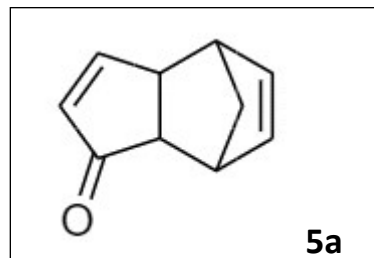
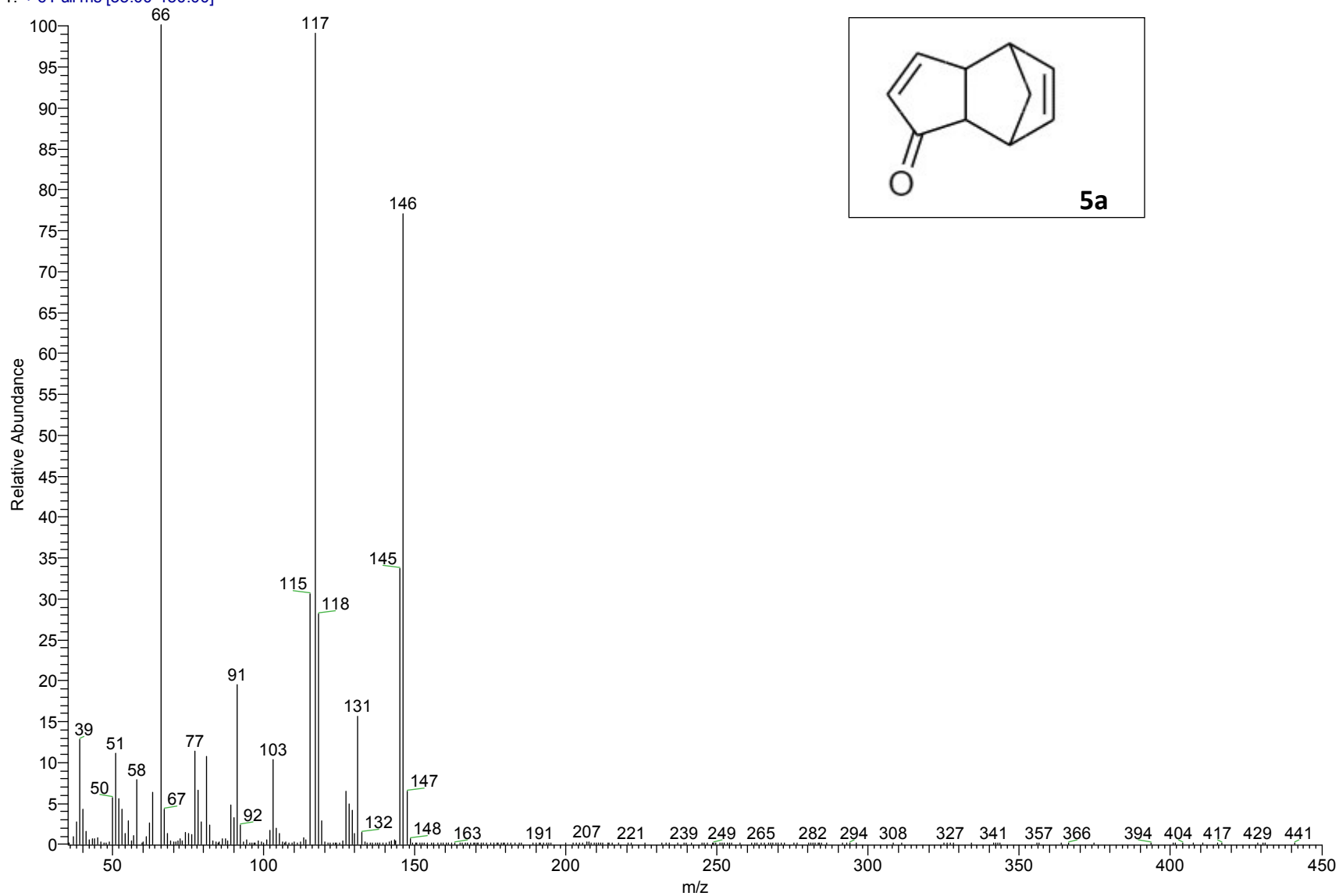
NL:
1.08E8
TIC MS
quadrelli39



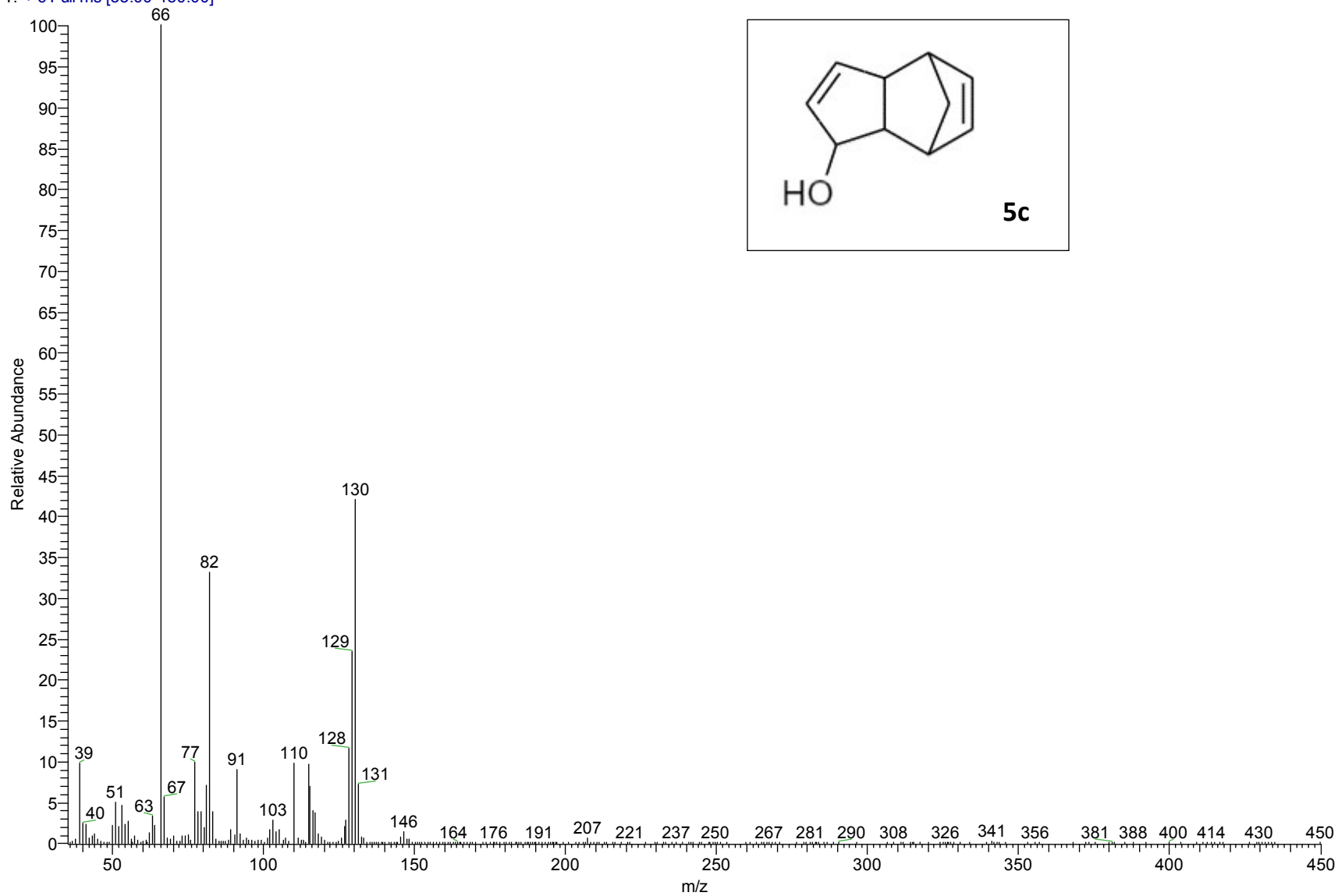
NL:
5.50E7
TIC MS
quadrelli58



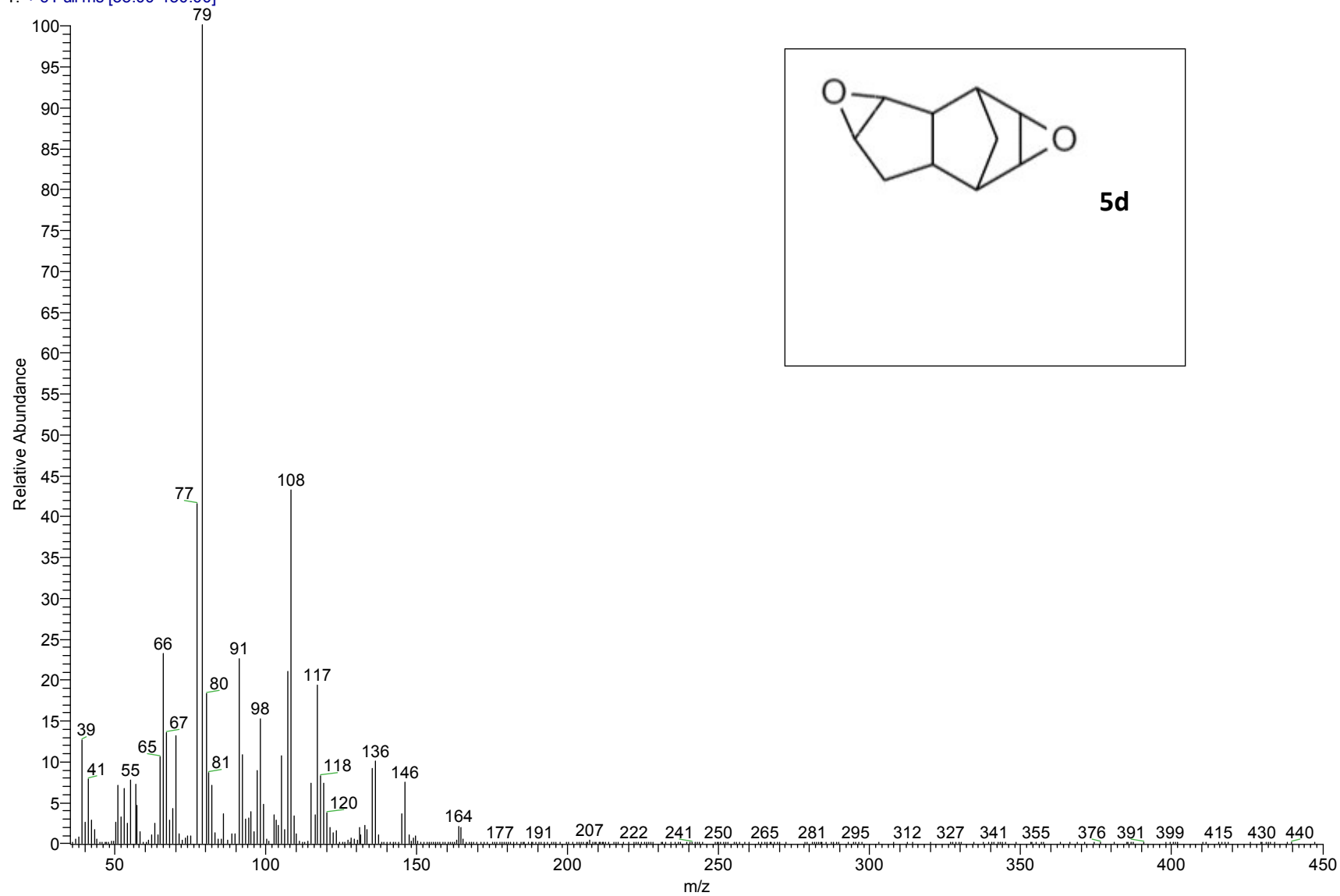
quadrelli39 #871 RT: 13.01 AV: 1 NL: 1.08E7
T: + c Full ms [35.00-450.00]



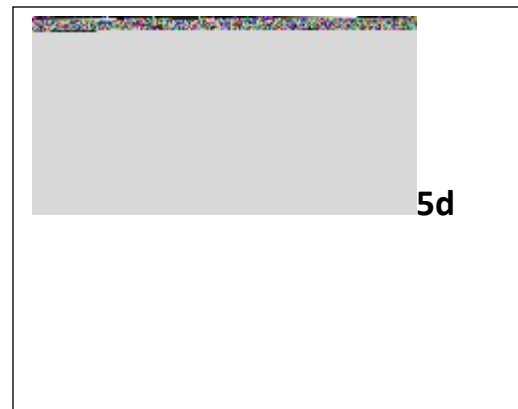
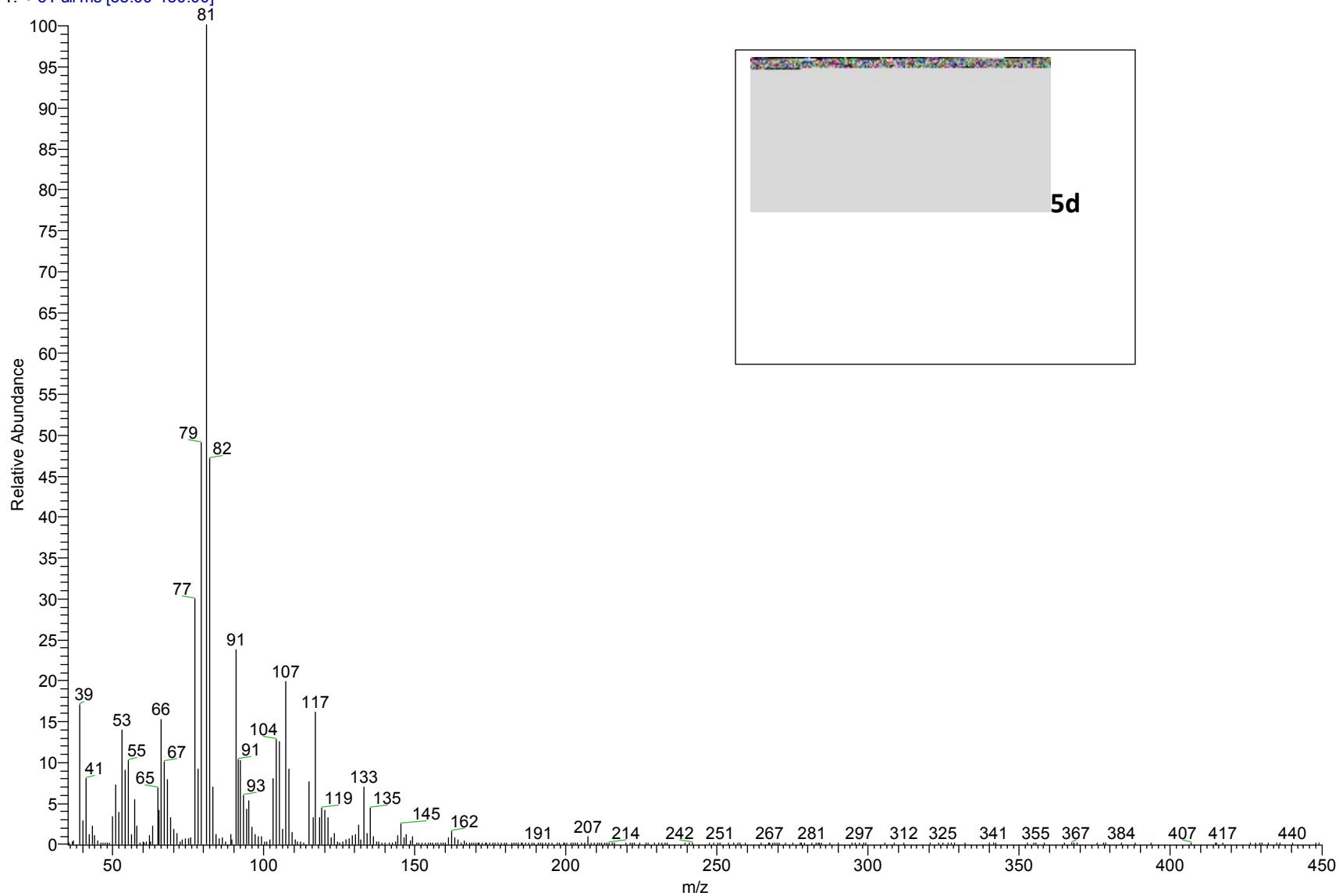
quadrelli39 #893 RT: 13.26 AV: 1 NL: 8.18E6
T: + c Full ms [35.00-450.00]



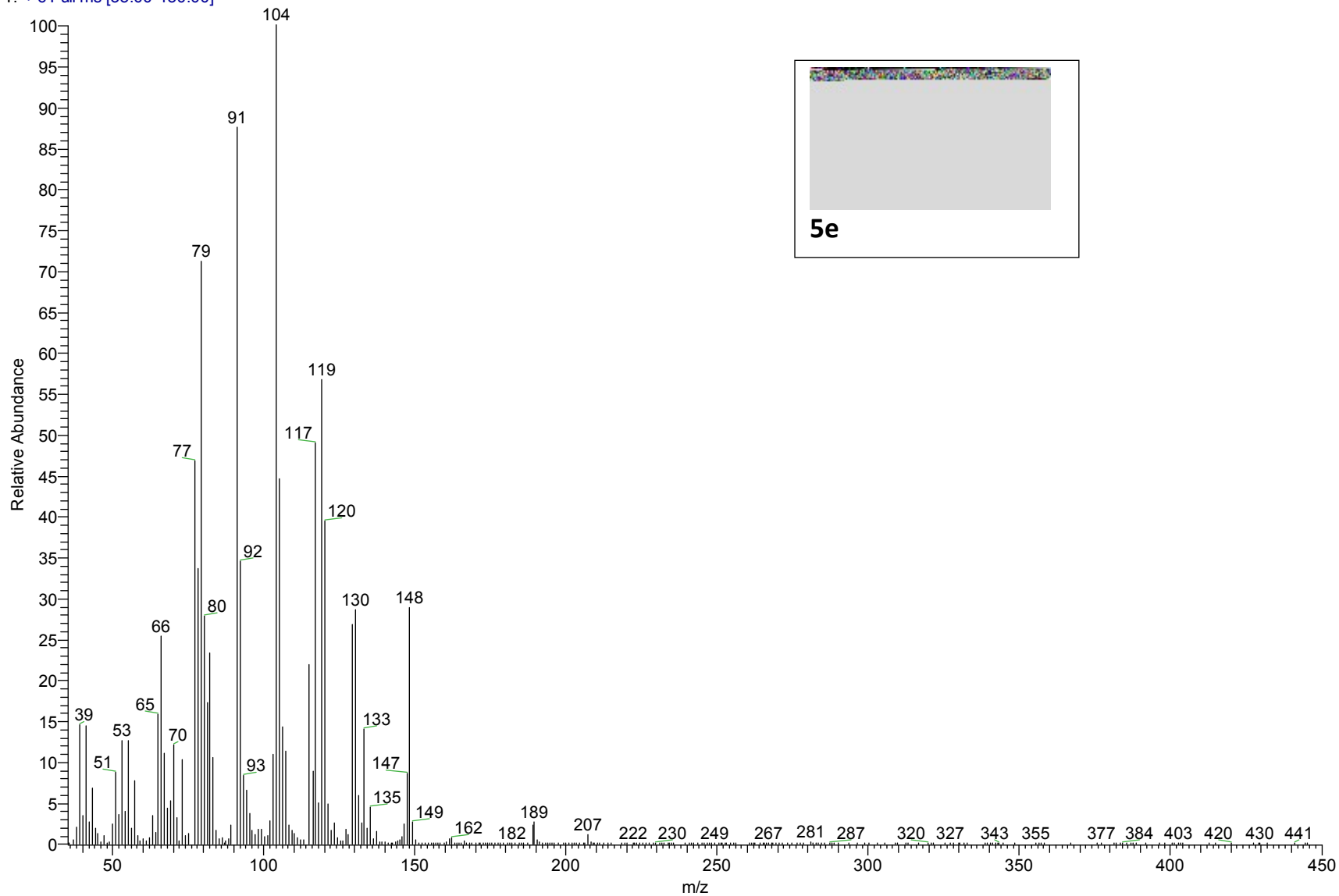
quadrelli39 #1081 RT: 15.42 AV: 1 NL: 1.17E7
T: + c Full ms [35.00-450.00]



quadrelli39 #1114 RT: 15.80 AV: 1 NL: 5.71E6
T: + c Full ms [35.00-450.00]



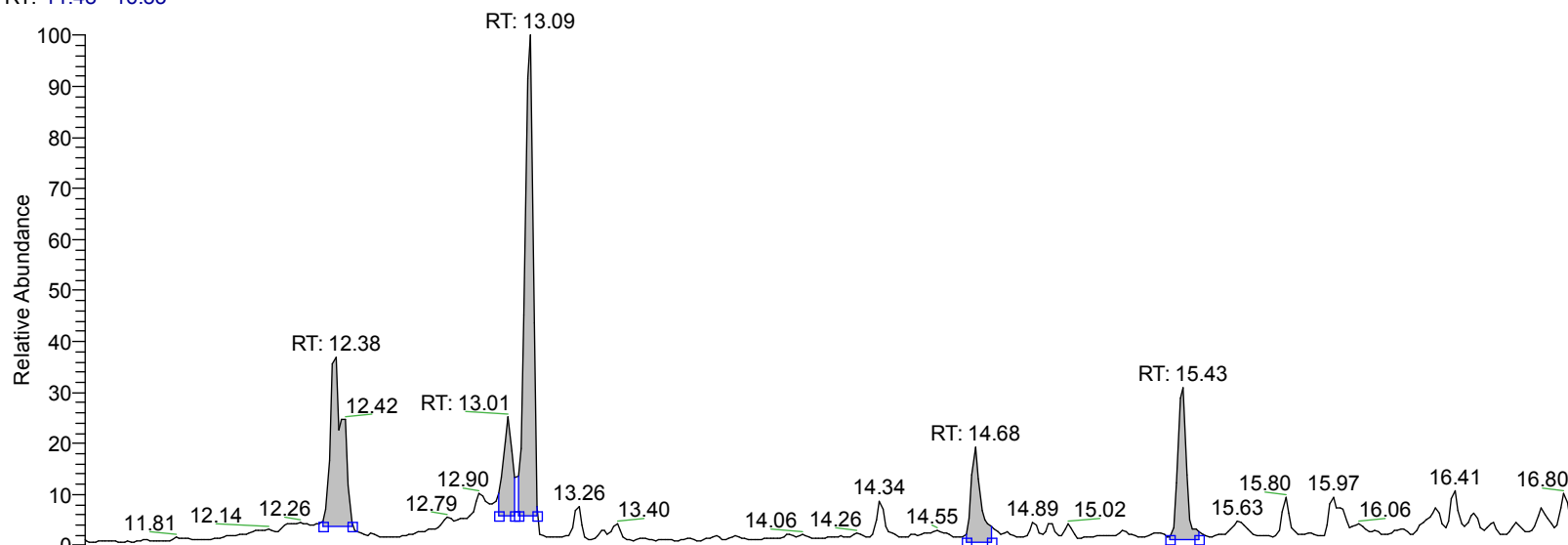
quadrelli39 #1167 RT: 16.41 AV: 1 NL: 4.58E6
T: + c Full ms [35.00-450.00]



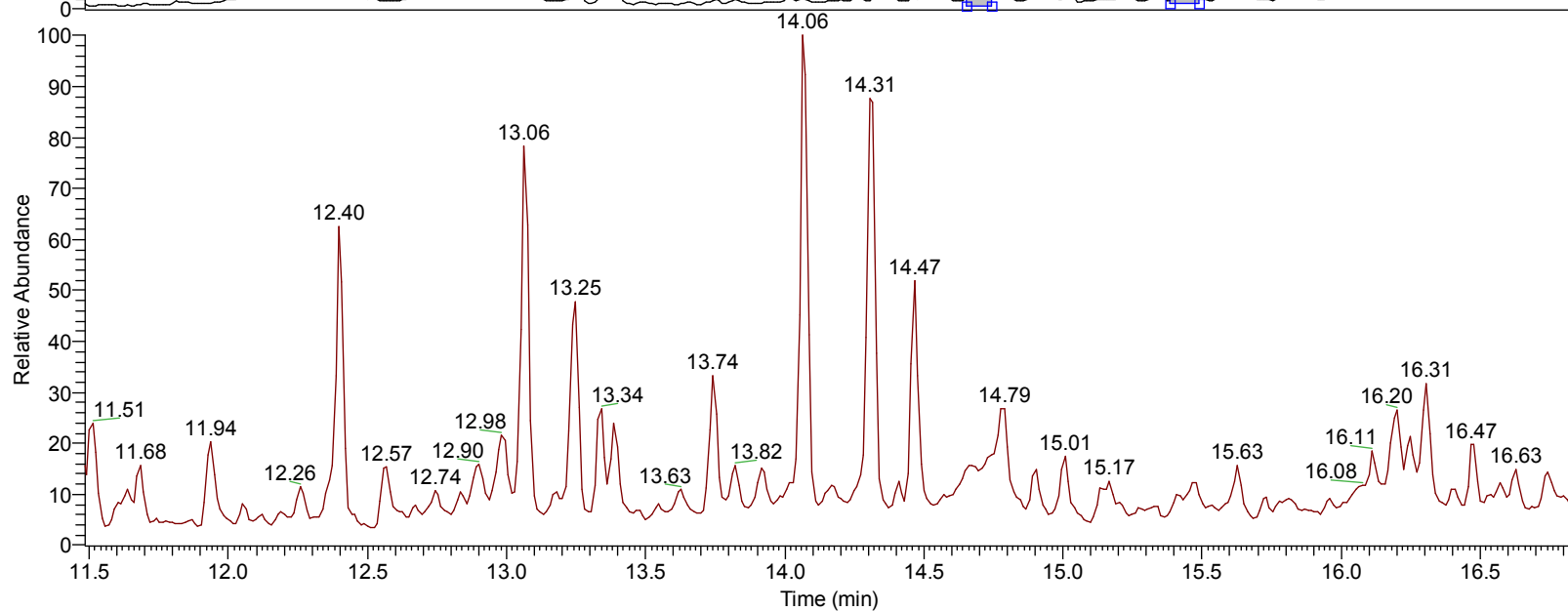
C4, reactions with cyclopentadiene

RT: 11.48 - 16.83

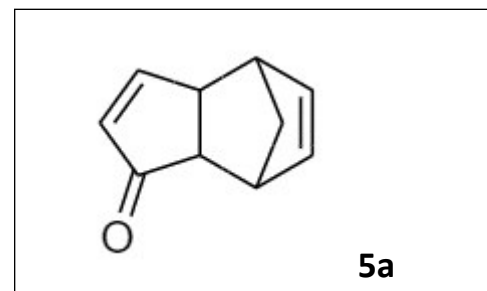
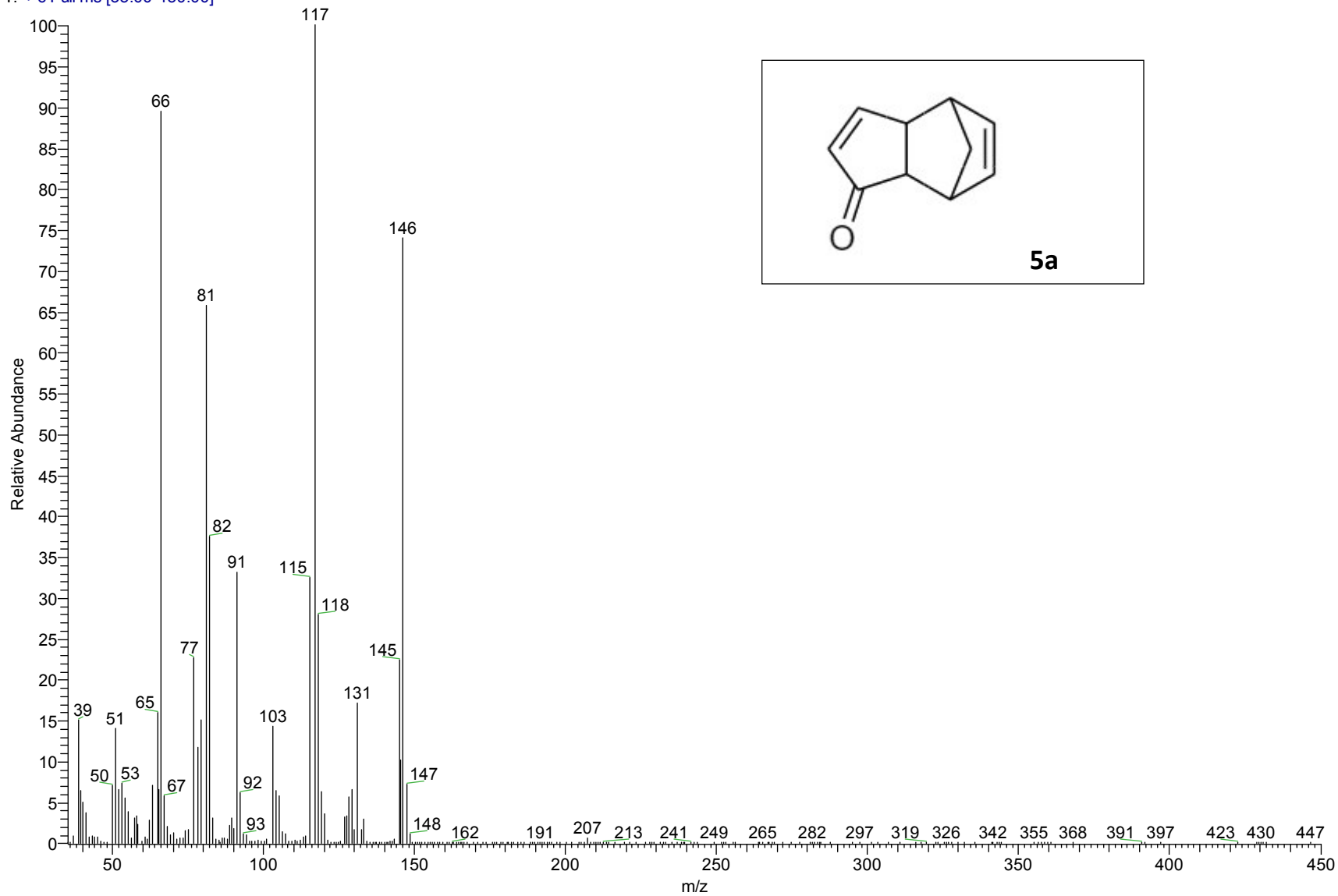
NL:
2.40E8
TIC MS
quadrelli41



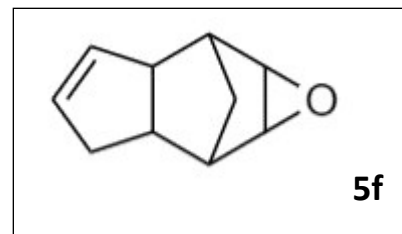
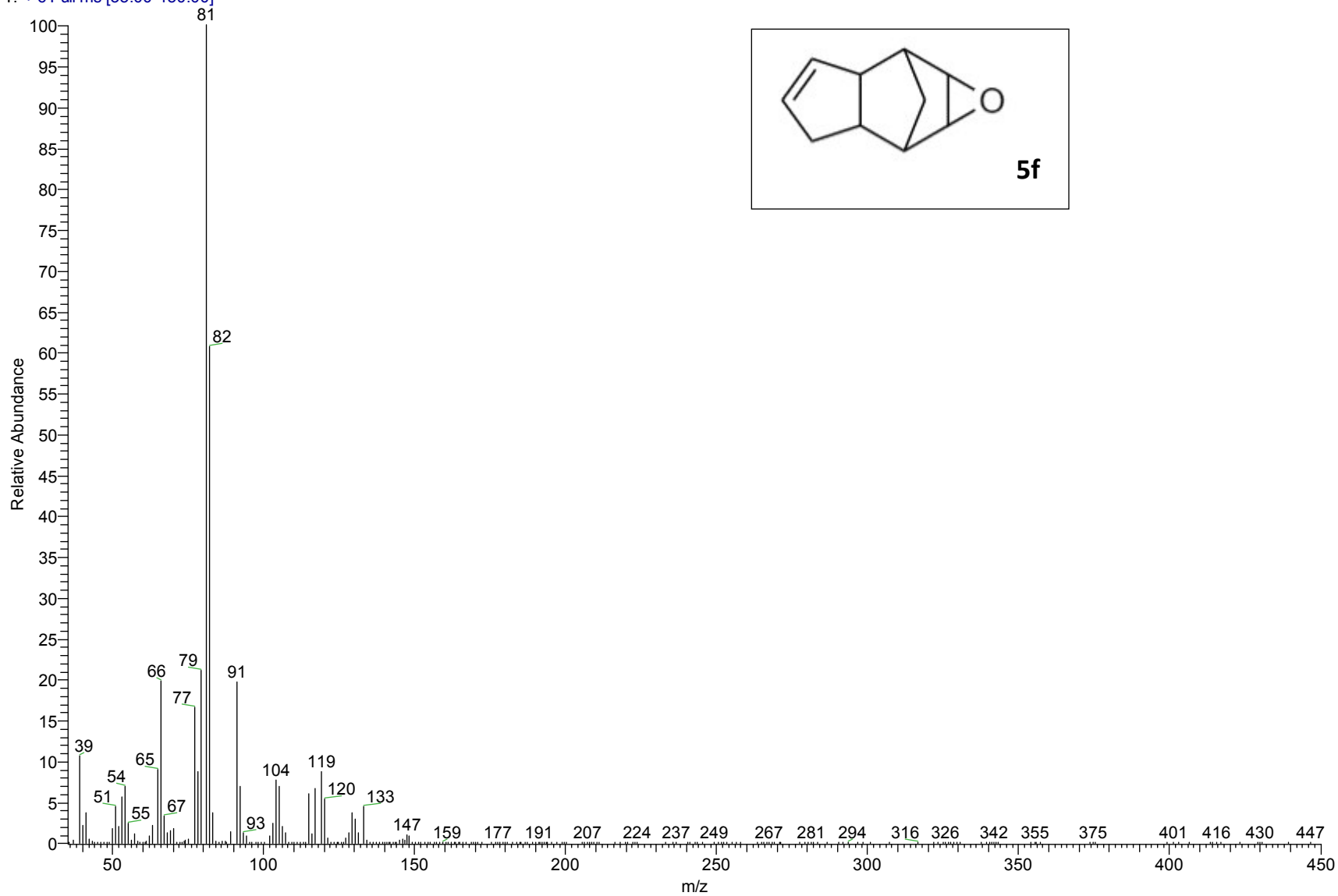
NL:
3.17E7
TIC MS
quadrelli62



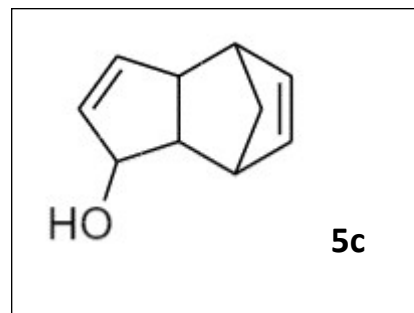
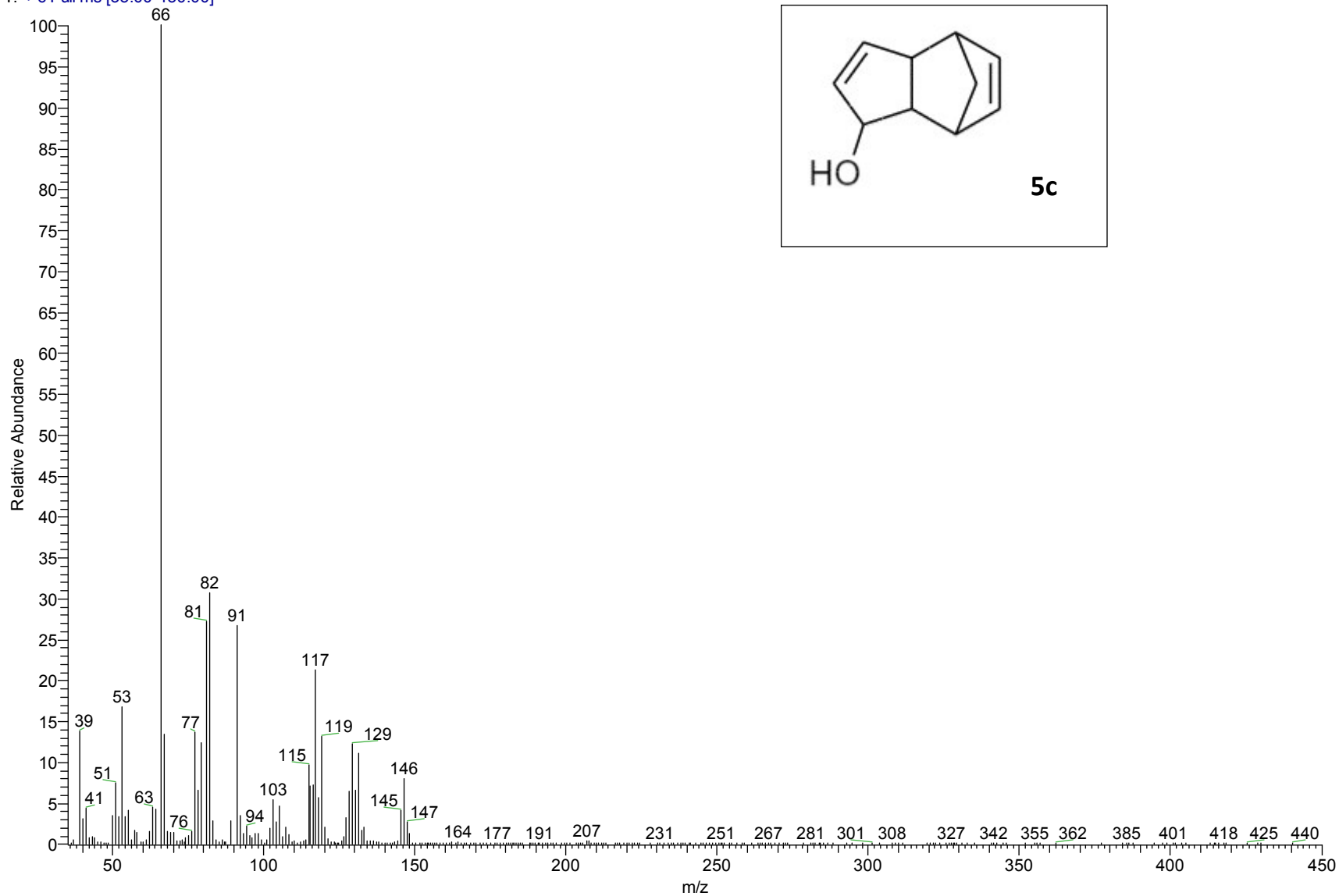
quadrelli41 #871 RT: 13.01 AV: 1 NL: 7.59E6
T: + c Full ms [35.00-450.00]



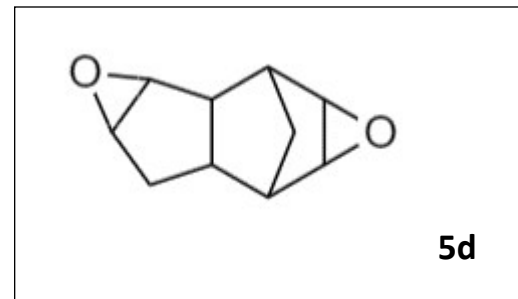
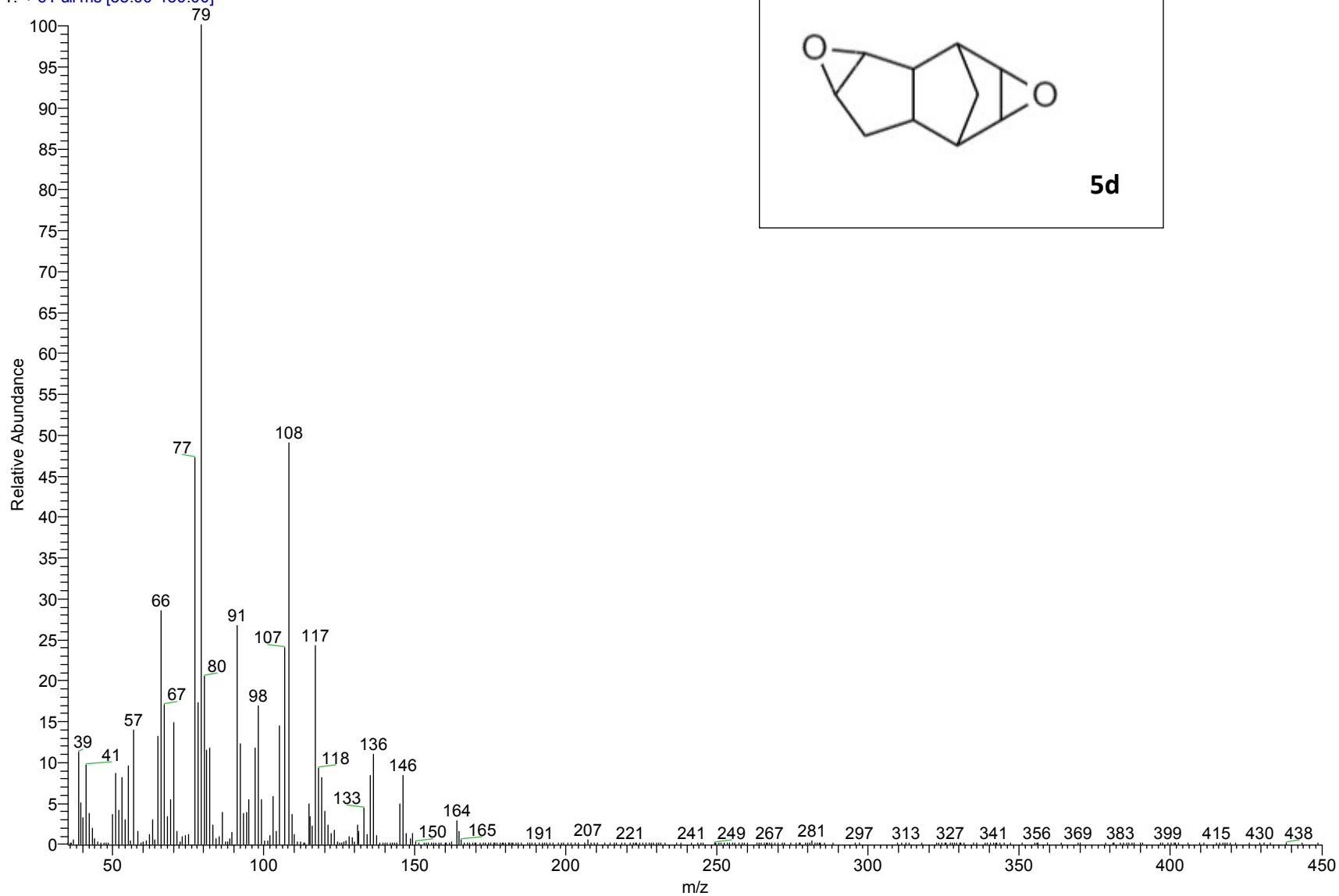
quadrelli41 #878 RT: 13.09 AV: 1 NL: 6.11E7
T: + c Full ms [35.00-450.00]



quadrelli41 #1017 RT: 14.68 AV: 1 NL: 9.50E6
T: + c Full ms [35.00-450.00]



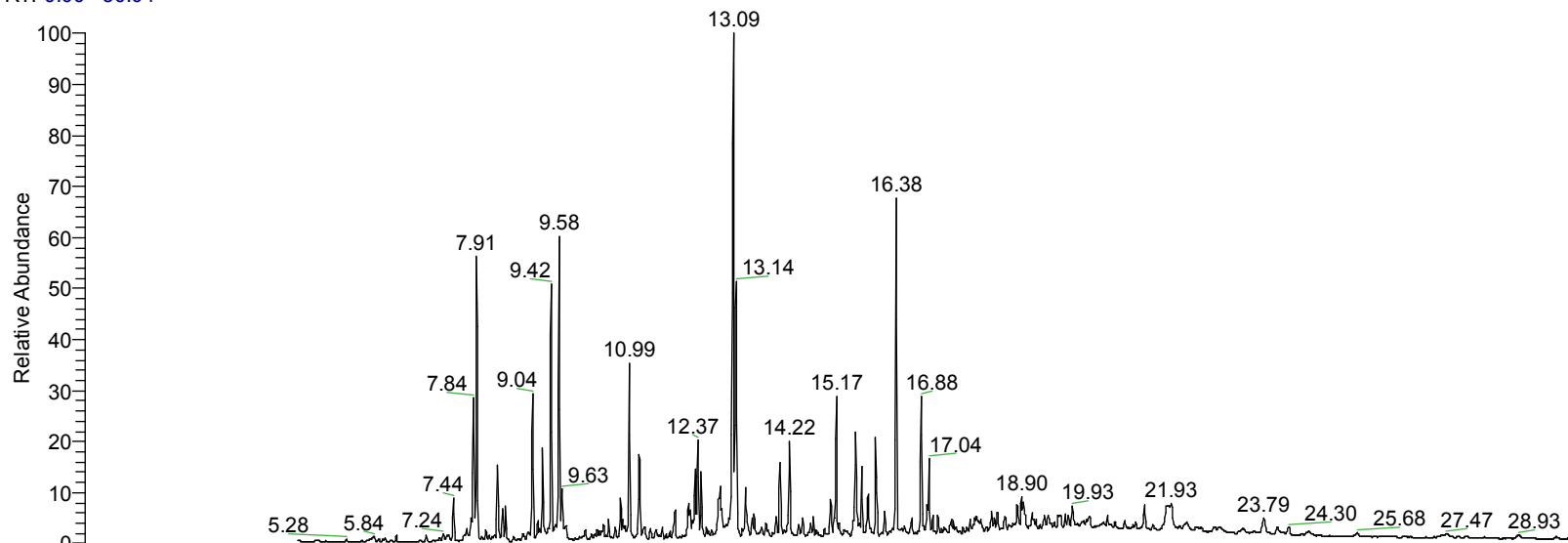
quadrelli41 #1082 RT: 15.43 AV: 1 NL: 1.05E7
T: + c Full ms [35.00-450.00]



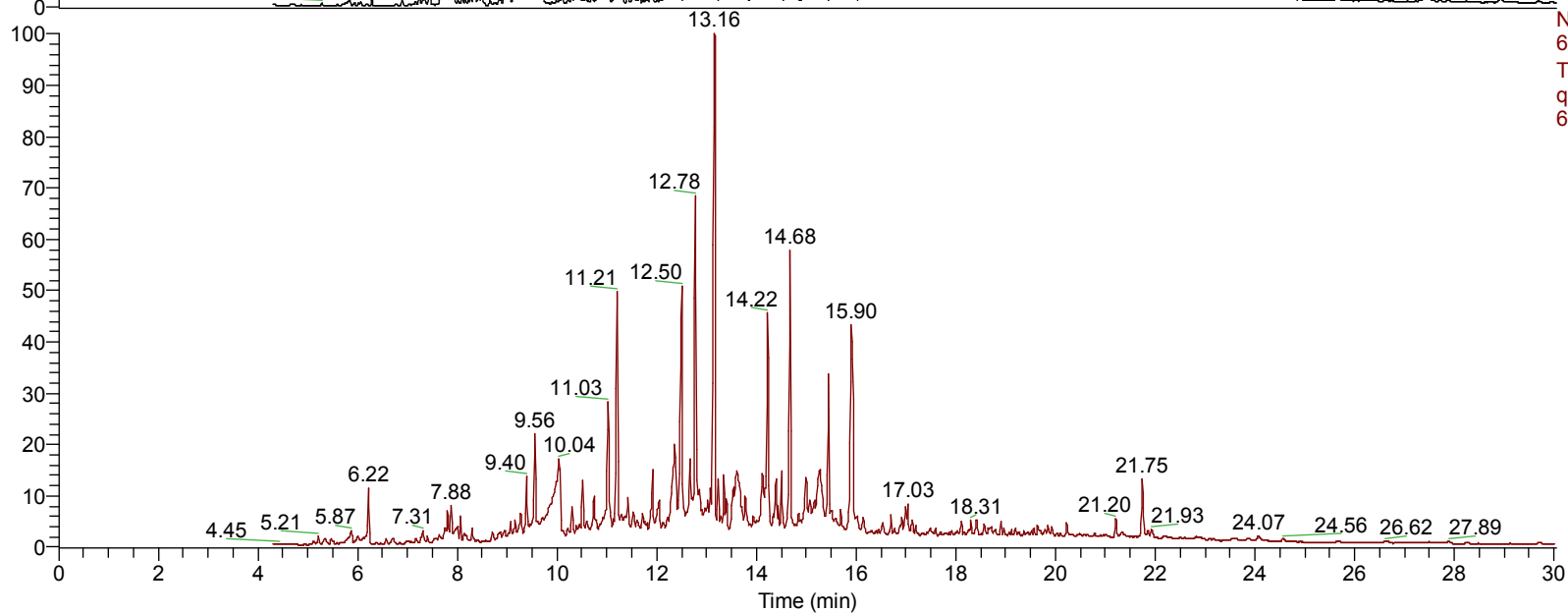
C4, reaction with 1-octene

RT: 0.00 - 30.04

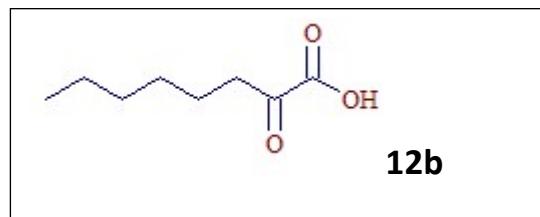
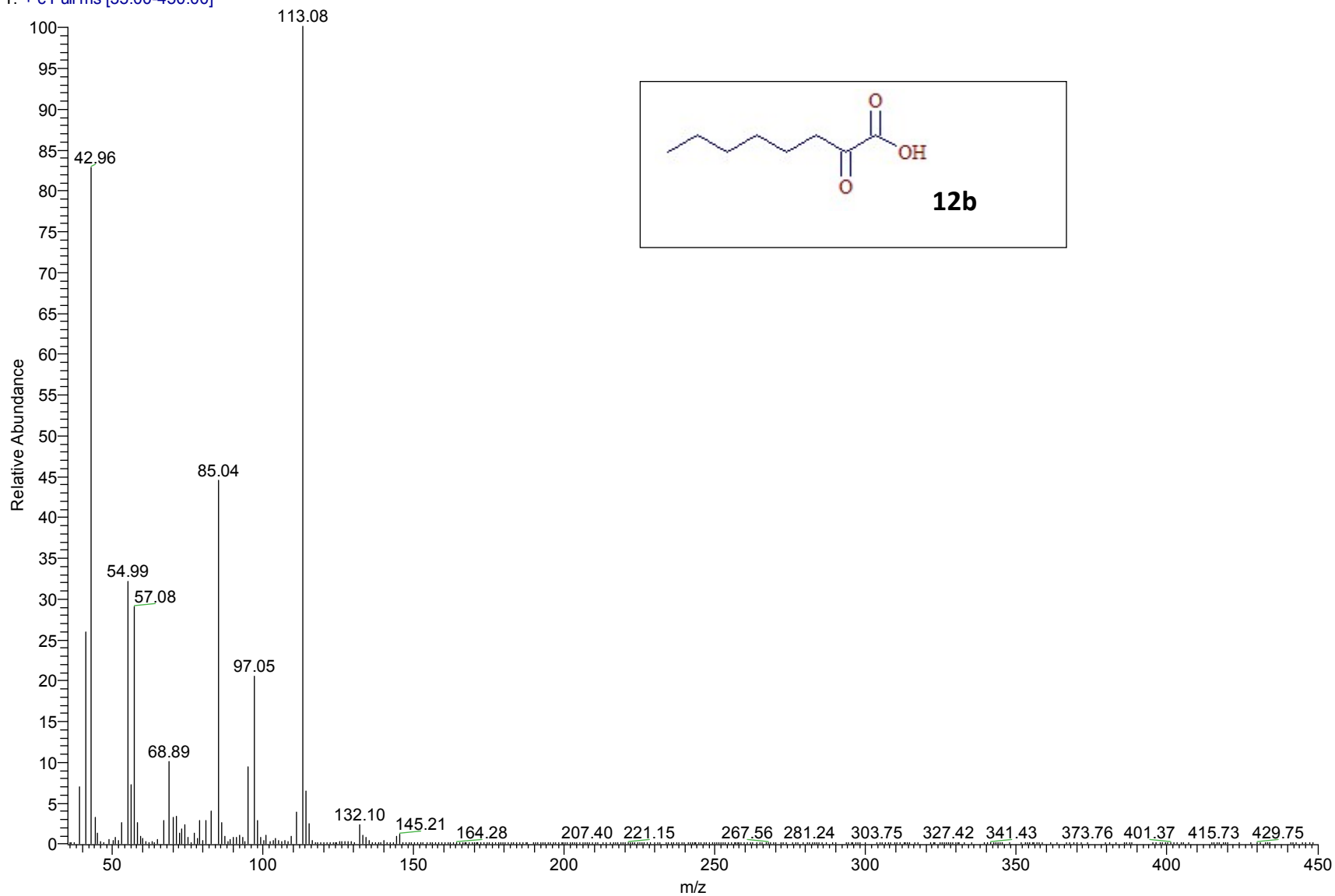
NL:
5.46E8
TIC MS
quadrelli17
5



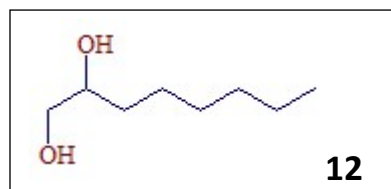
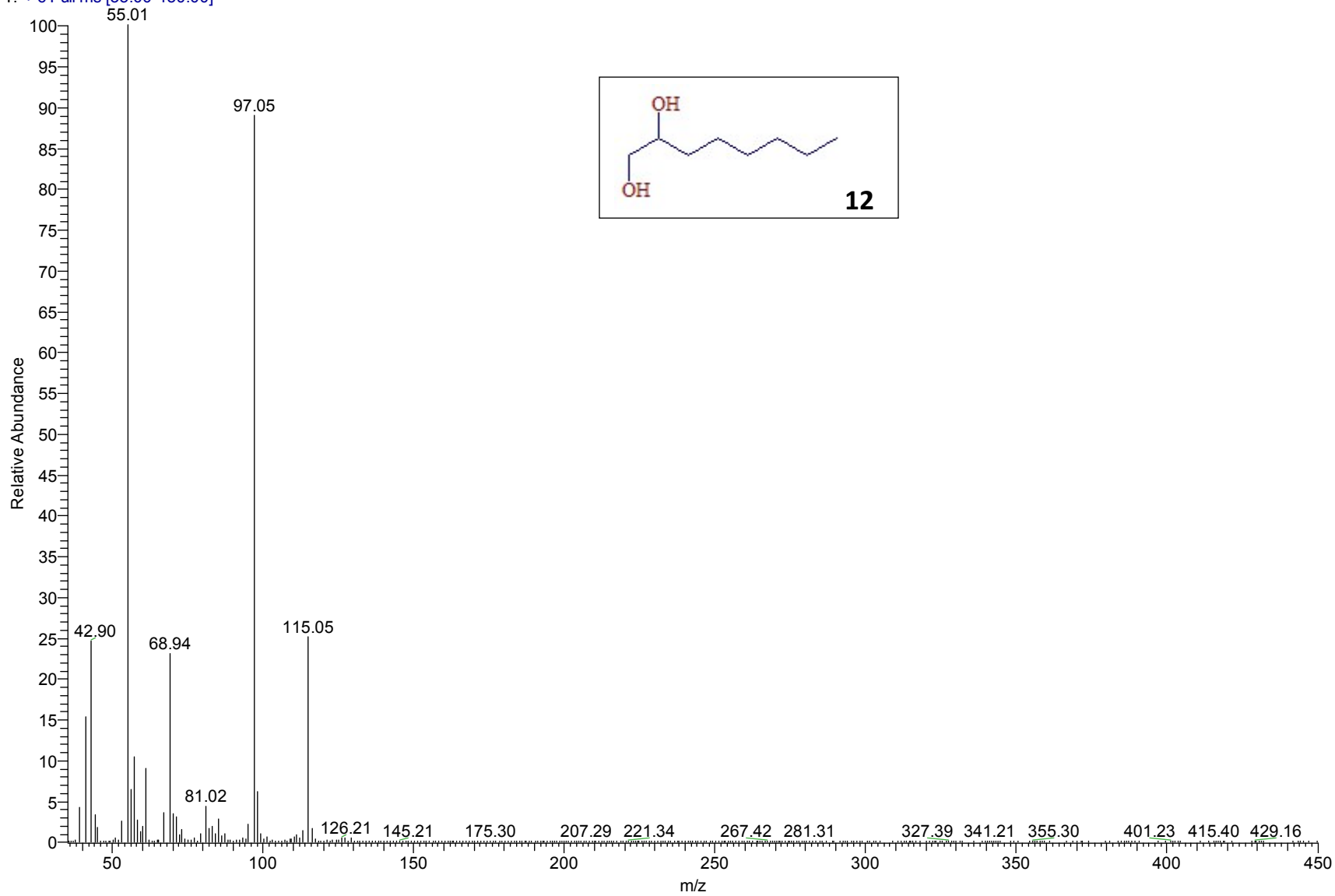
NL:
6.13E8
TIC MS
quadrelli17
6



quadrelli174 #602 RT: 11.21 AV: 1 NL: 8.45E7
T: + c Full ms [35.00-450.00]



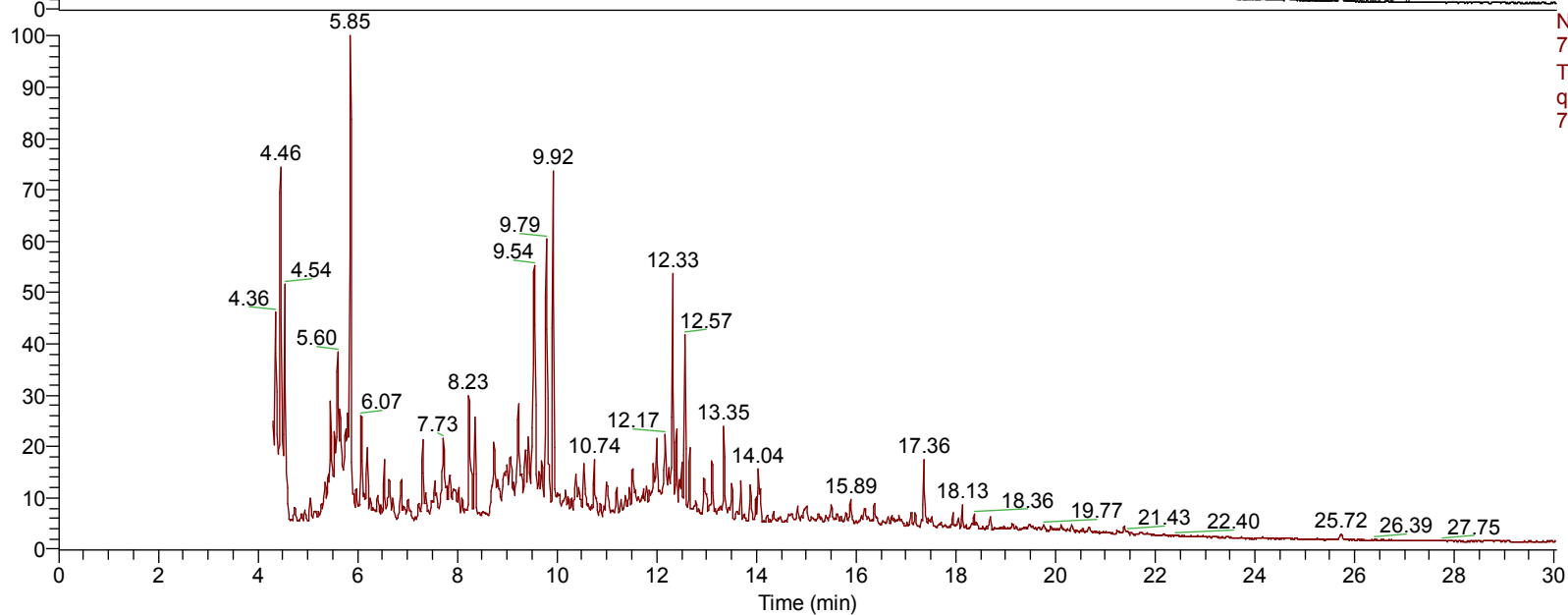
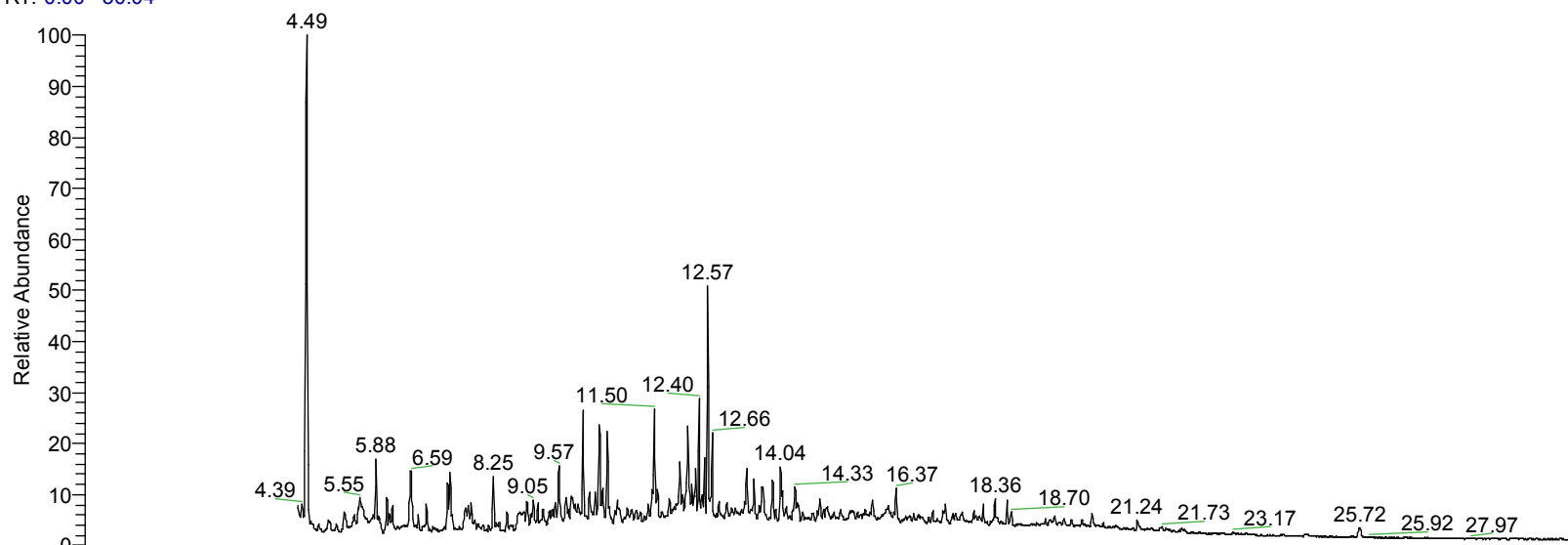
quadrelli174 #714 RT: 12.50 AV: 1 NL: 7.95E7
T: + c Full ms [35.00-450.00]



C4, reaction with trimethyl ethylene (tme)

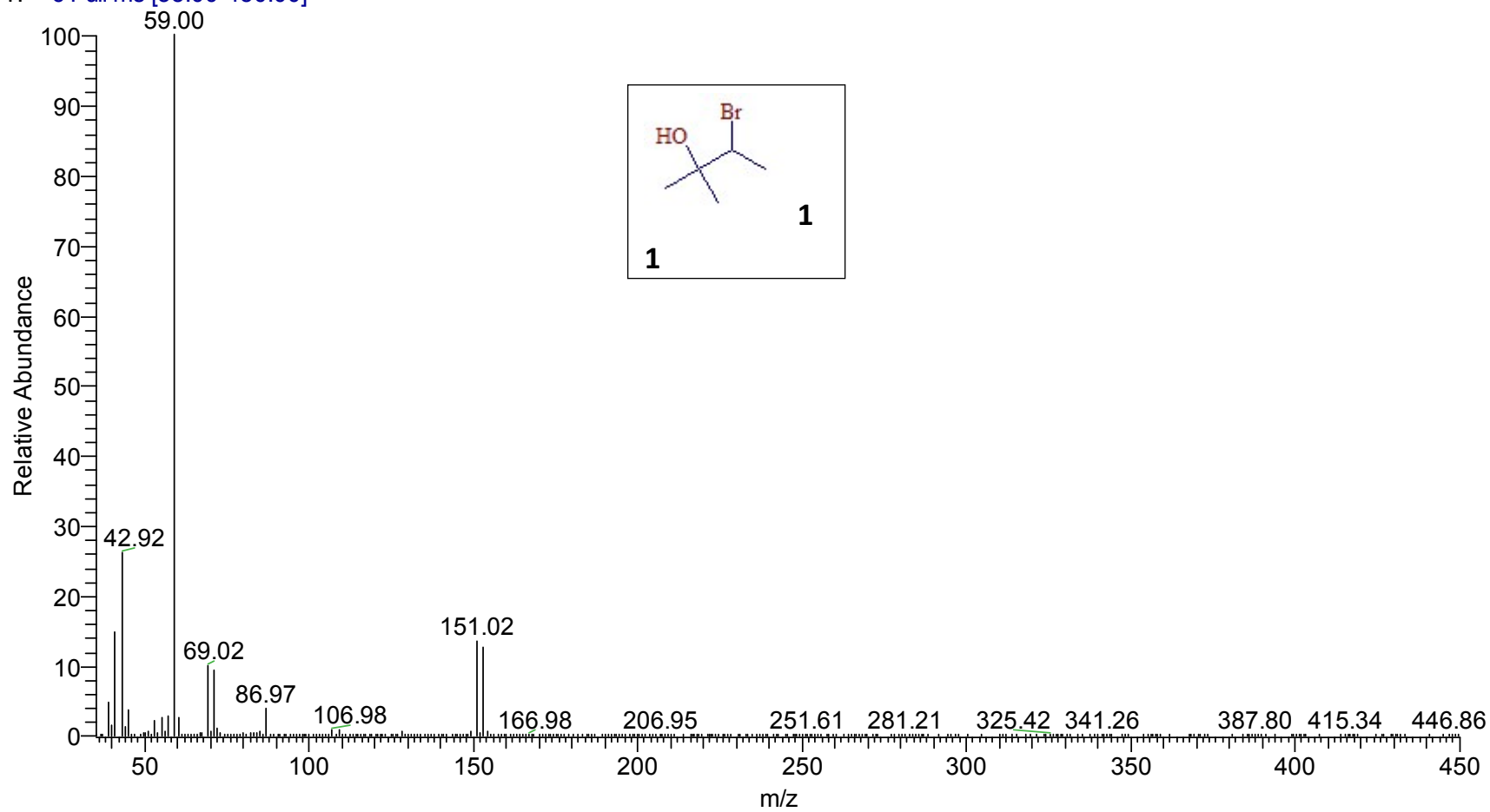
RT: 0.00 - 30.04

NL:
1.24E8
TIC MS
quadrelli12
3



quadrelli127 #136 RT: 5.85 AV: 1 NL: 3.14E7

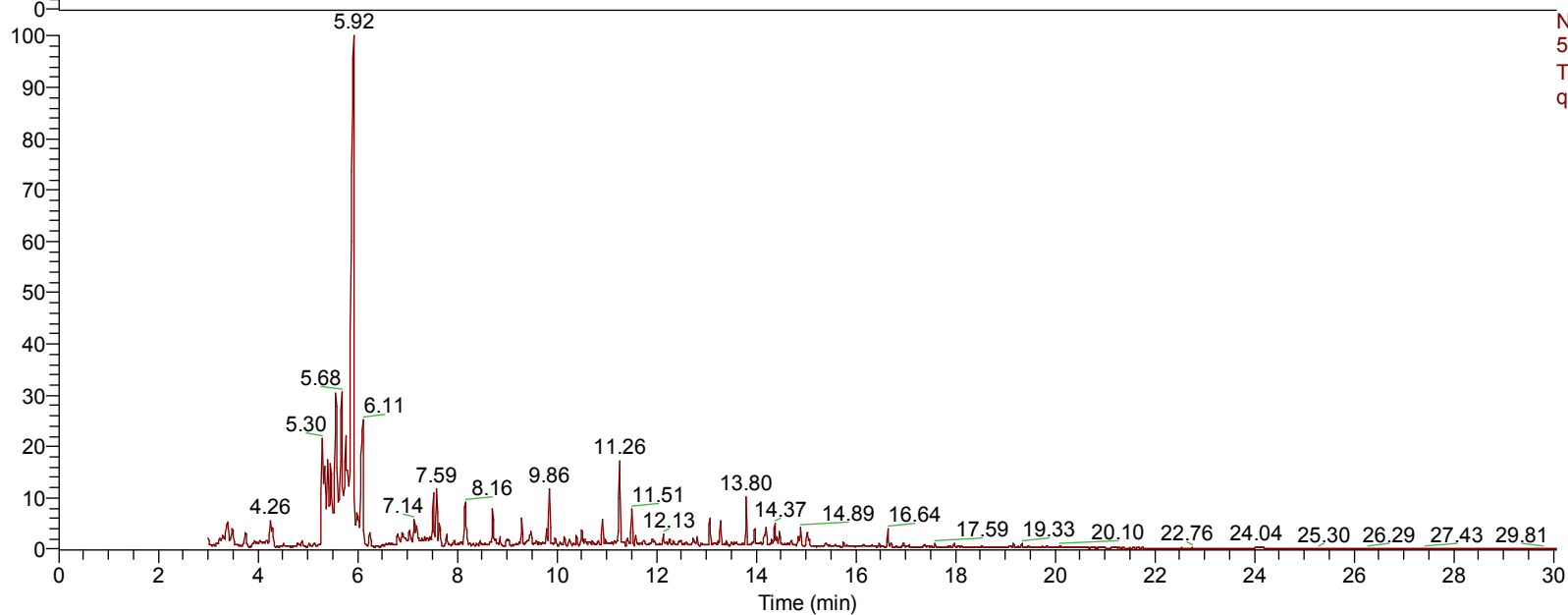
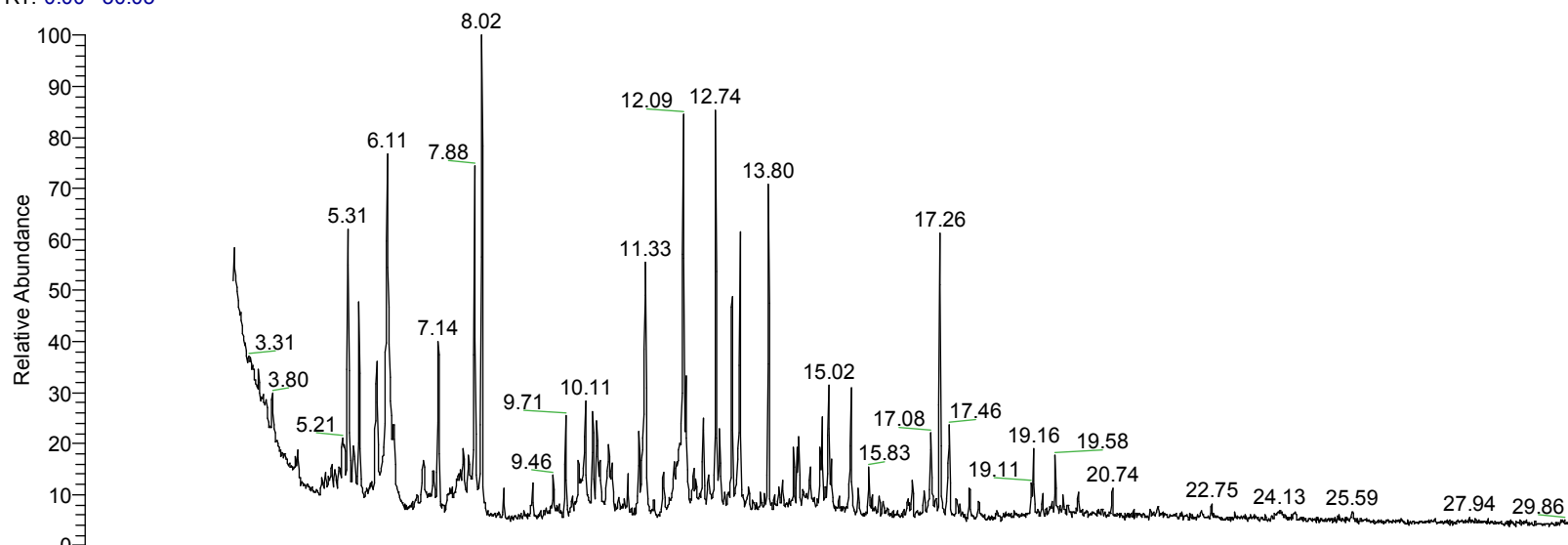
T: + c Full ms [35.00-450.00]



C4, reaction with tetramethyl ethylene (TME)

RT: 0.00 - 30.05

NL:
5.78E6
TIC MS
quadrelli86

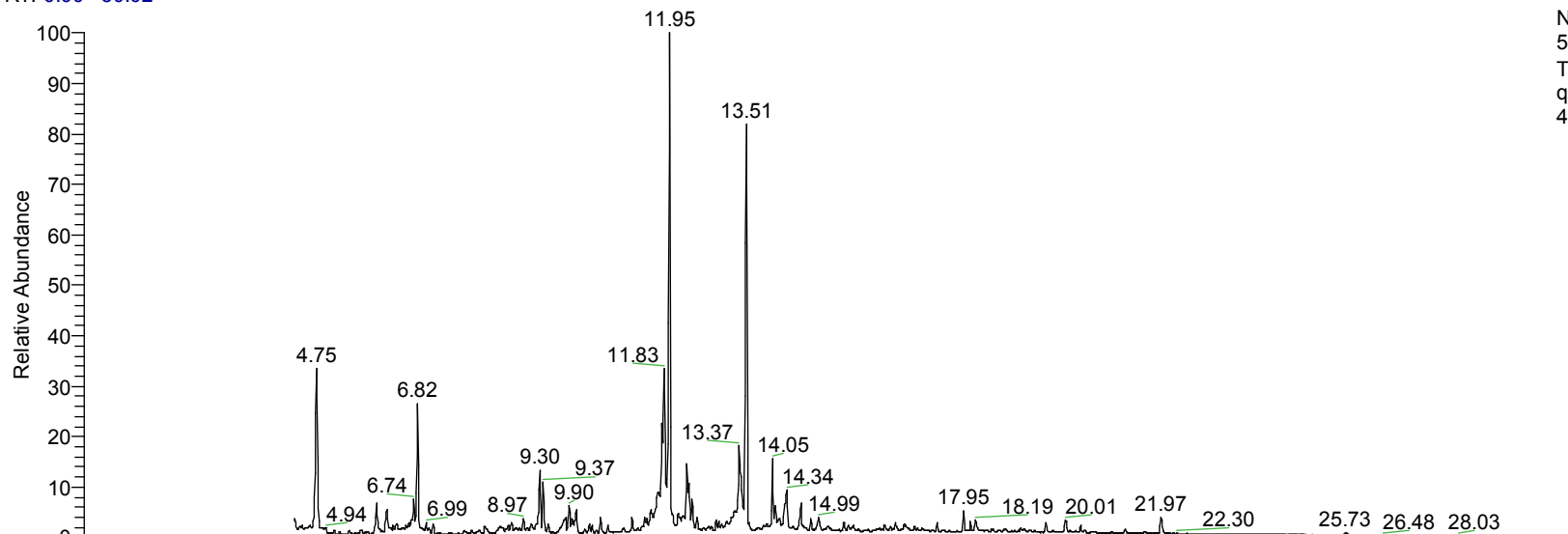


No results

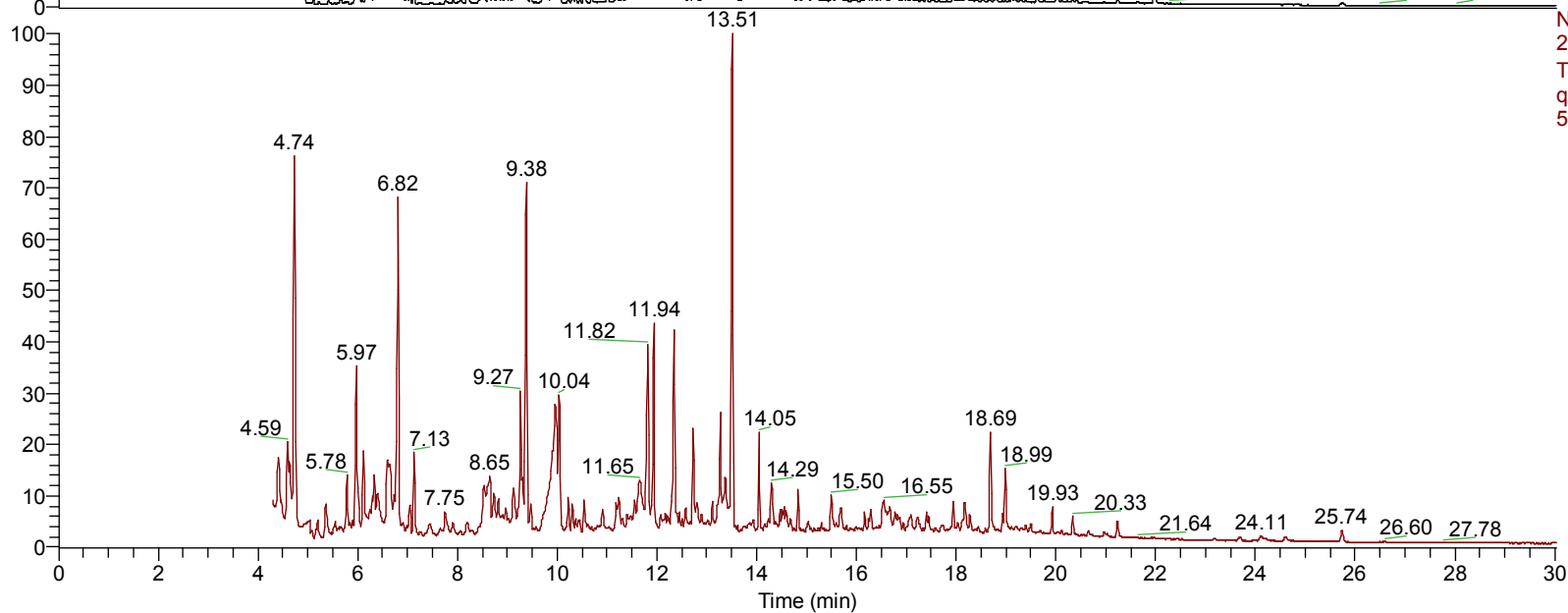
C4, reaction with cyclopentene

RT: 0.00 - 30.02

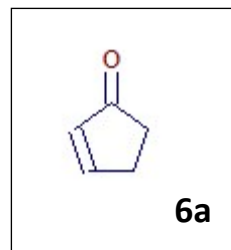
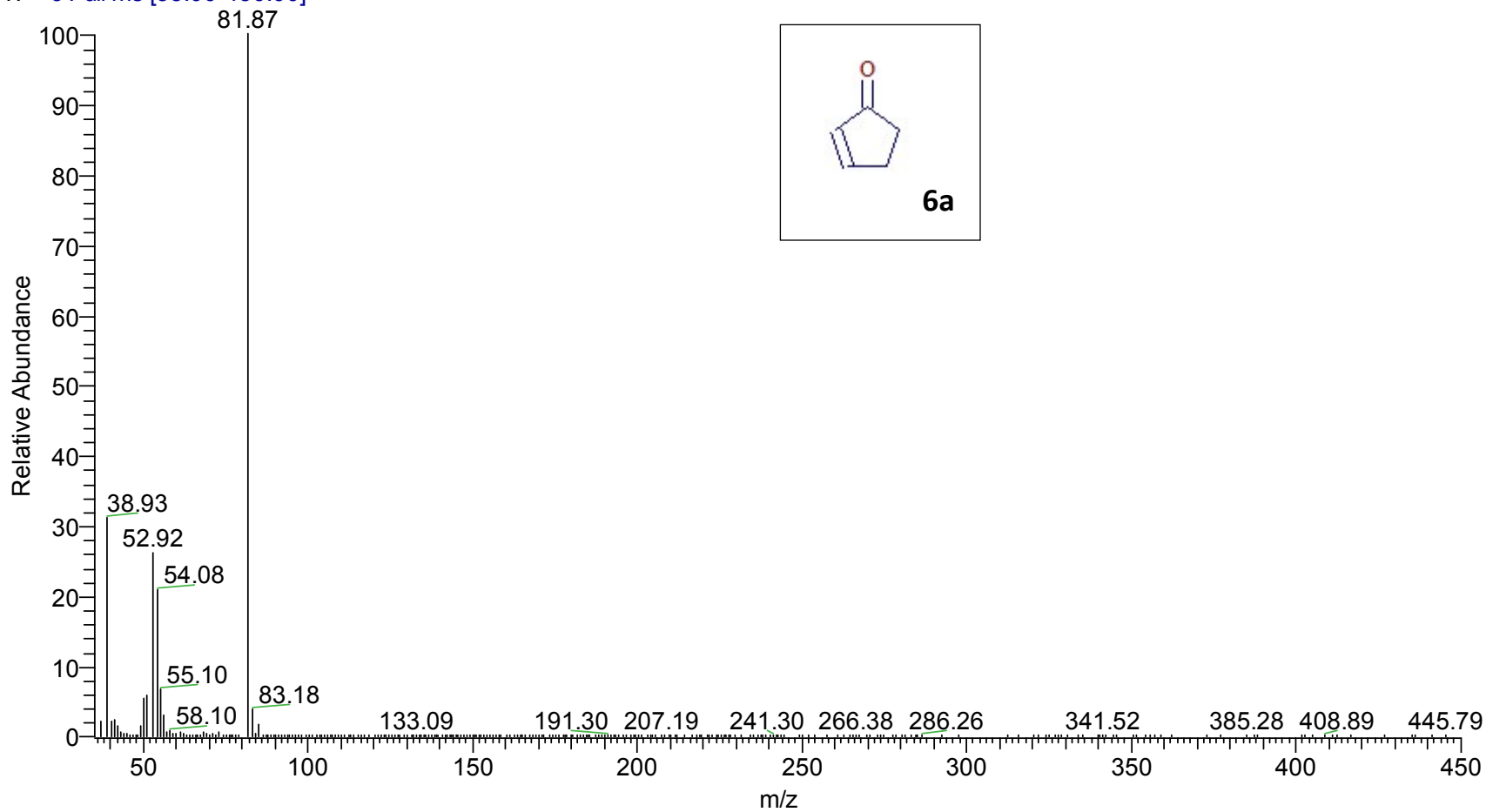
NL:
5.66E8
TIC MS
quadrelli11
4



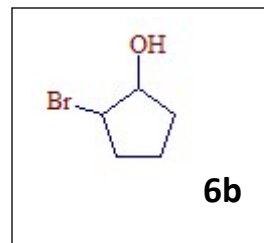
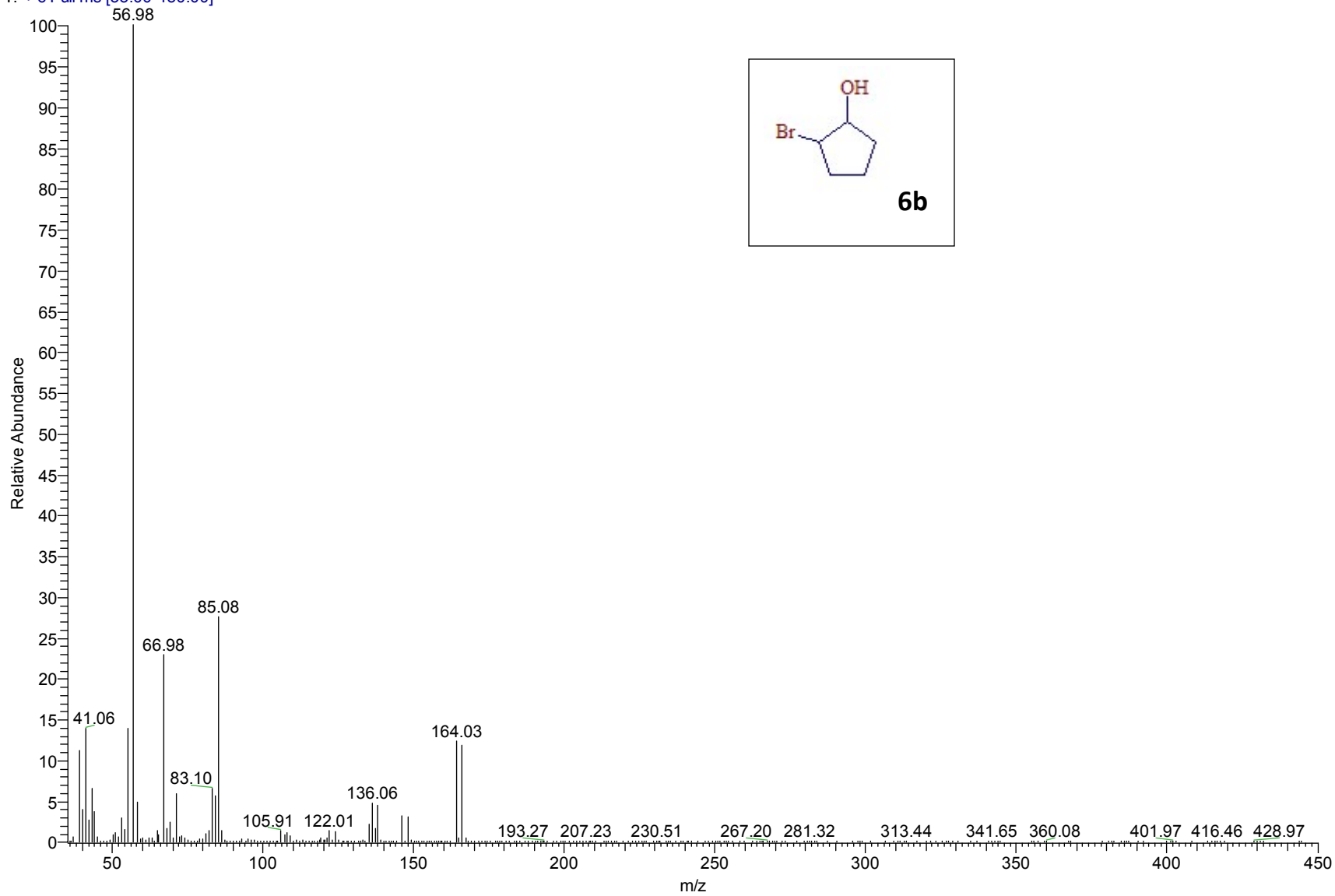
NL:
2.76E8
TIC MS
quadrelli11
5



quadrelli139 #44 RT: 4.80 AV: 1 NL: 8.17E7
T: + c Full ms [35.00-450.00]

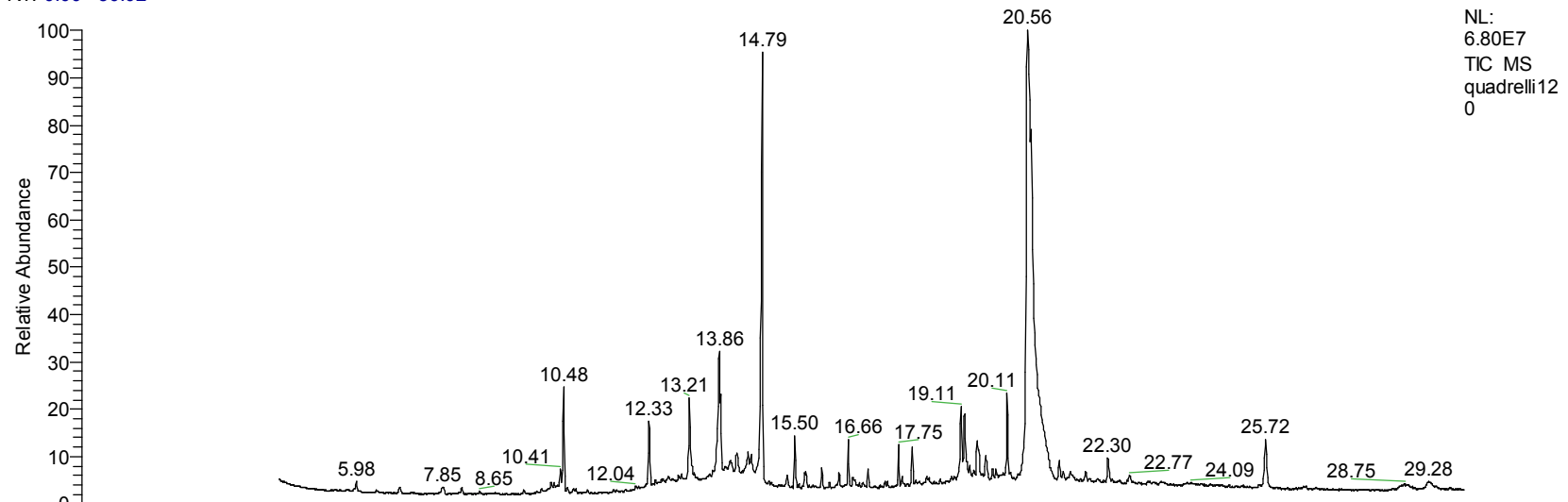


quadrelli139 #442 RT: 9.37 AV: 1 NL: 2.49E7
T: + c Full ms [35.00-450.00]

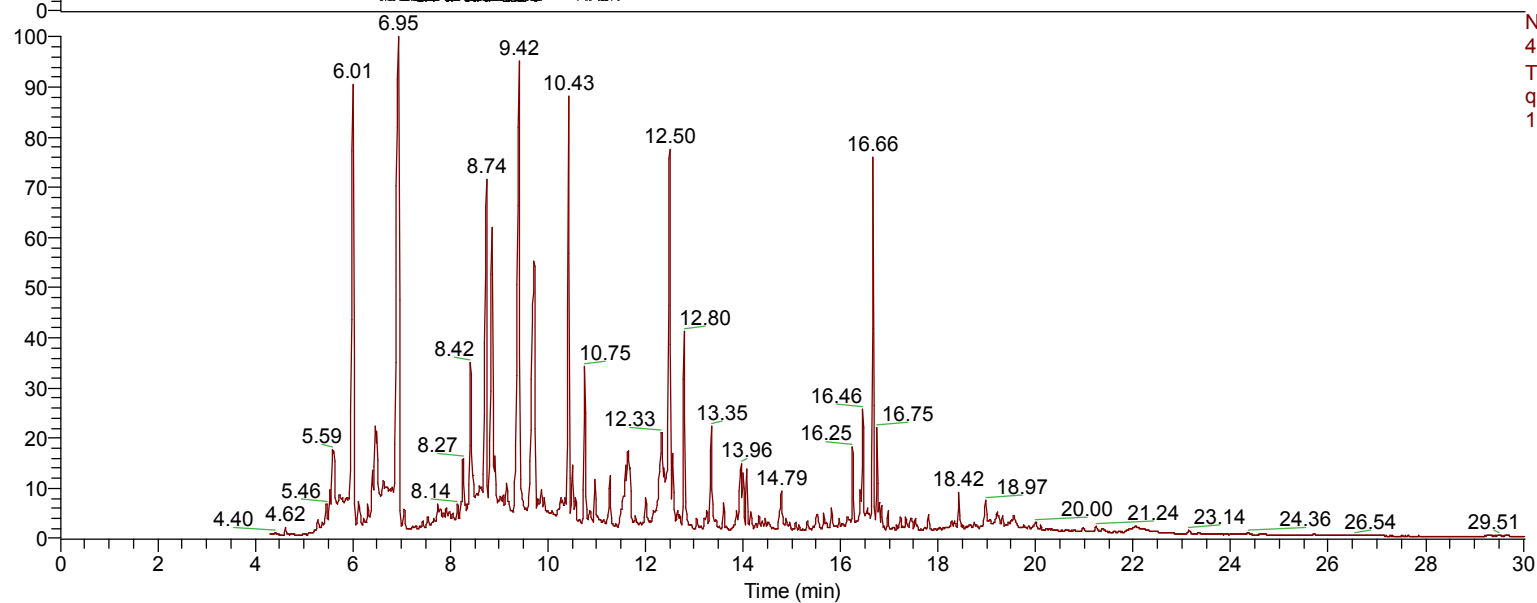


C4, reaction with cyclohexene

RT: 0.00 - 30.02

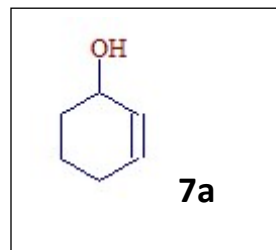
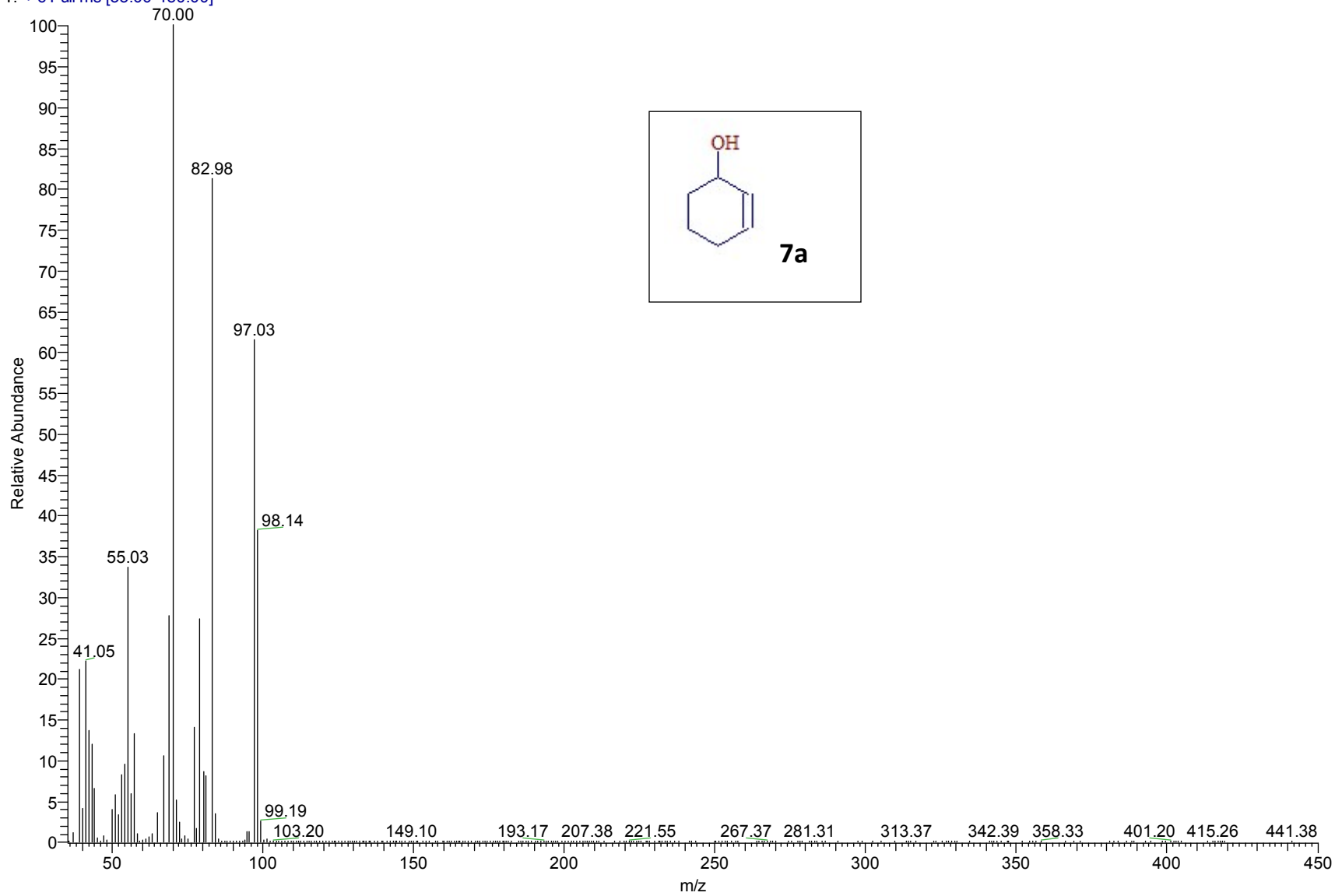


NL:
6.80E7
TIC MS
quadrelli12
0

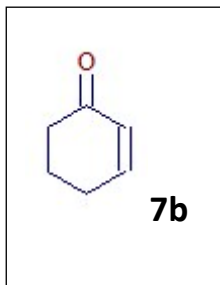
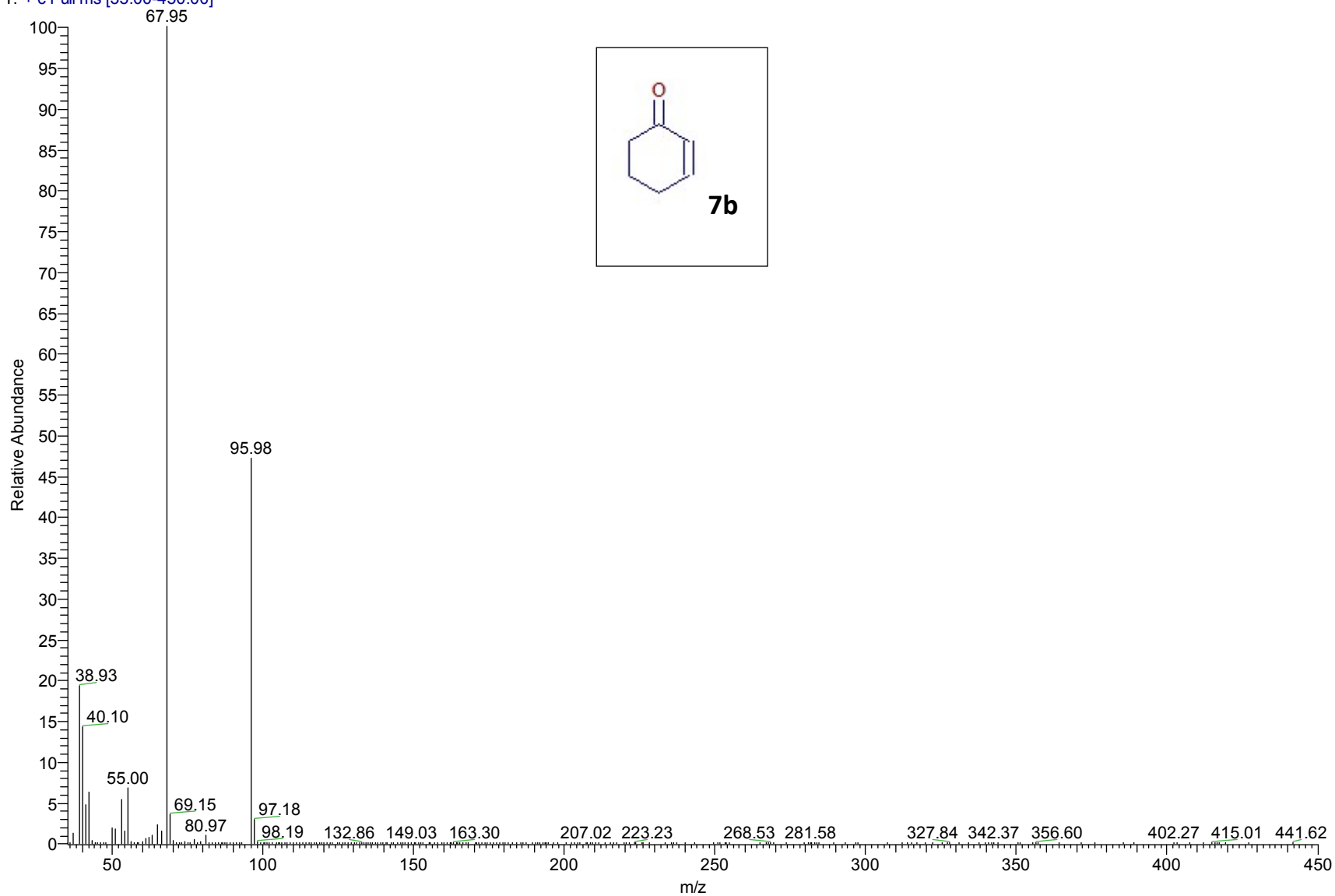


NL:
4.60E8
TIC MS
quadrelli12
1

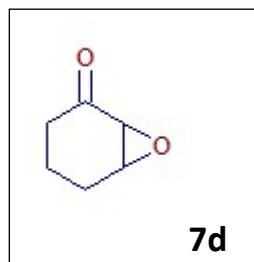
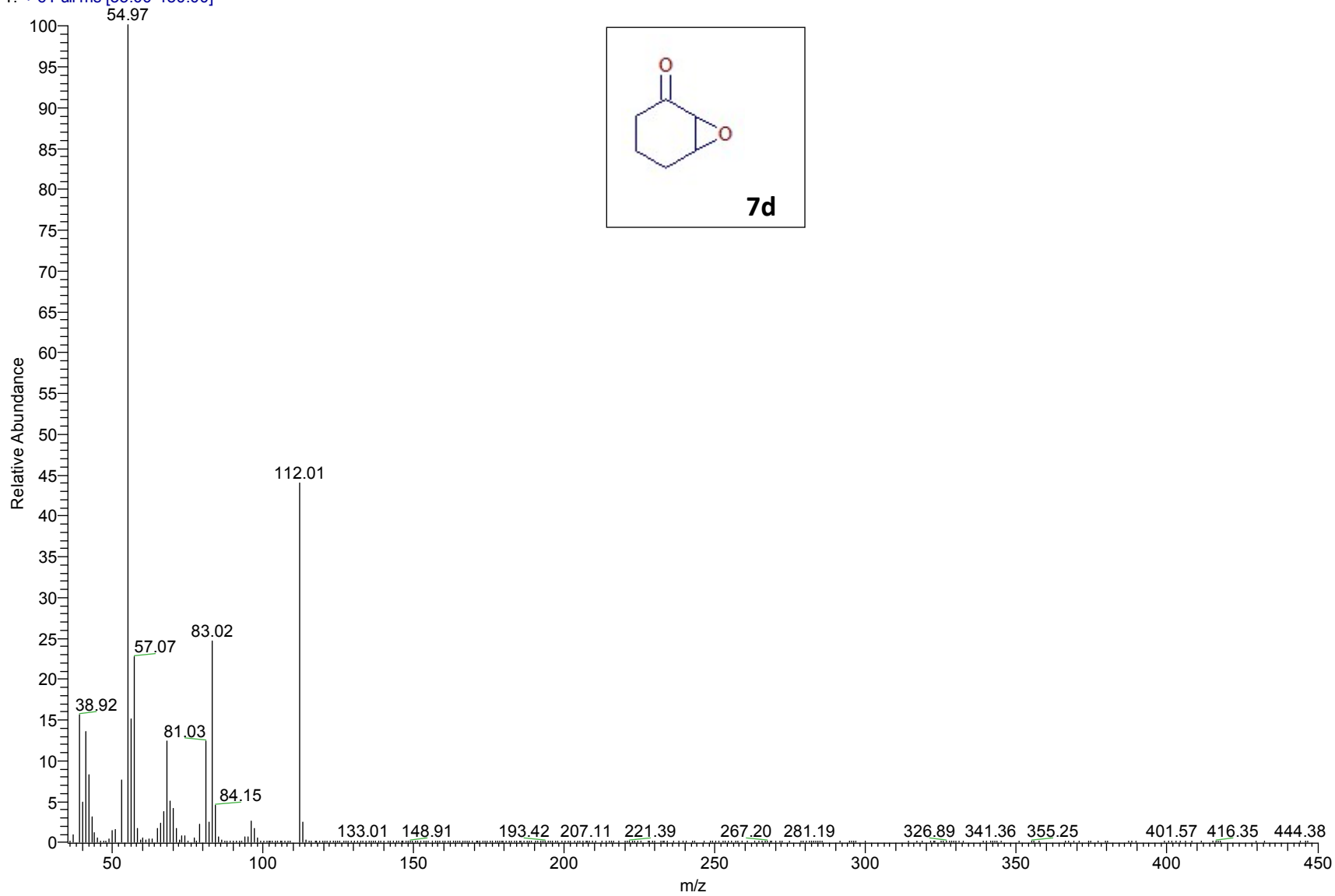
quadrelli121 #149 RT: 6.00 AV: 1 NL: 7.30E7
T: + c Full ms [35.00-450.00]



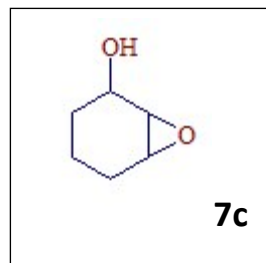
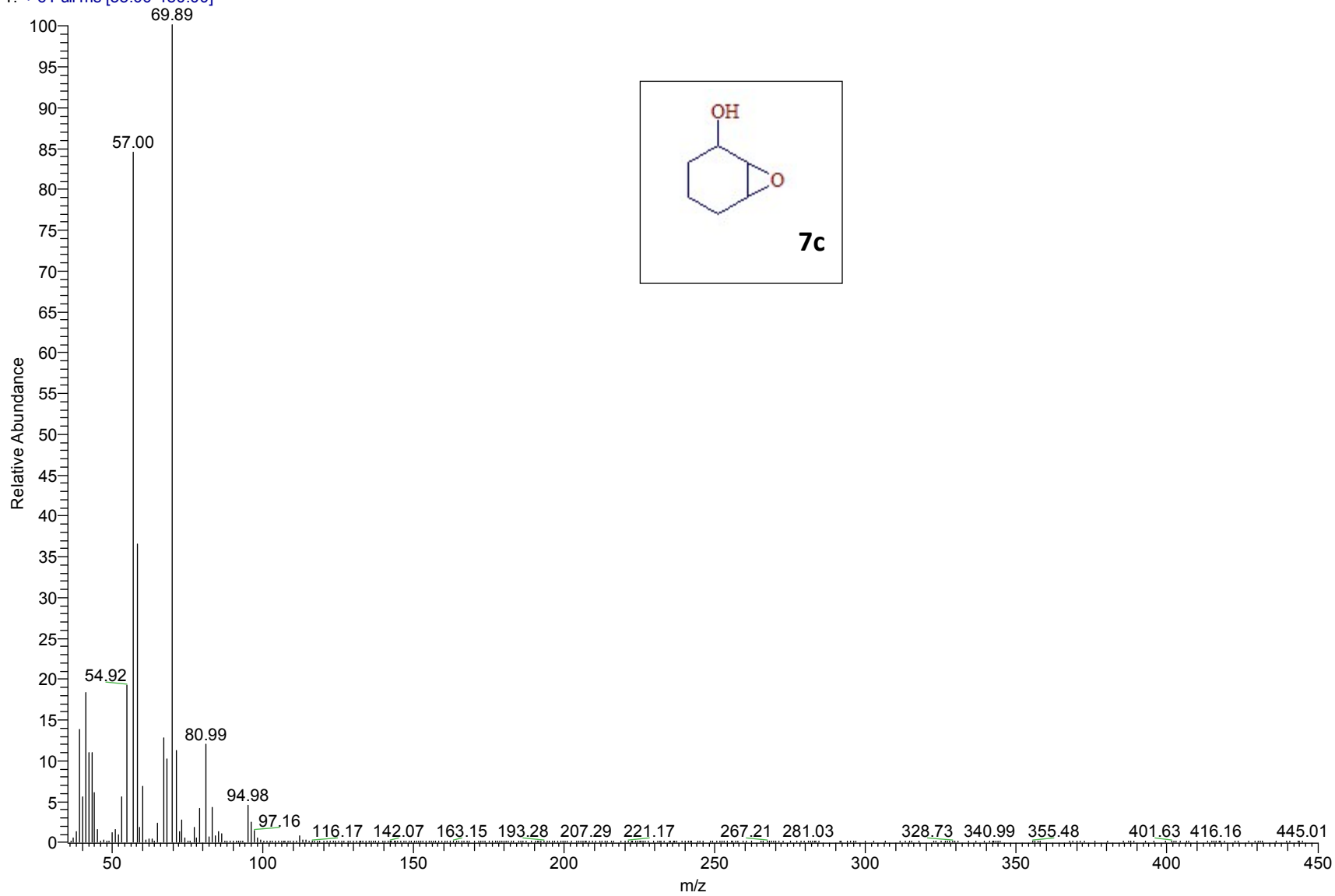
quadrelli121 #230 RT: 6.93 AV: 1 NL: 2.02E8
T: + c Full ms [35.00-450.00]



quadrelli121 #385 RT: 8.72 AV: 1 NL: 7.32E7
T: + c Full ms [35.00-450.00]

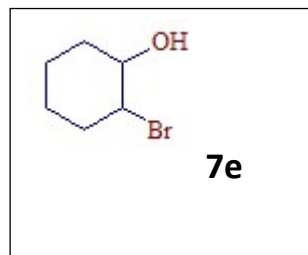
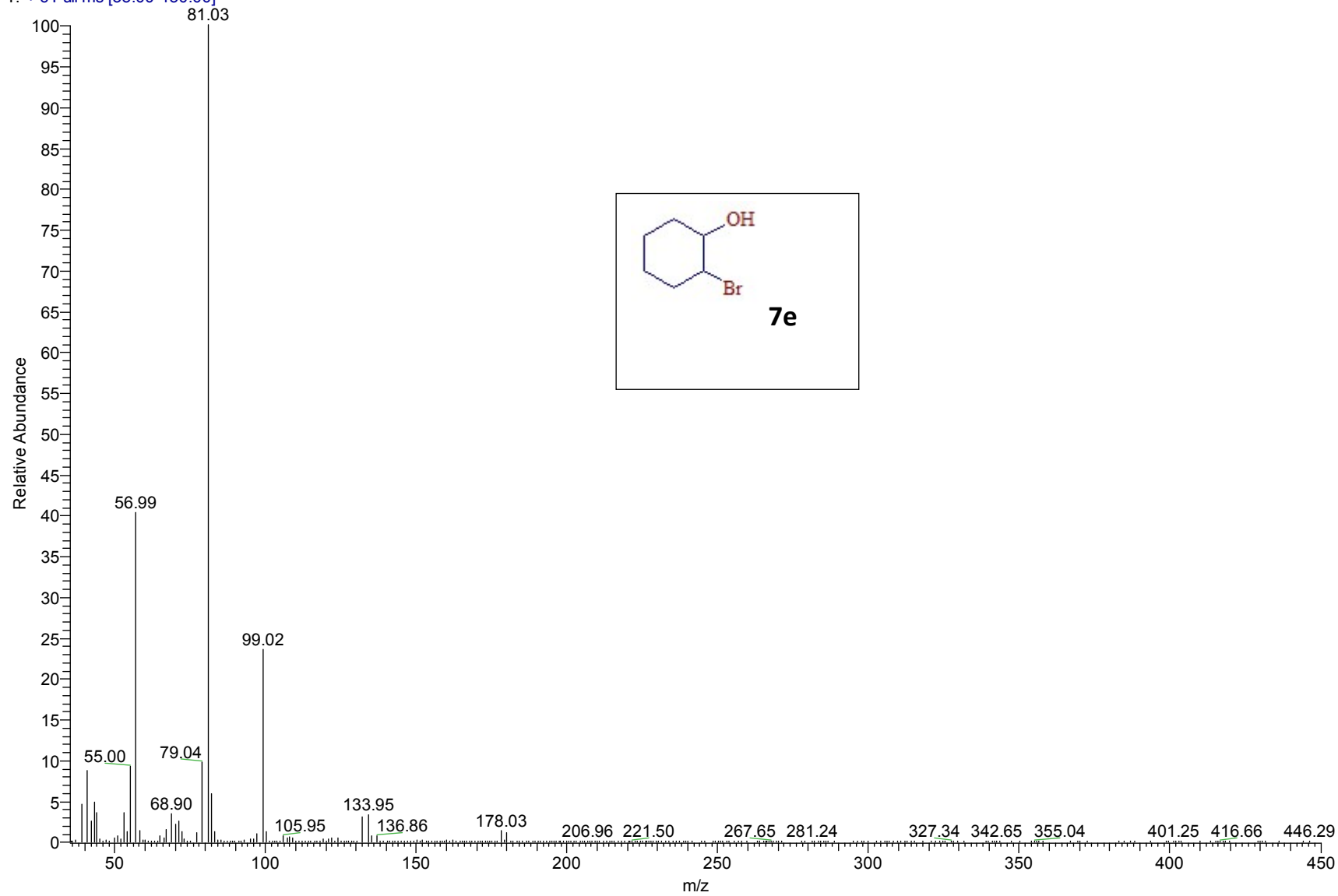


quadrelli121 #396 RT: 8.84 AV: 1 NL: 6.01E7
T: + c Full ms [35.00-450.00]

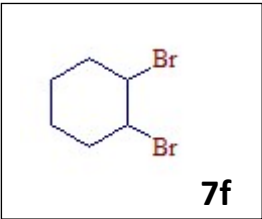
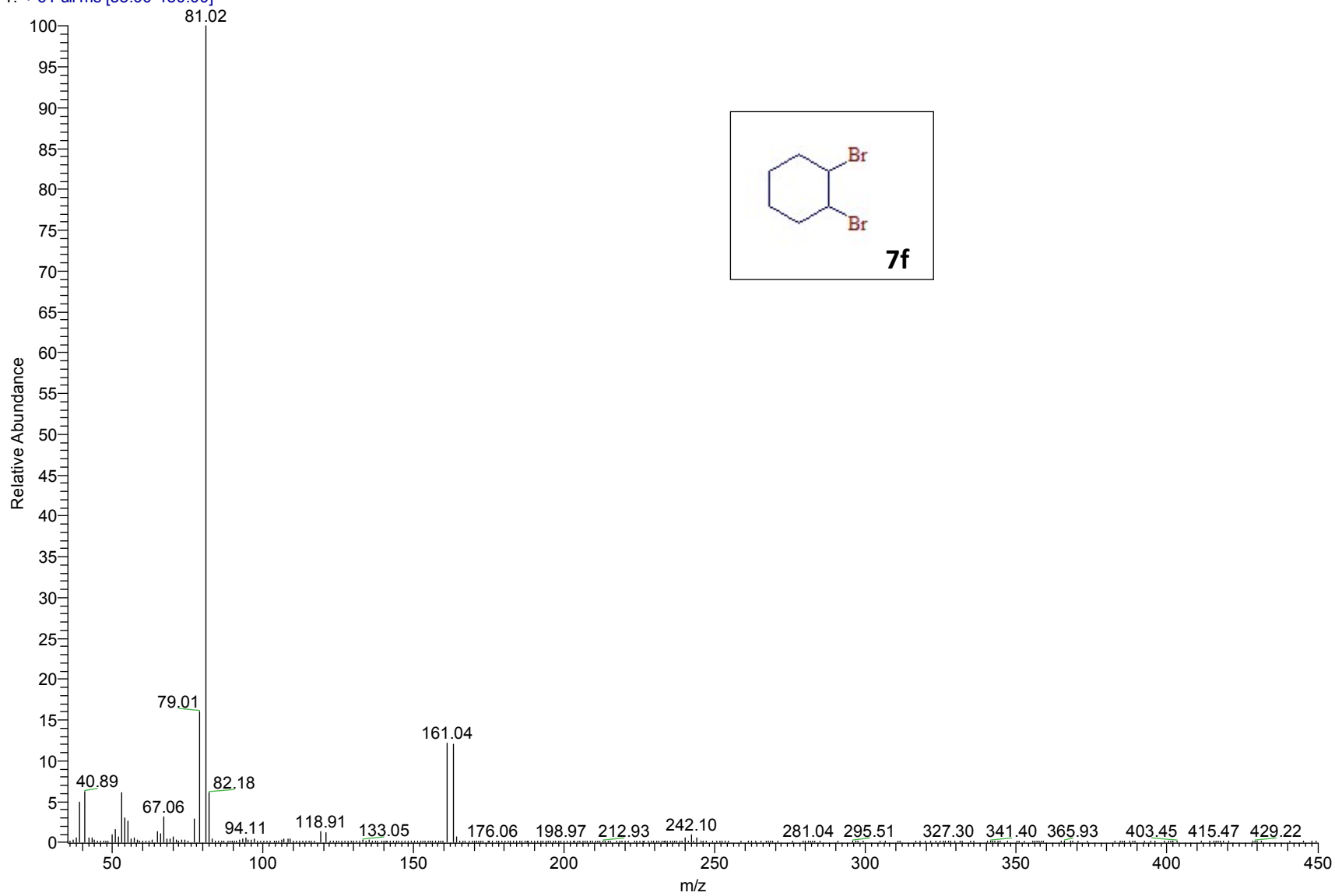


quadrelli121 #534 RT: 10.43 AV: 1 NL: 1.58E8

T: + c Full ms [35.00-450.00]



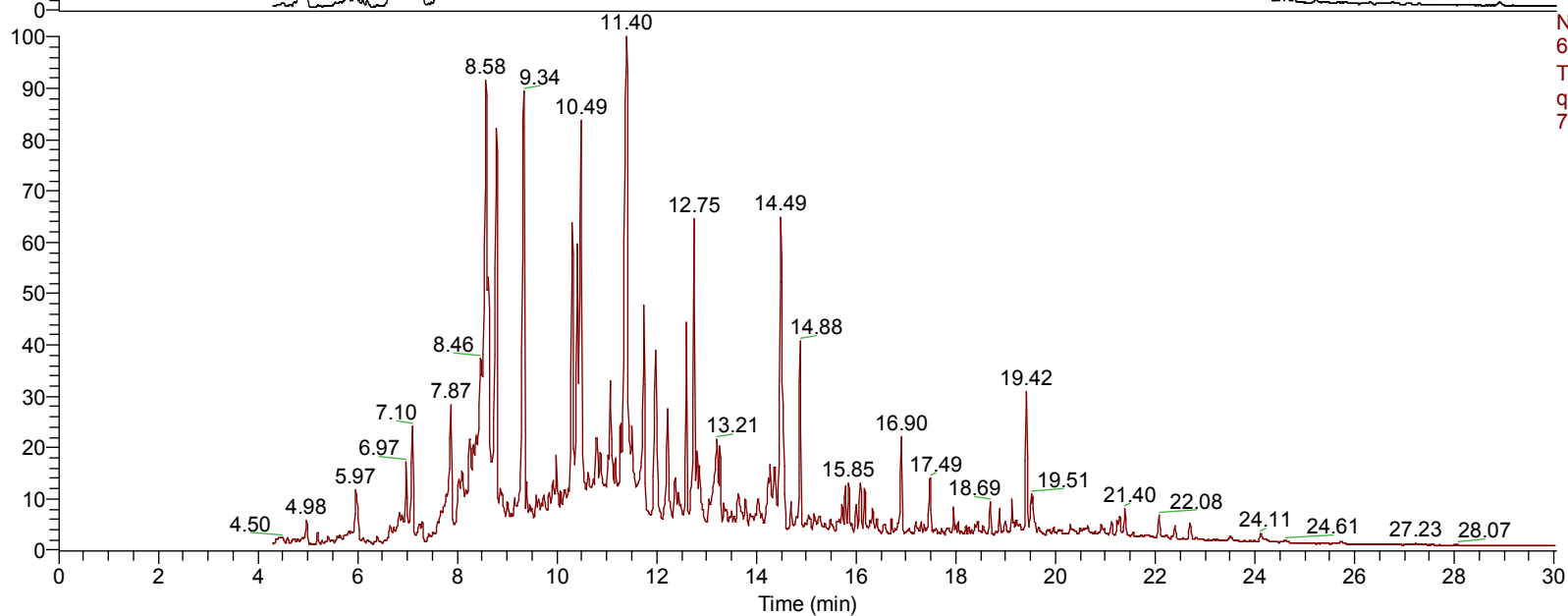
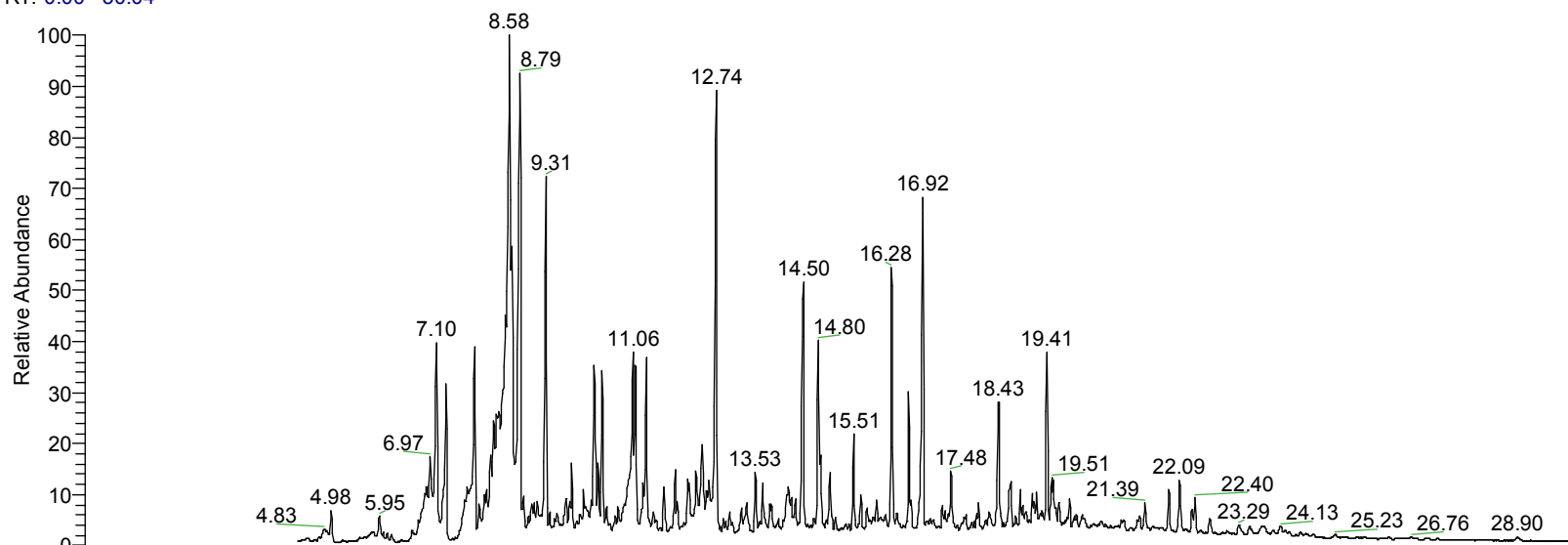
quadrelli121 #714 RT: 12.50 AV: 1 NL: 1.84E8
T: + c Full ms [35.00-450.00]



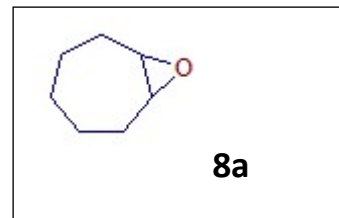
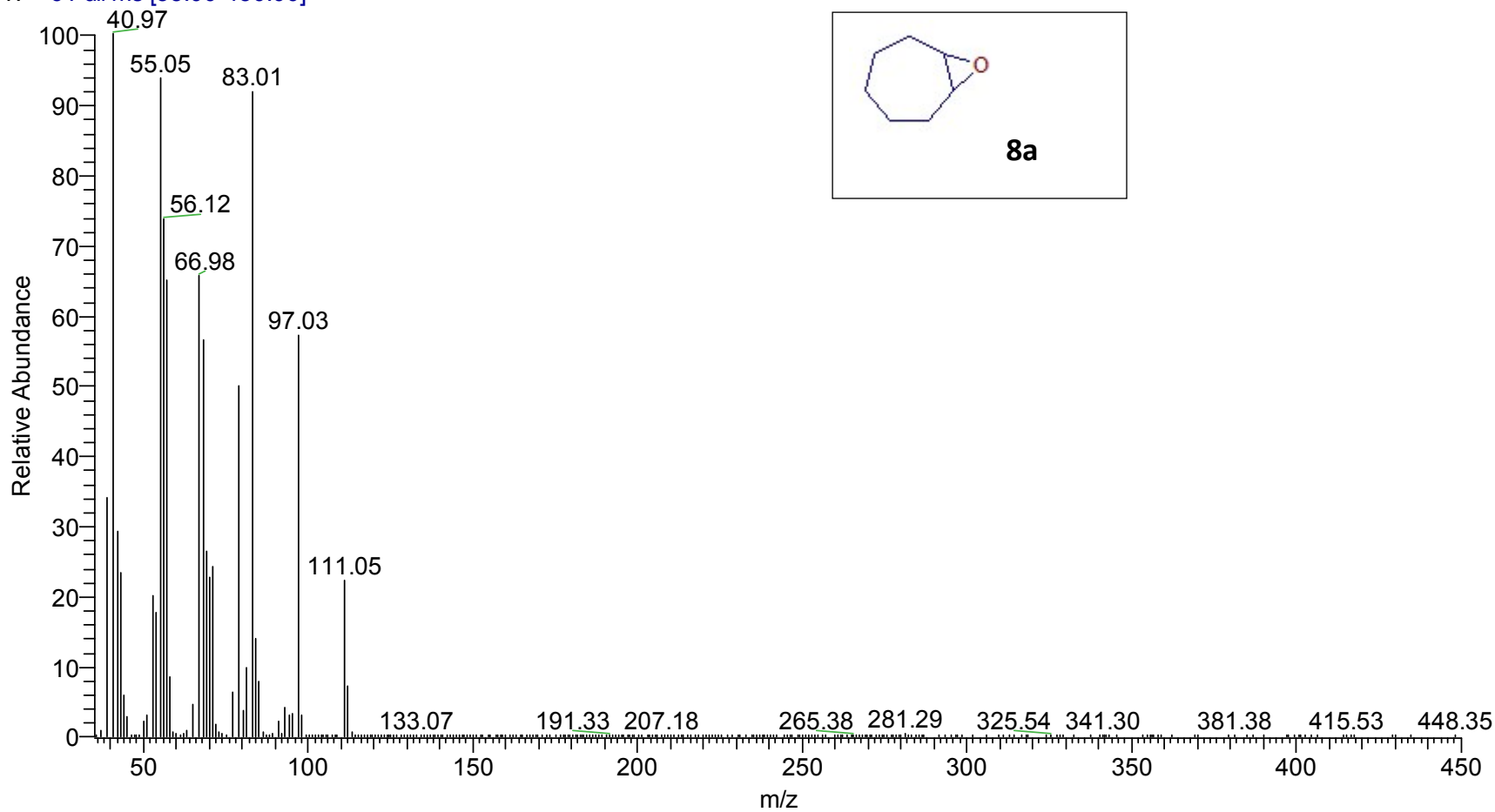
C4, reaction with cyclooptene

RT: 0.00 - 30.04

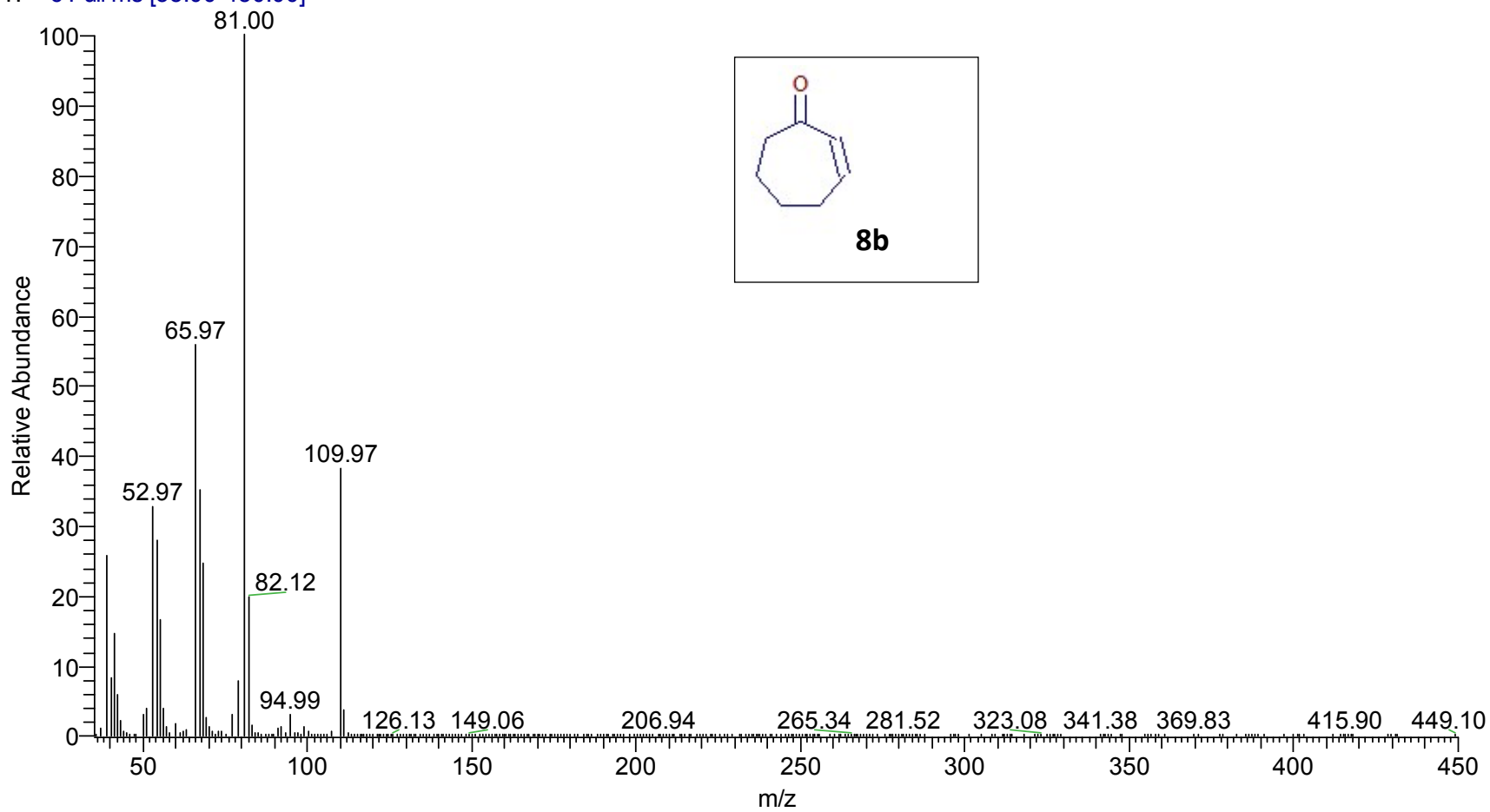
NL:
6.08E8
TIC MS
quadrelli10
6



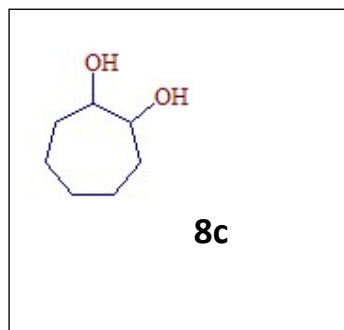
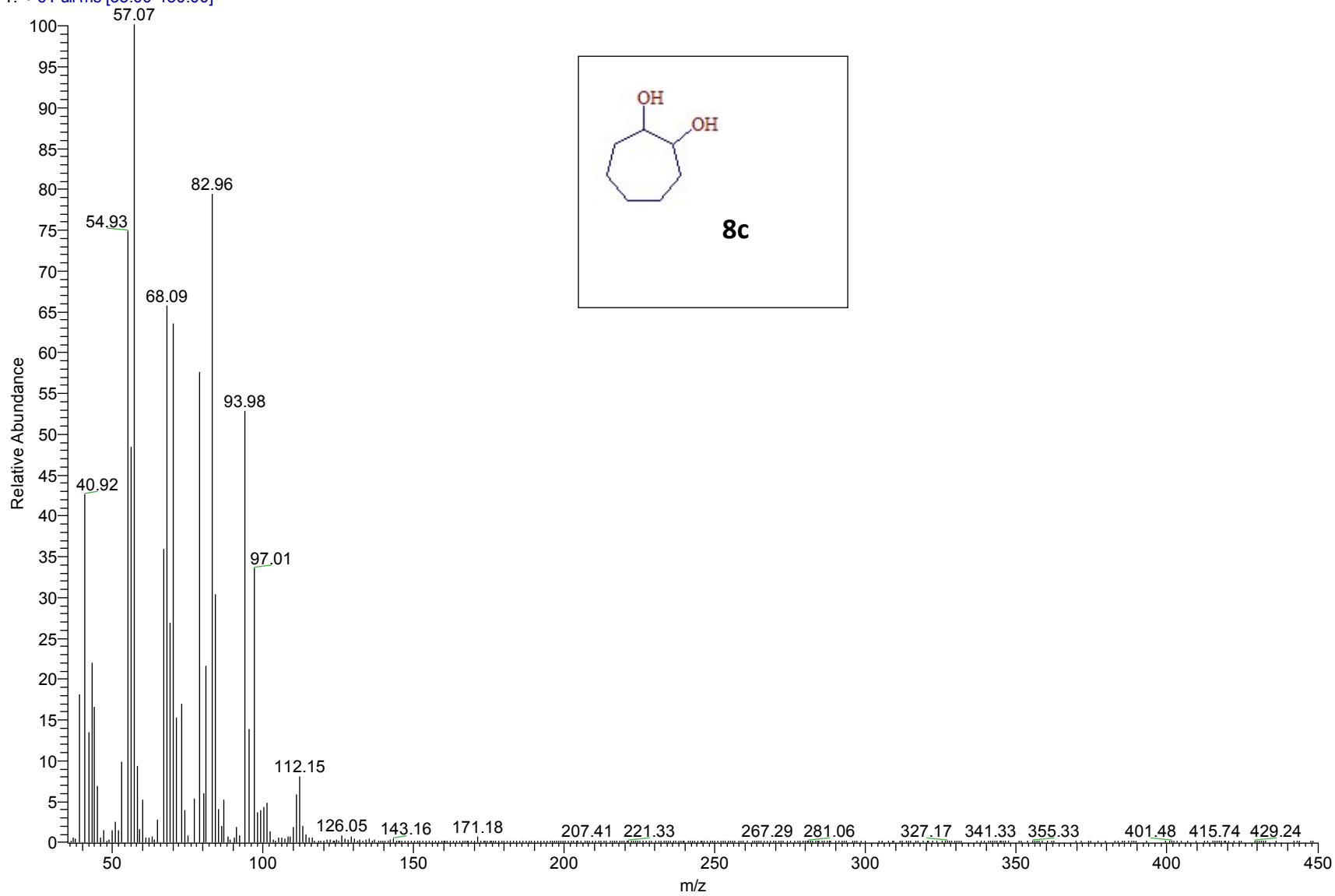
quadrelli95 #316 RT: 7.92 AV: 1 NL: 8.13E7
T: + c Full ms [35.00-450.00]



quadrelli95 #445 RT: 9.41 AV: 1 NL: 1.65E8
T: + c Full ms [35.00-450.00]



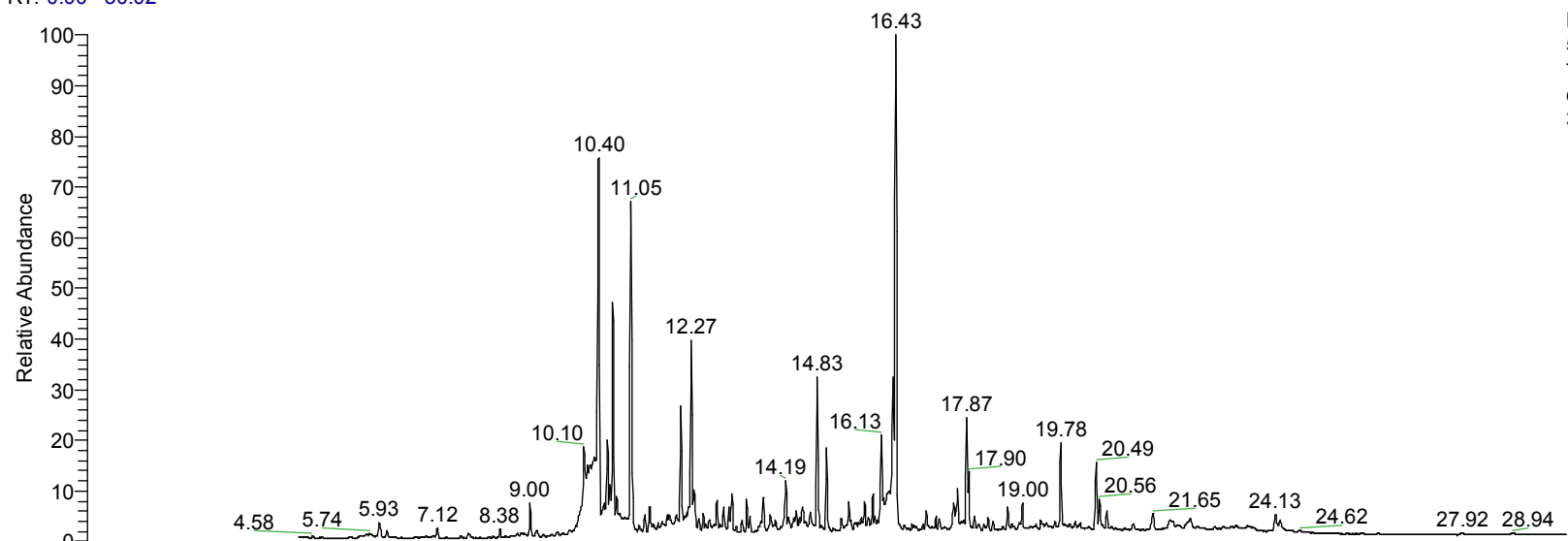
quadrelli188 #666 RT: 11.95 AV: 1 NL: 2.82E7
T: + c Full ms [35.00-450.00]



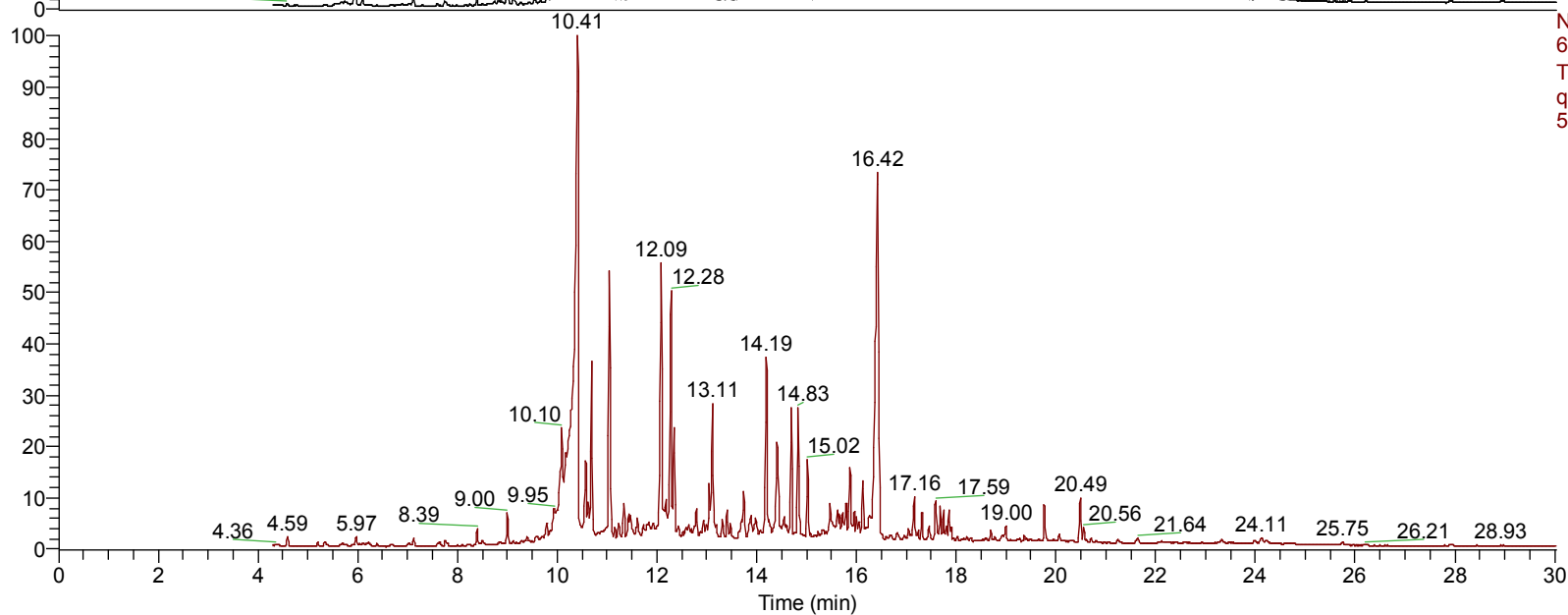
C4, reaction with cyclooctene

RT: 0.00 - 30.02

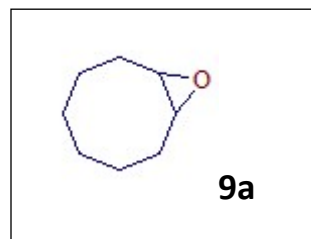
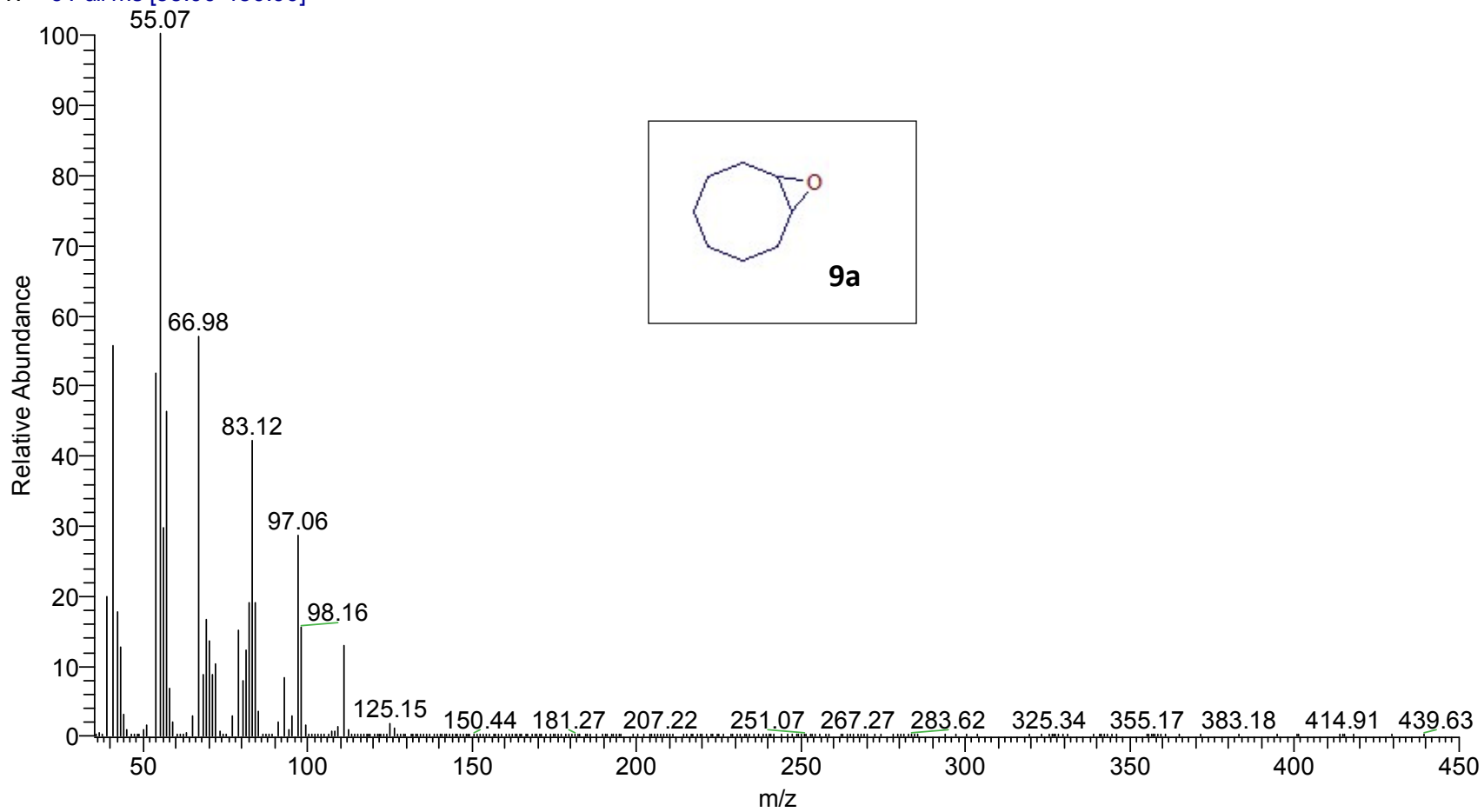
NL:
5.82E8
TIC MS
quadrelli10
3



NL:
6.74E8
TIC MS
quadrelli10
5

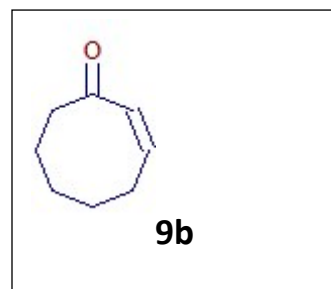
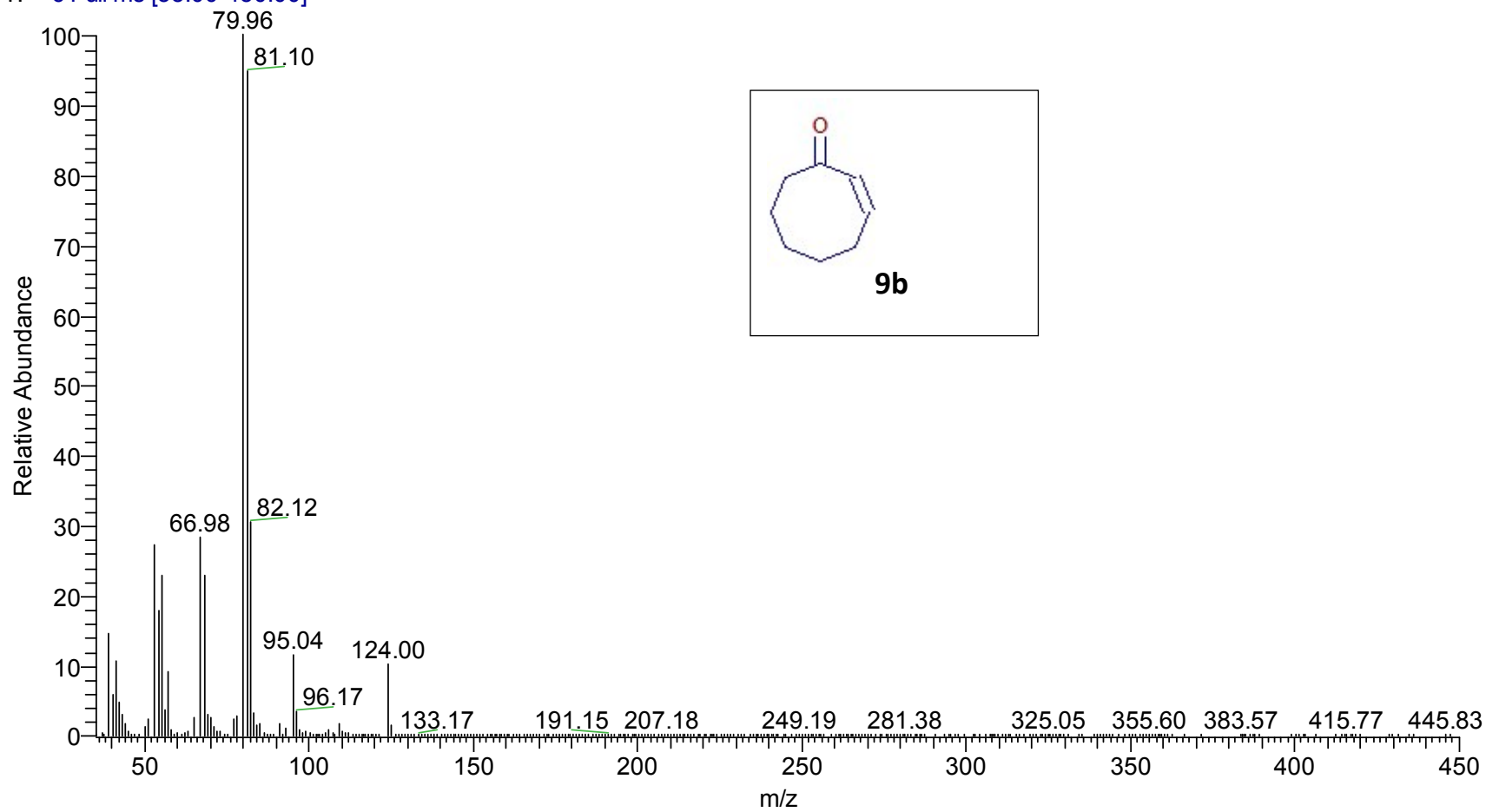


quadrelli105 #532 RT: 10.41 AV: 1 NL: 1.01E8
T: + c Full ms [35.00-450.00]

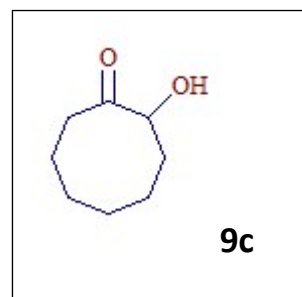
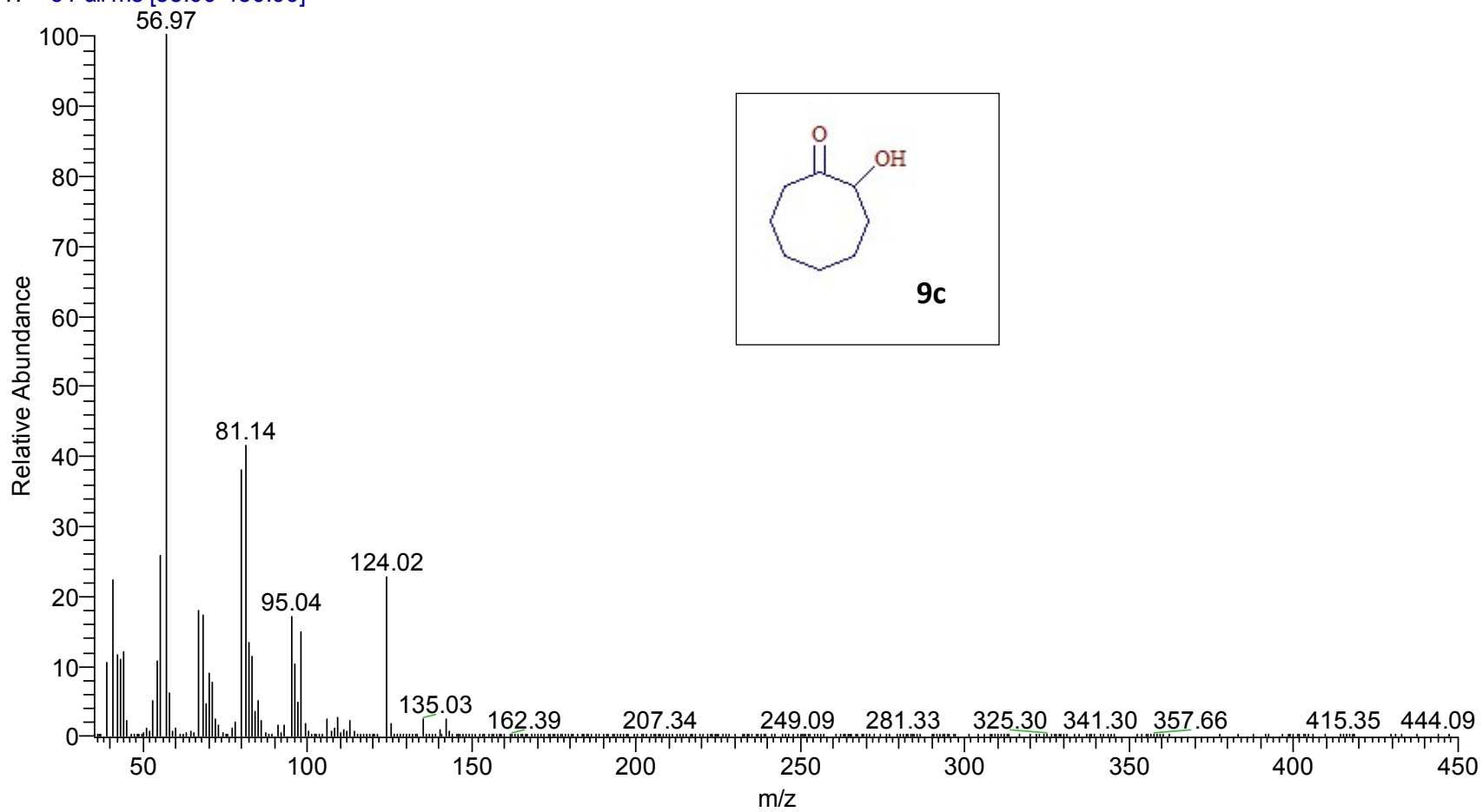


quadrelli94 #704 RT: 11.09 AV: 1 NL: 1.55E8

T: + c Full ms [35.00-450.00]



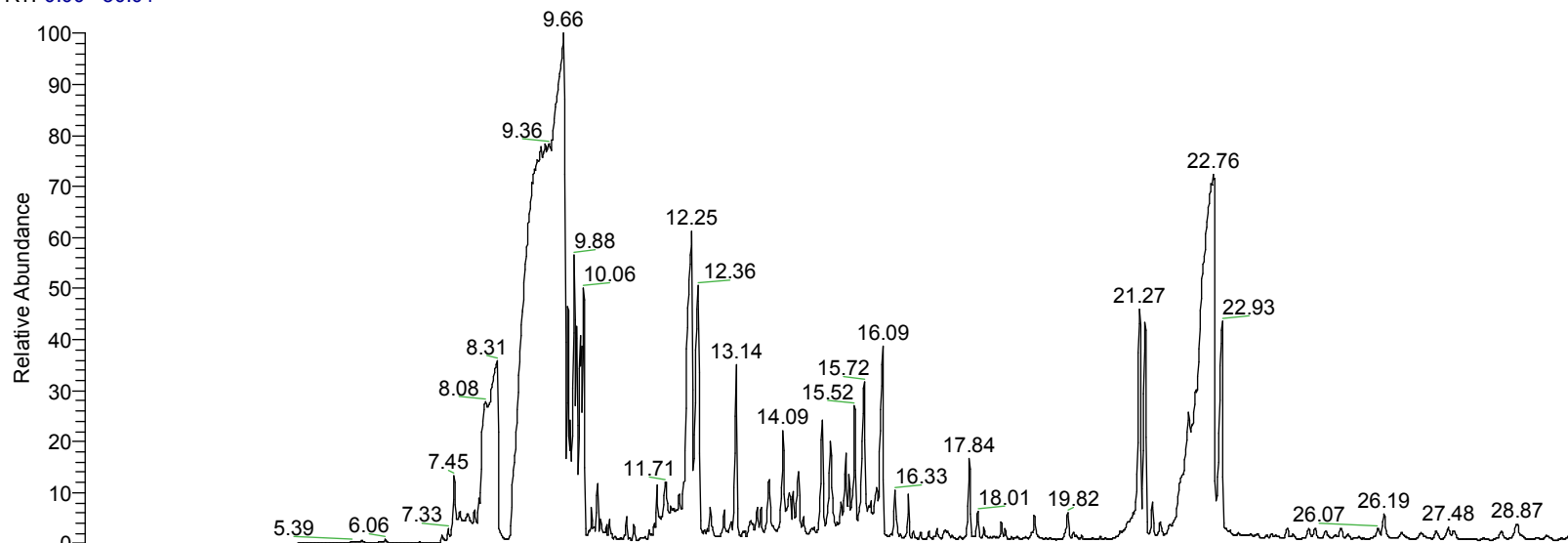
quadrelli105 #695 RT: 12.28 AV: 1 NL: 6.87E7
T: + c Full ms [35.00-450.00]



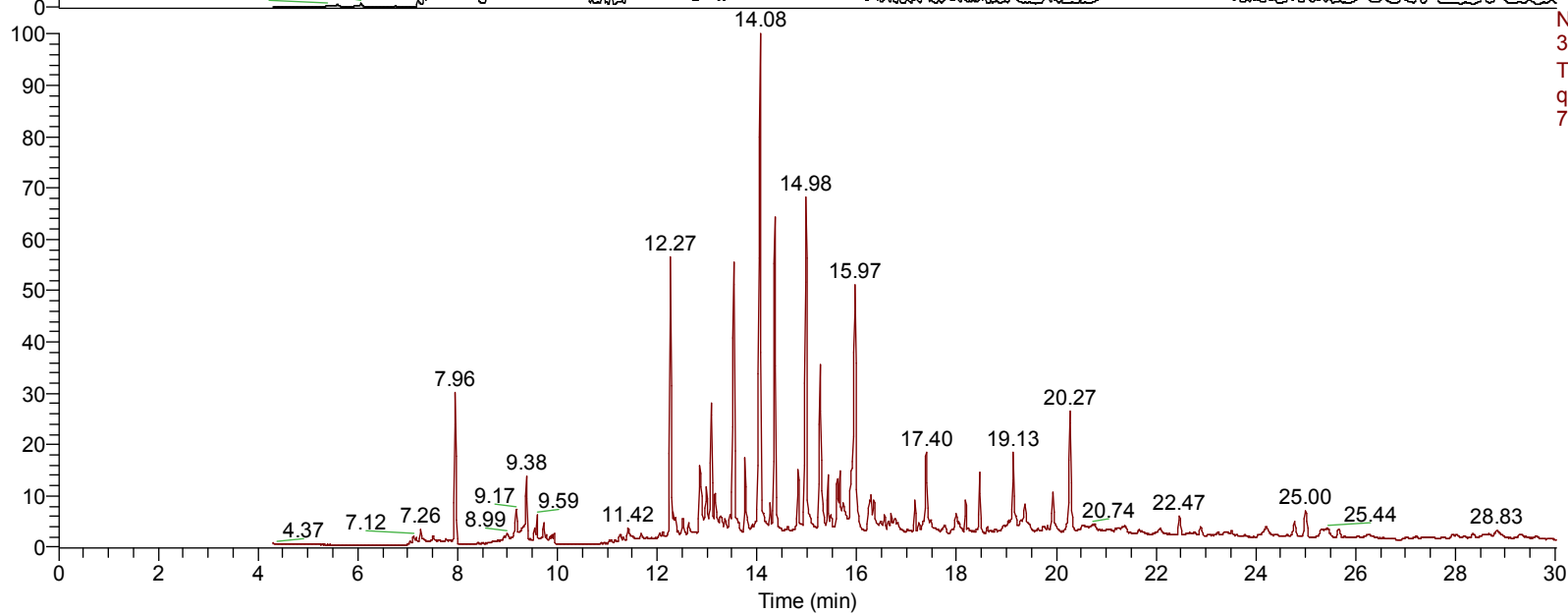
C4, reaction with indene

RT: 0.00 - 30.01

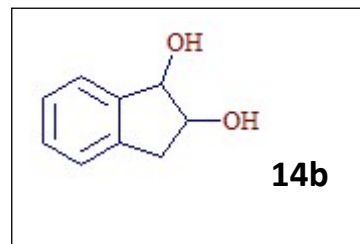
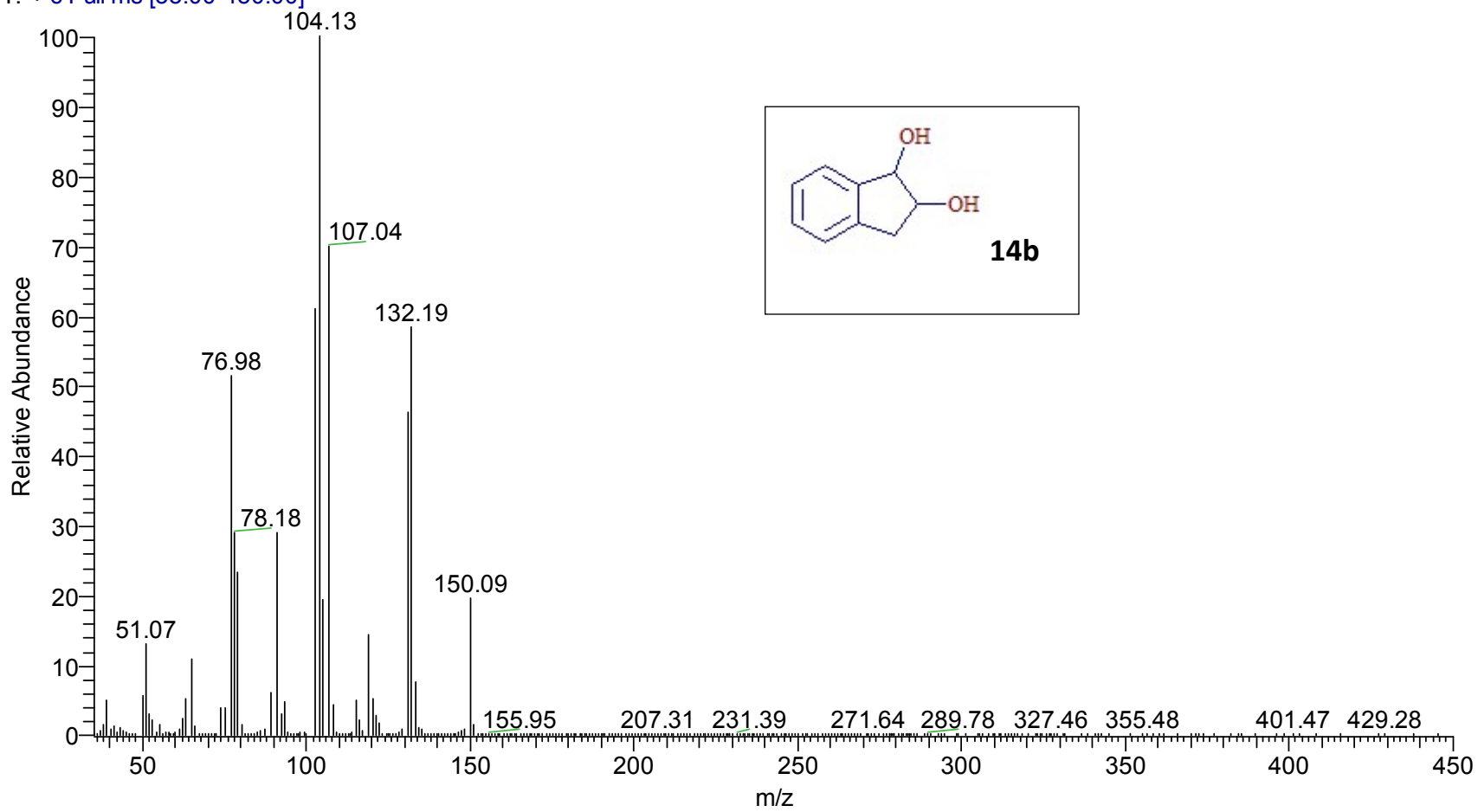
NL:
1.37E9
TIC MS
quadrelli15
6



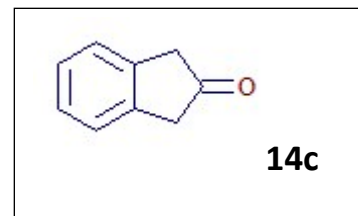
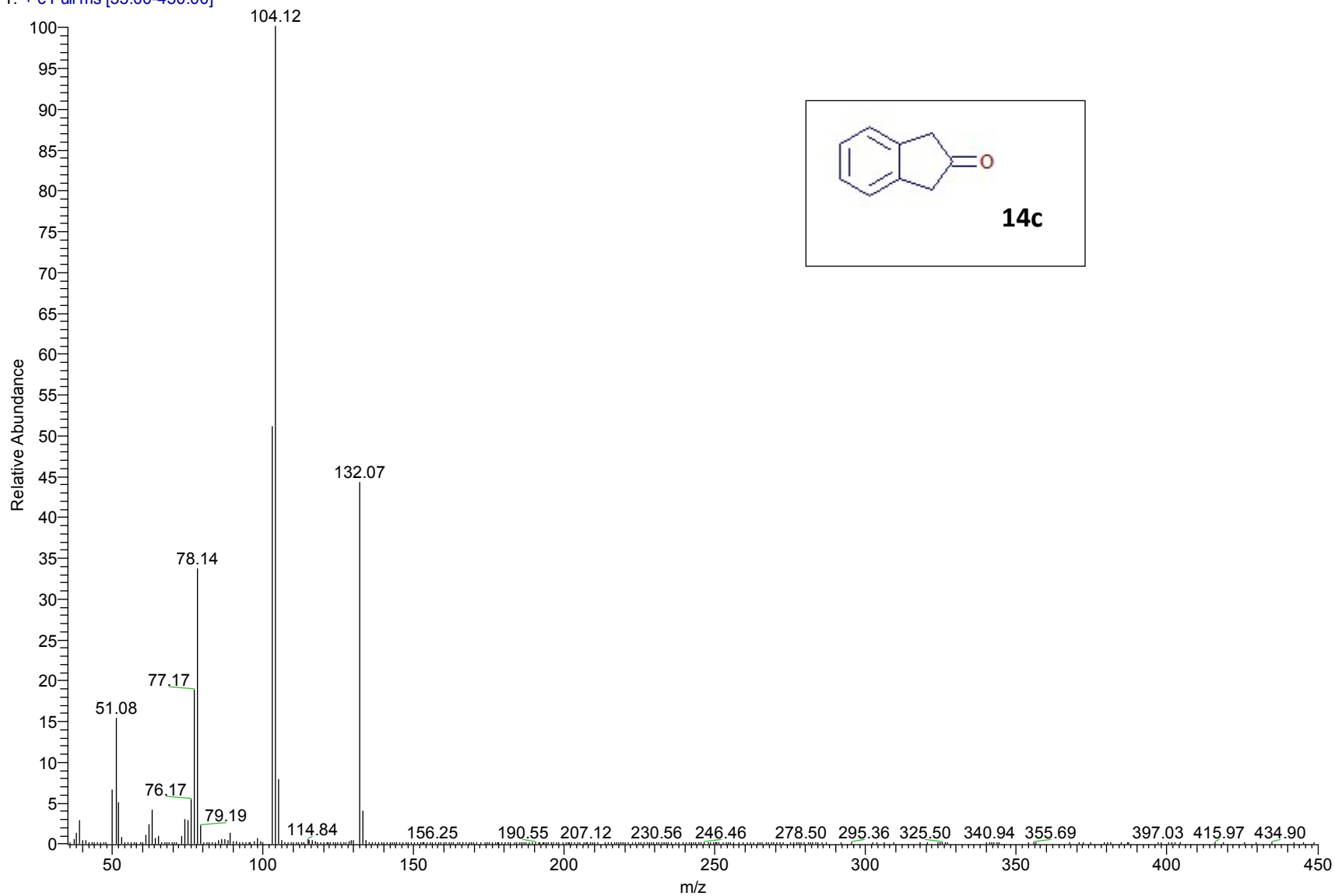
NL:
3.04E8
TIC MS
quadrelli15
7



quadrelli157 #930 RT: 14.98 AV: 1 NL: 3.22E7
T: + c Full ms [35.00-450.00]

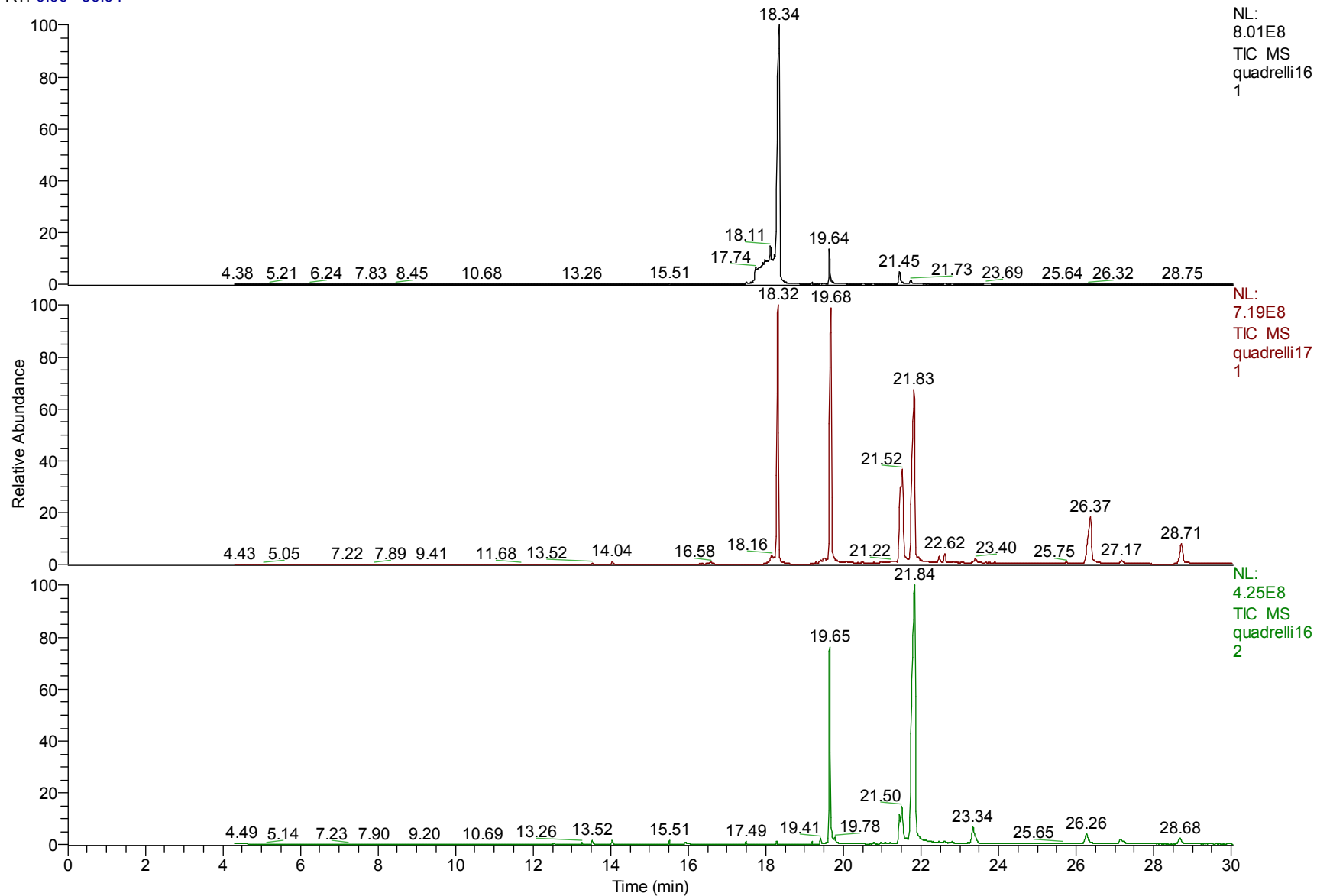


quadrelli157 #694 RT: 12.27 AV: 1 NL: 5.30E7
T: + c Full ms [35.00-450.00]

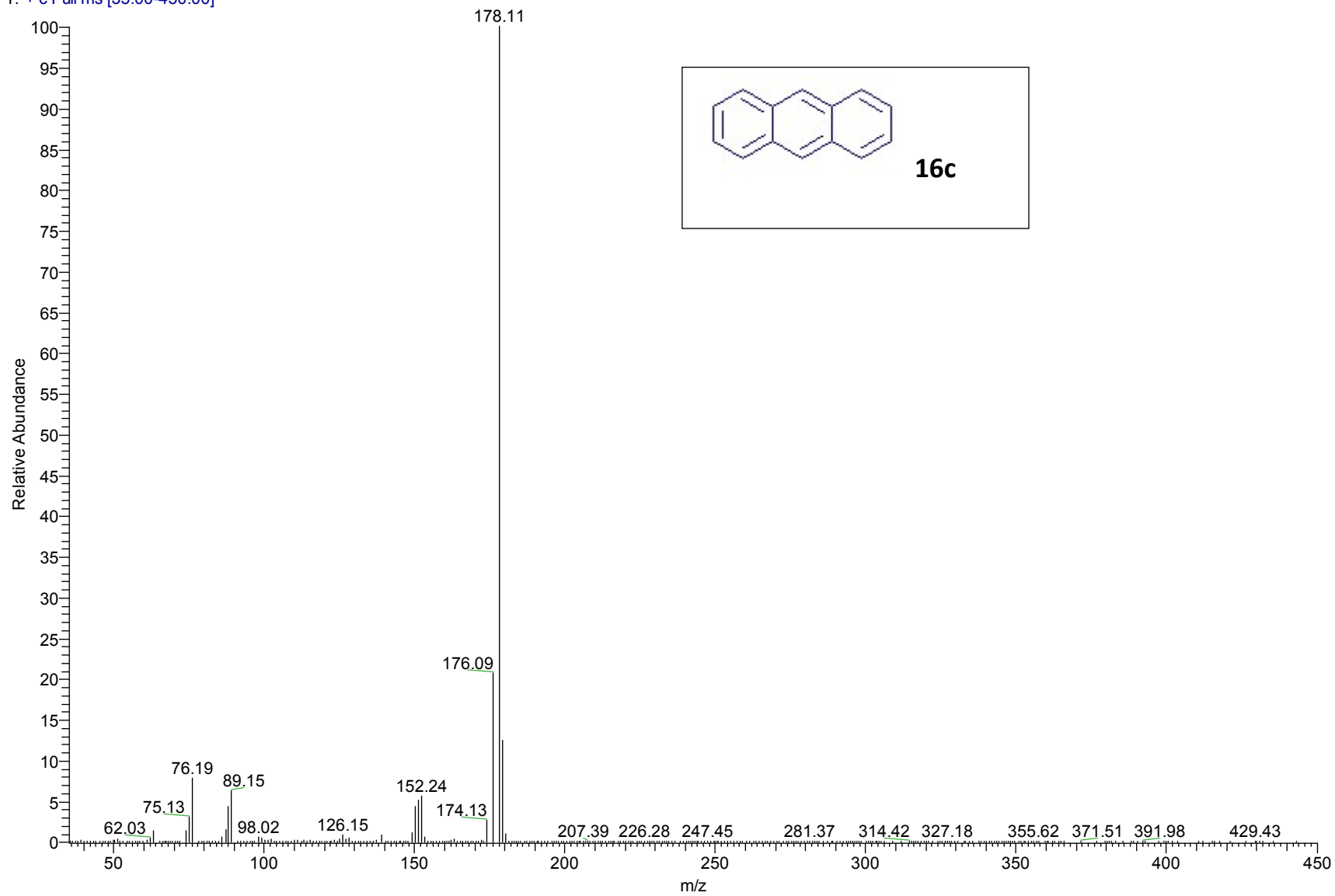


C4, reaction with 9,10-dihydroanthracene

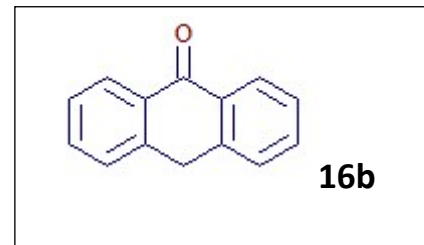
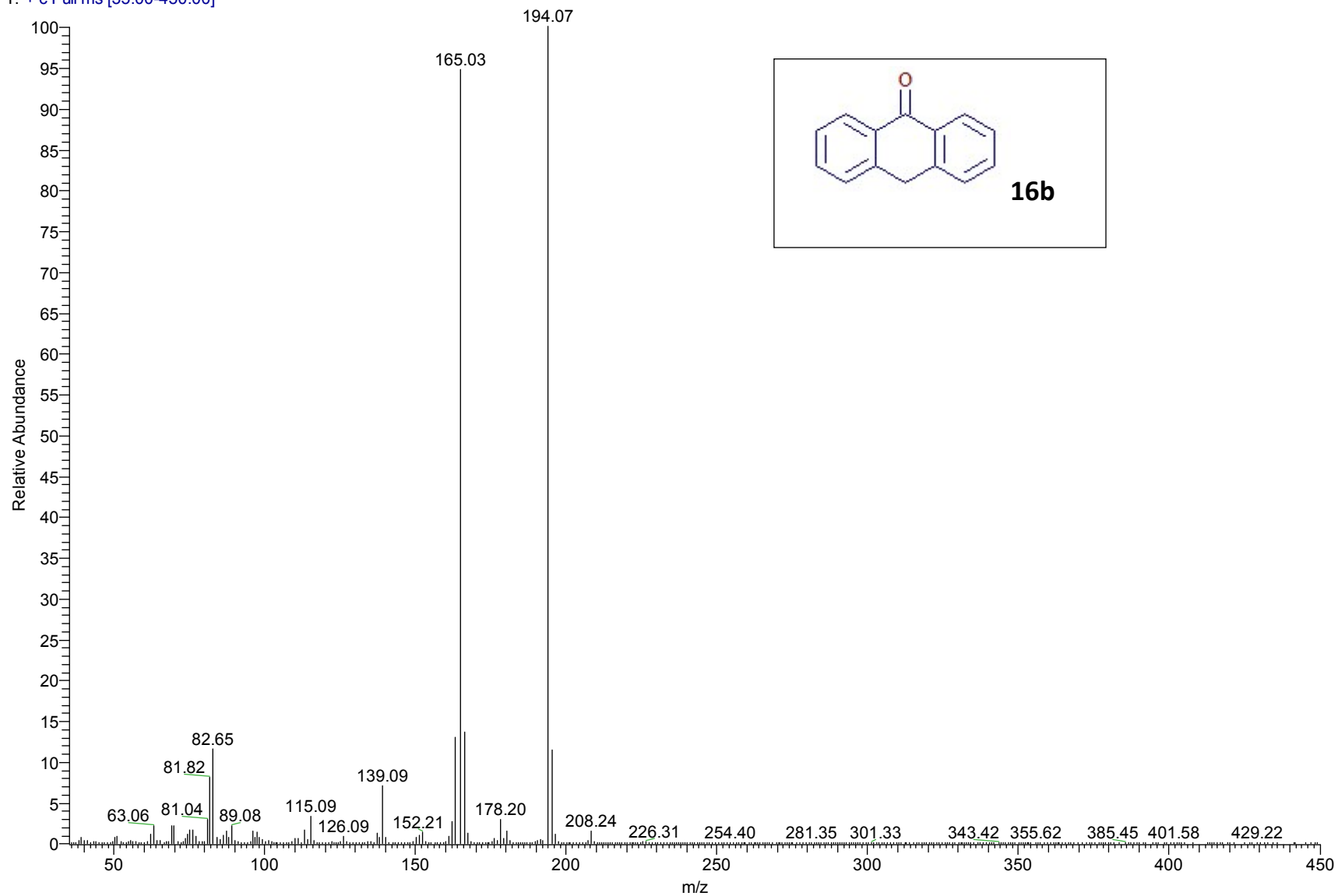
RT: 0.00 - 30.04



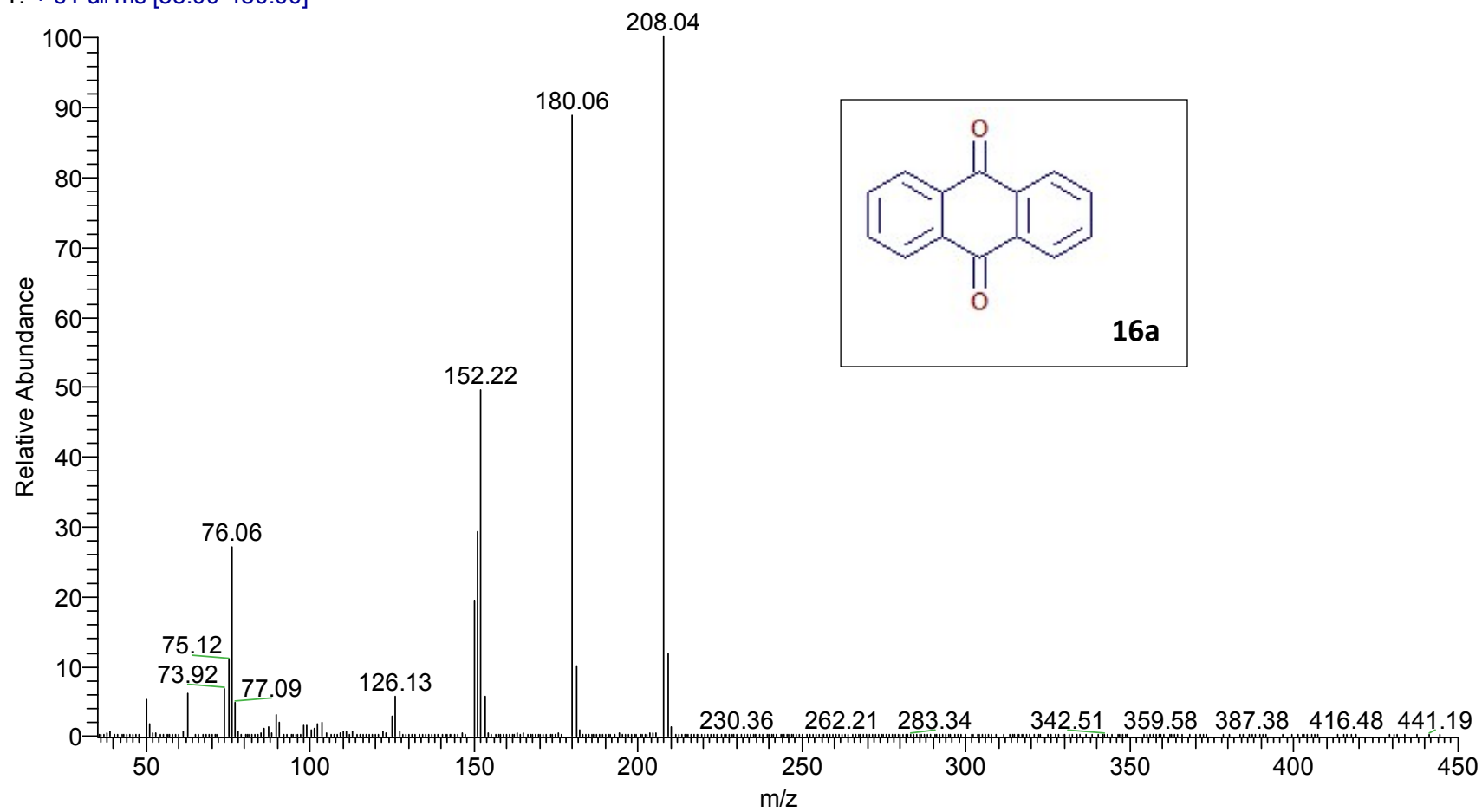
quadrelli162 #1335 RT: 19.64 AV: 1 NL: 1.67E8
T: + c Full ms [35.00-450.00]



quadrelli170 #1493 RT: 21.46 AV: 1 NL: 2.32E7
T: + c Full ms [35.00-450.00]

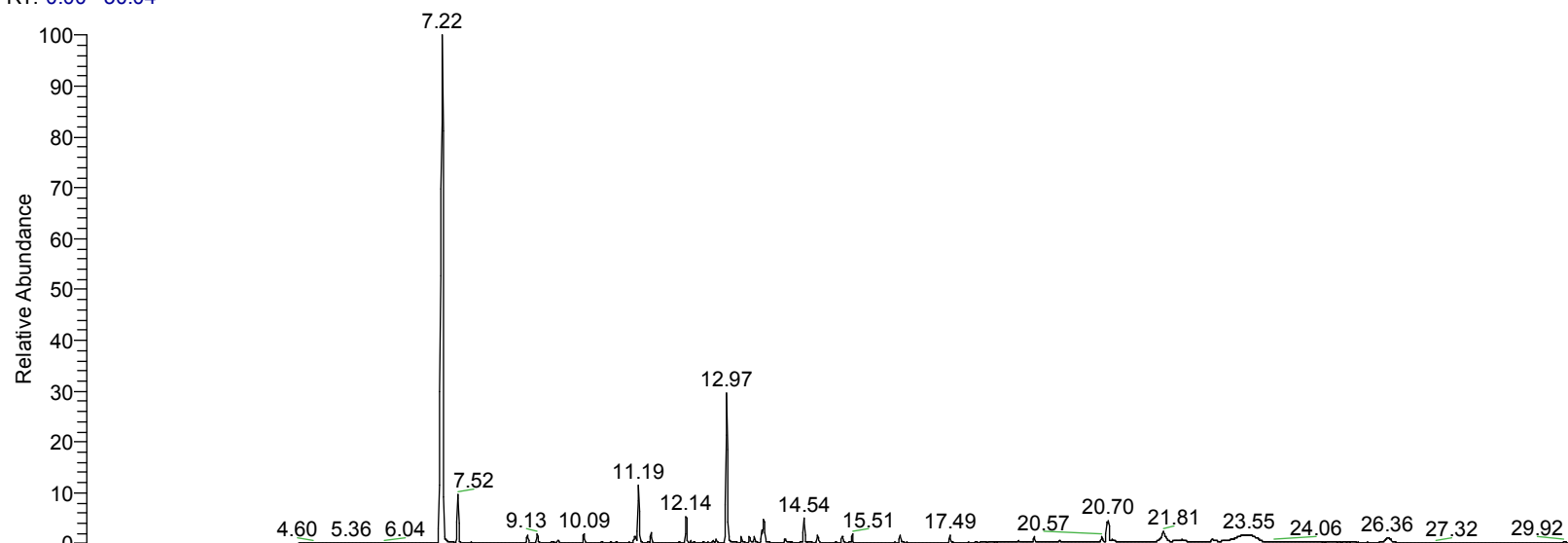


quadrelli162 #1522 RT: 21.79 AV: 1 NL: 8.27E7
T: + c Full ms [35.00-450.00]

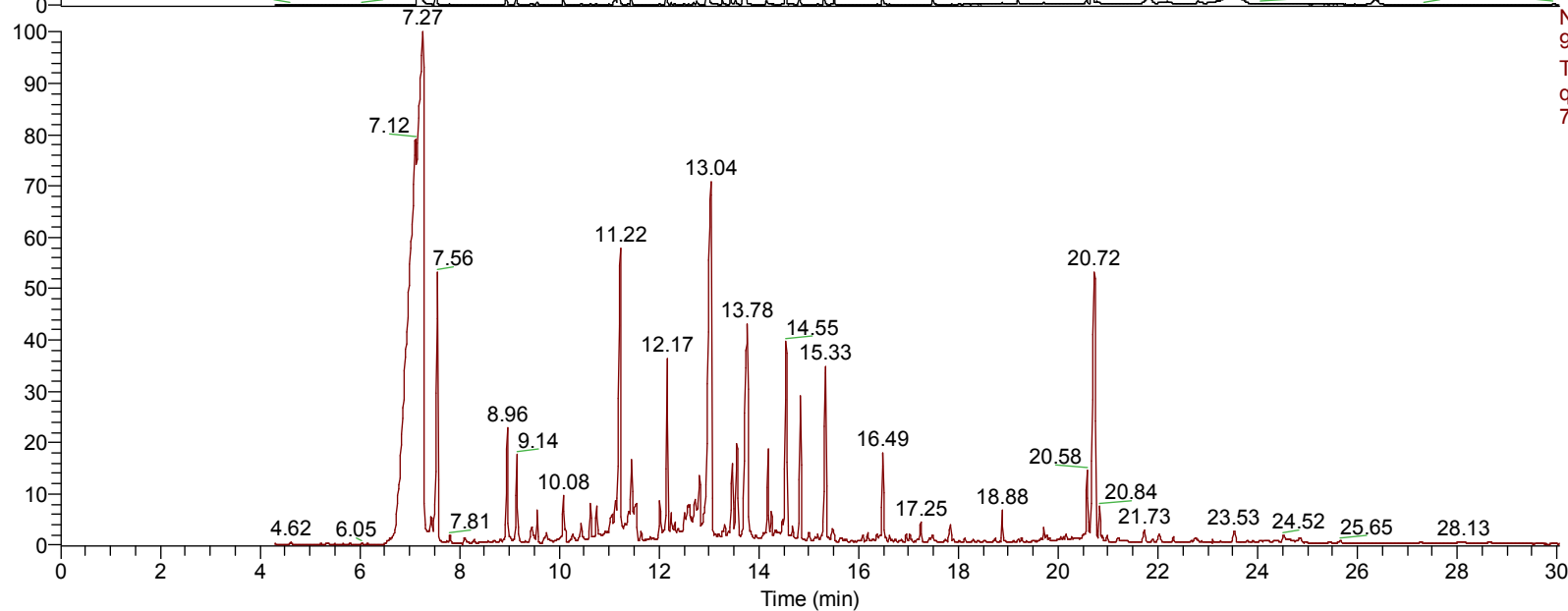


C4, reaction with allyl-benzene

RT: 0.00 - 30.04

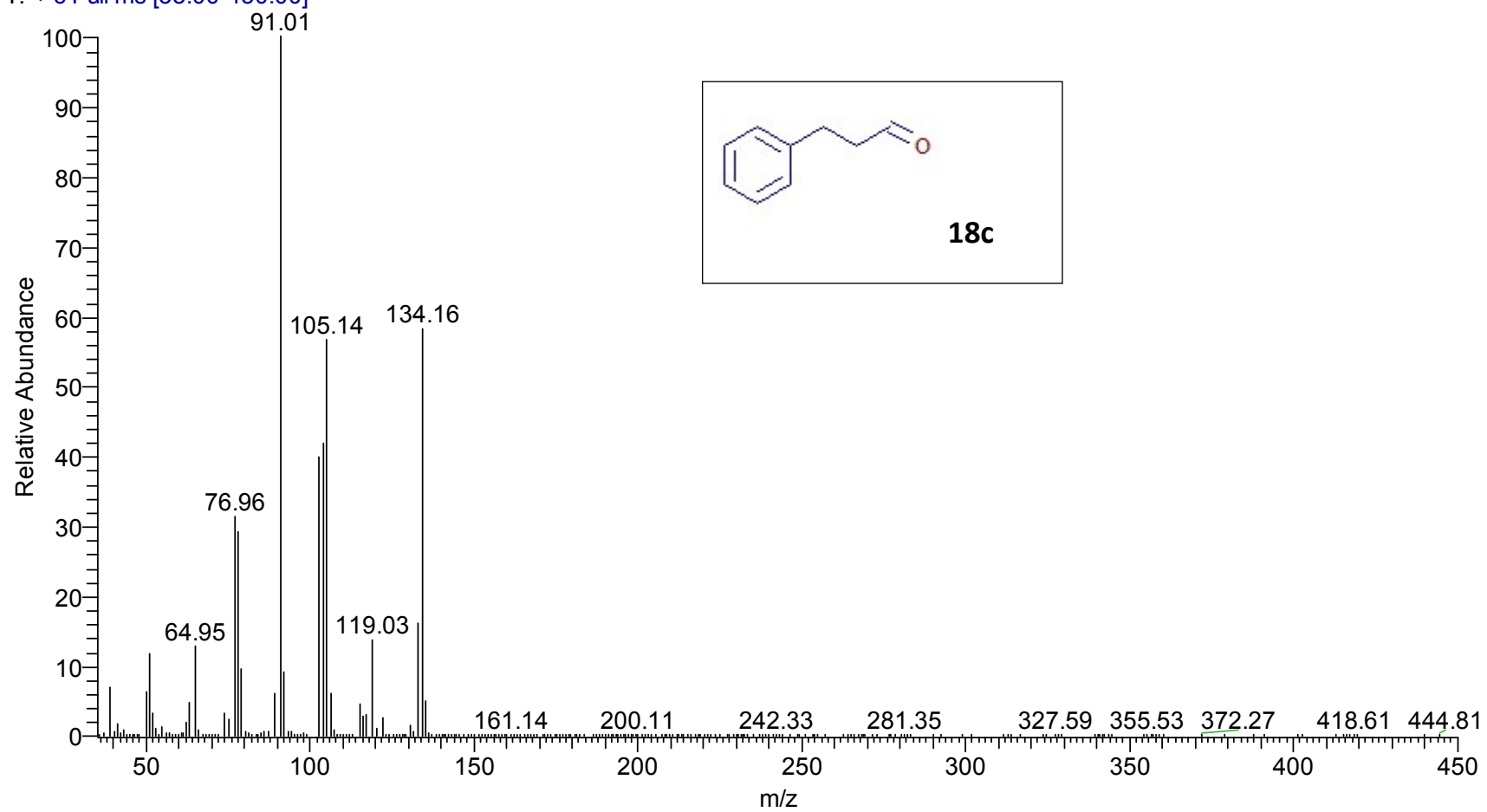


NL:
8.46E8
TIC MS
quadrelli16
6

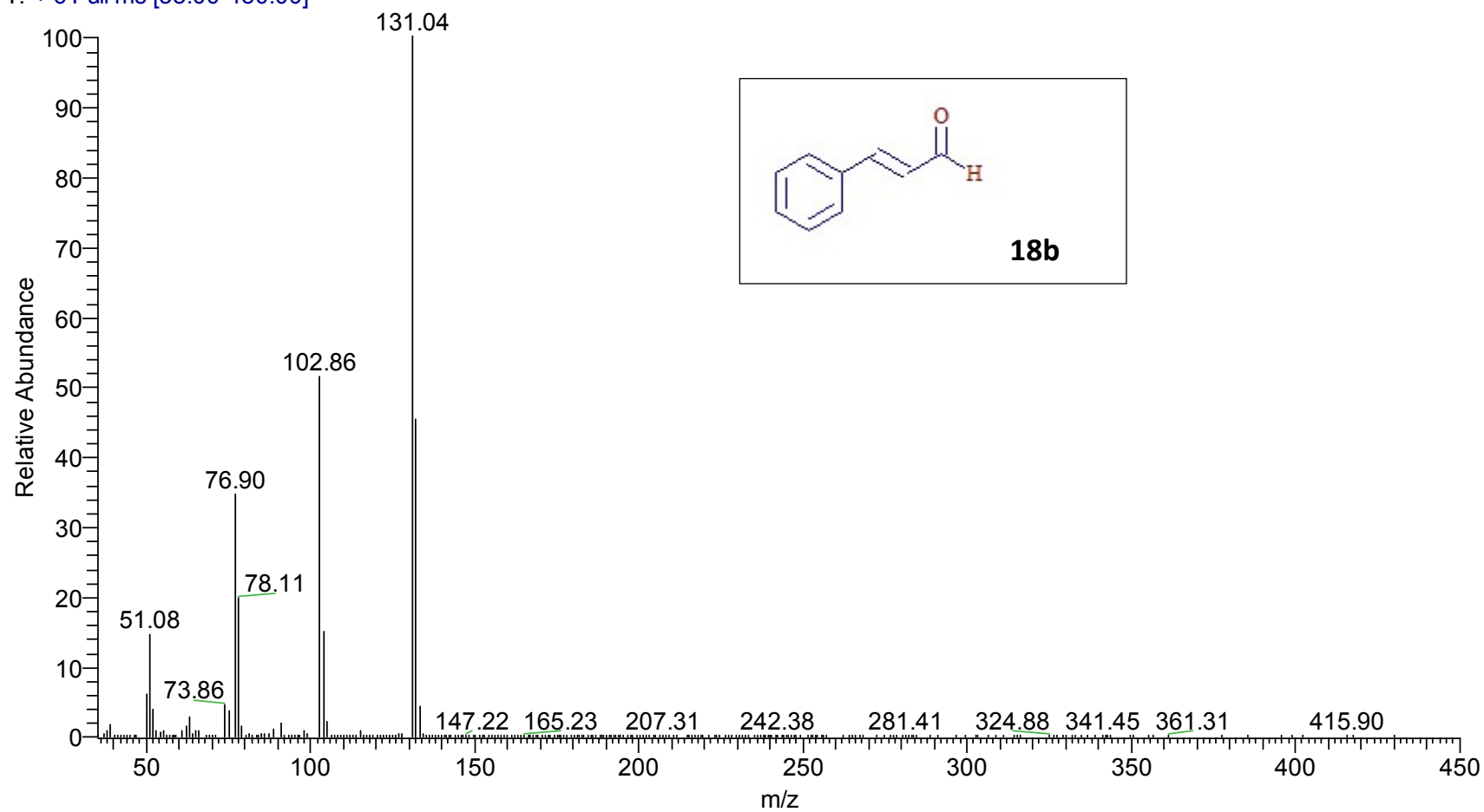


NL:
9.66E8
TIC MS
quadrelli16
7

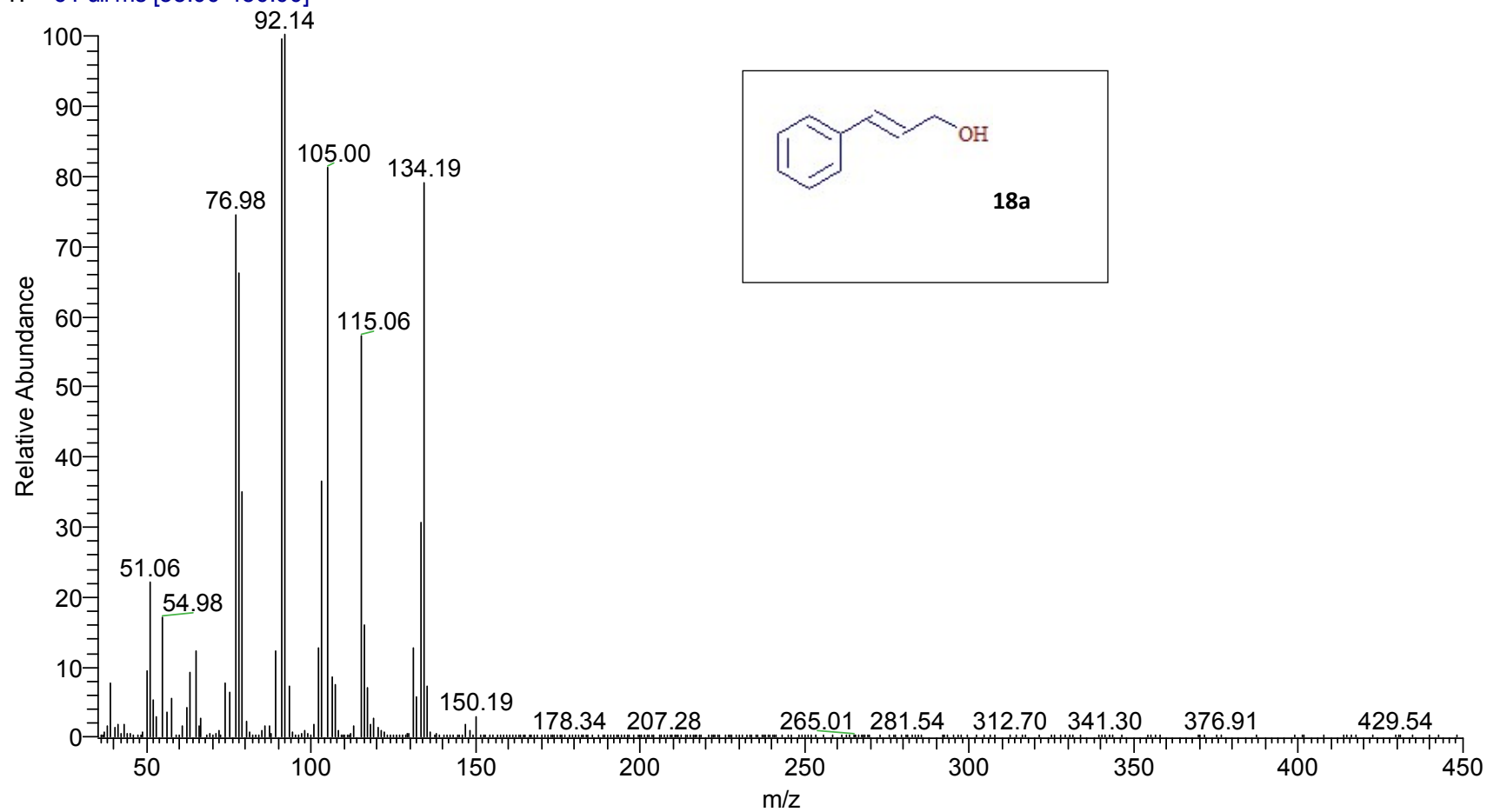
quadrelli167 #603 RT: 11.22 AV: 1 NL: 1.11E8
T: + c Full ms [35.00-450.00]



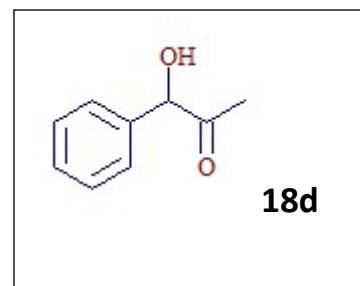
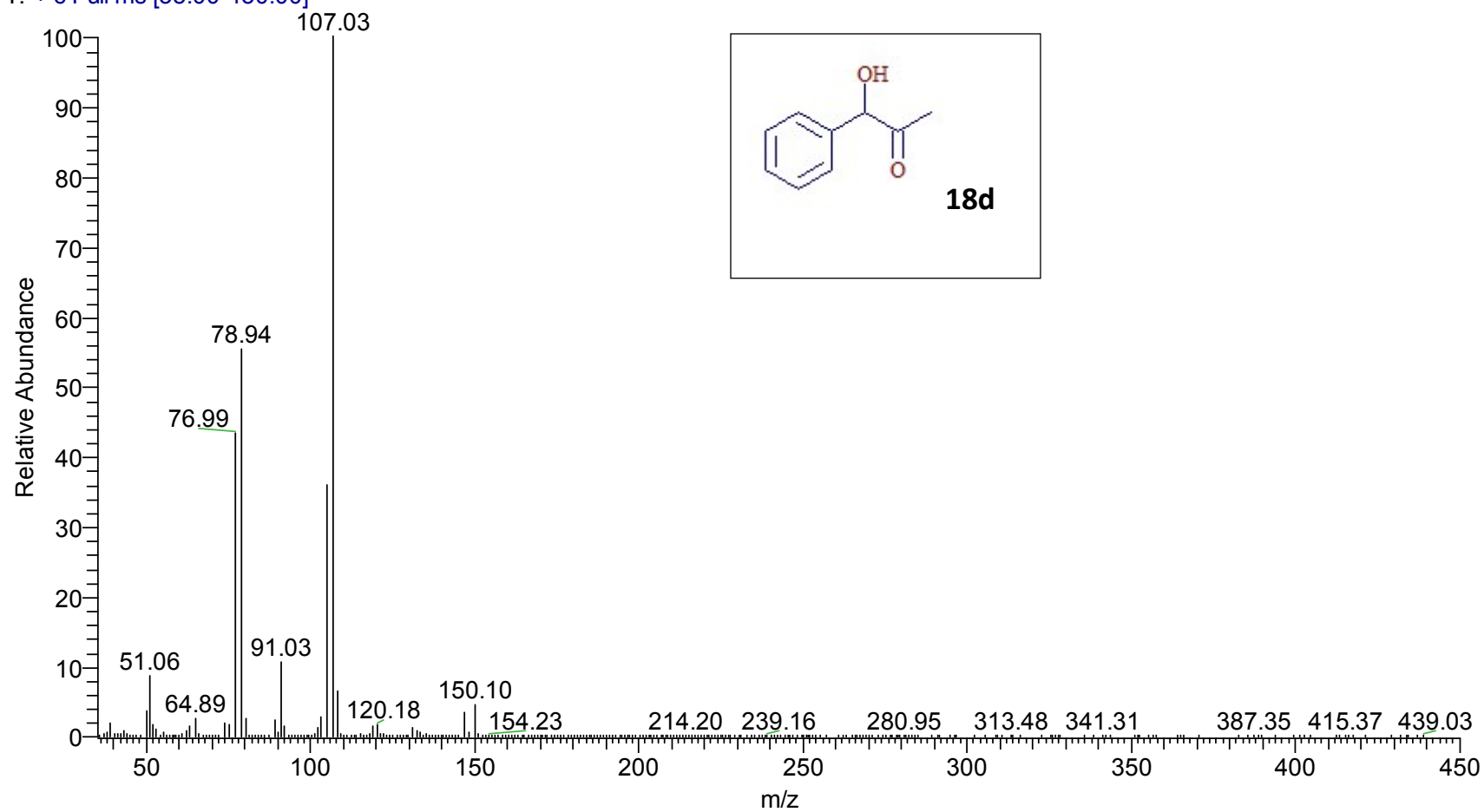
quadrelli167 #760 RT: 13.03 AV: 1 NL: 1.98E8
T: + c Full ms [35.00-450.00]



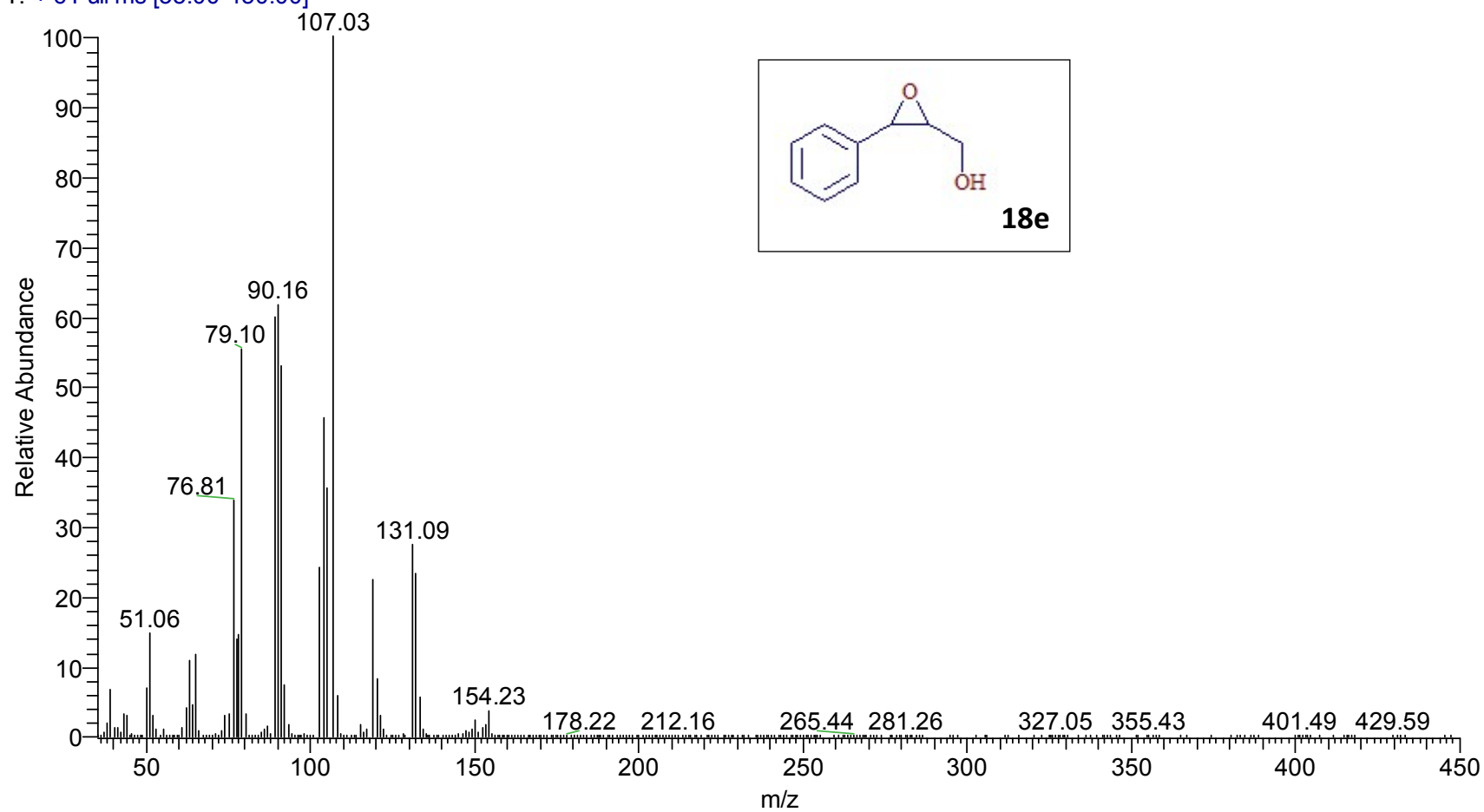
quadrelli167 #798 RT: 13.47 AV: 1 NL: 1.69E7
T: + c Full ms [35.00-450.00]



quadrelli167 #825 RT: 13.78 AV: 1 NL: 1.34E8
T: + c Full ms [35.00-450.00]



quadrelli167 #860 RT: 14.18 AV: 1 NL: 2.52E7
T: + c Full ms [35.00-450.00]



quadrelli167 #960 RT: 15.33 AV: 1 NL: 1.19E8
T: + c Full ms [35.00-450.00]

