NHC catalyzed enantioselective Coates-Claisen rearrangement : A rapid access to the dihydropyran core for Oleuropein based Secoiridoids

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Supporting Information

Table of Contents:

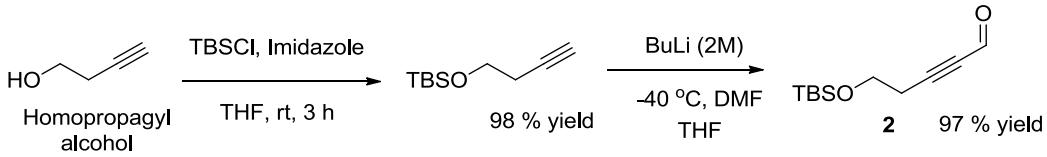
I. General methods:

General: All the reactions were carried out in a flame or oven dried glassware under an argon or nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 nm). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using base solution of potassium permanganate. Technical grade solvents were used for chromatography and were distilled prior to use. NMR spectra were recorded at room temperature on 300 MHz Bruker ACF 300, 400 MHz Bruker DPX 400, 500 MHz Bruker AMX 500, and 400 MHz JEOL ECA 400 NMR spectrometers. The residual solvent signals were taken as the reference (7.26 ppm for ^{1}H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$, 2.5 ppm for ^{1}H NMR spectra and 39.5 ppm for ^{13}C NMR spectra in DMSO-d_6). Sometimes the TMS signal at 0.0 ppm was used an internal standard for ^{1}H NMR spectra. Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal. HR-MS (ESI) spectra were recorded on a Waters Q-Tof premier^{TM} mass spectrometer.

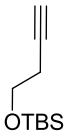
Materials: All solvents were distilled under argon from the following drying agents immediately before use: tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl; dichloromethane was distilled from calcium hydride. All the starting materials were purchased from commercial suppliers and used without further purification. All the NHC catalyses were purchased from commercial suppliers and catalyst **G** and **H** was prepared from standard literature procedure.[1]

Experimental Sections

Synthesis of Propagyl fragment 2:



But-3-yn-1-yloxy)(tert-butyl)dimethylsilane:[2]



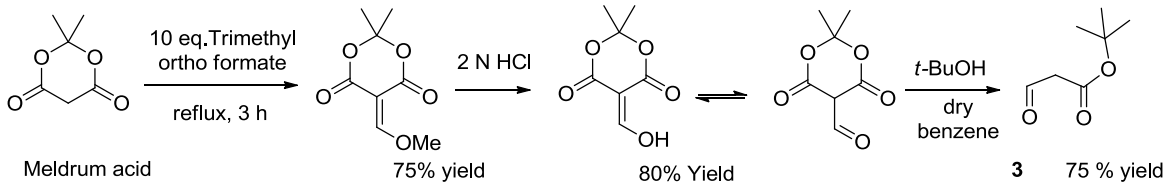
To a solution of 3-butyn-1-ol (9.26 g, 132.1 mmol) and imidazole (21.59 g, 317.1 mmol) in tetrahydrofuran (200 mL) was added *tert*-butyl-dimethyl-silyl chloride (TBSCl) (23.90 g, 158.5 mmol). After stirring at ambient temperature for 3 h, the reaction mixture was filtered through a pad of silica and concentrated under reduced pressure. Gradient flash chromatography (Petroleum ether/Ethyl acetate, 100:0 → 95:5) afforded the alkyne (23.62 g, 98 %) as a clear colorless oil: **^{1}H NMR** (400 MHz, CDCl3) δ 3.74 (t, J = 7.1 Hz, 2 H), 2.40 (dt, J_1 = 7.1, J_2 = 2.6 Hz, 2H), 1.95 (t, J = 2.6 Hz, 1 H), 0.89 (s, 9 H), 0.07 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 81.5, 69.2, 61.7, 25.8, 22.8, 18.3; **HRMS** (ESI) m/z $[M+H]^+$: calcd. for $C_{10}H_{21}OSi$: 185.1330, found: 185.1324.

5-((Tert-butyldimethylsilyl)oxy)pent-2-ynal (2):[3]

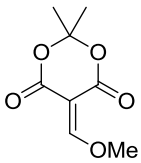
The alkyne (5 g, 27.0 mmol) was dissolved in dry THF (50 mL) and the solution was cooled to −40 °C under nitrogen. n-Butyl lithium (2 M in cyclohexane, 14.2 mL, 28.3 mmol) was added dropwise over 2 minutes maintaining the temperature between −35 and −40 °C. After completion of the addition, anhydrous DMF (4.16 mL, 54.0 mmol, 2 equiv) was added in one portion and the cold bath was removed. The reaction mixture was allowed to warm to room temperature and aged for 30 minutes. The THF solution was poured into a vigorously stirred biphasic solution prepared from a 10 % aqueous solution of KH_2PO_4 (150

mL, 100 mmol) and methyl *tert*-butyl ether (MTBE) (150 mL) cooled over ice to +5 ^{o}C. Layers were separated and the organic extract was washed with water (2x200 mL). Combined aqueous layers were back extracted with MTBE (150 mL). Combined organic layers were dried over $MgSO_4$, filtered and concentrated to give the crude acetylenic aldehyde as oil which was purified by column chromatography. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.1 (s, 1 H), 3.80 (t, J = 6.7 Hz, 2 H), 2.62 (dt, J_1 = 6.7, J_2 = 0.7 Hz, 2H), 0.89 (s, 1 H), 0.08 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 96.2, 82.2, 60.5, 25.7, 23.7, 23.5, 18.2; **HRMS** (ESI) m/z $[M+H]^+$: calcd. for $C_{11}H_{21}O_2Si$: 213.1388, found: 213.1331. Spectra consistent with known data.

Synthesis of fragment 3:

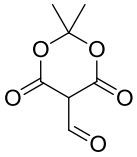


5-(methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione:[4]



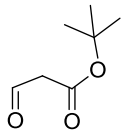
A mixture of Meldrum's acid (15 g, 104.1 mmol) and 50 g. of $CH(OMe)_3$ was heated for 3 h at 85−95 ^{o}C. After complete conversion of starting material by checking the TLC, $CH(OMe)_3$ was removed and through rotavap. The light brown oil was diluted with 100 mL of 5 % CH_2Cl_2 in hexane and scratch the sides using spatula to obtained yellow solid which is filtered through Buchner to obtained (Methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione. The product was obtained as yellow solid; (17.6 g, 91 % yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 4.29 (s, 3H), 1.74 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.0, 163.2, 158.6, 104.8, 96.8, 66.3, 27.3; **HRMS** (ESI) m/z $[M+Na]^+$: calcd. for $C_8H_{10}O_5Na$: 209.0401, found: 209.0411. Spectra consistent with known data.

2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-carbaldehyde:[4]



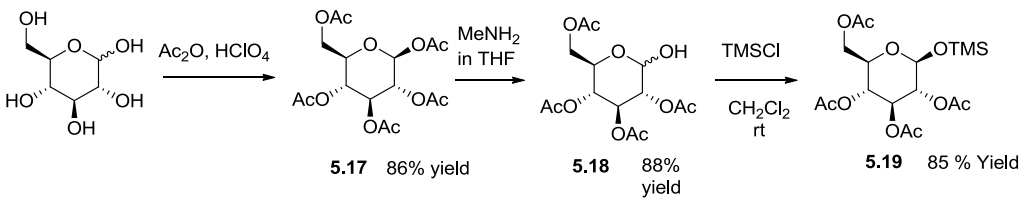
(Methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (10 g, 53.7 mmol) which upon treatment with 2N HCl (30 mL) for 2 h obtained hydrolyzed product. The reaction mixture was diluted with ethyl acetate (200 mL) and separated through separating funnel. The aqueous layer again extracted with (2x50 mL) of ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated to obtained light brown solid; (8.13 g, 88 % yield); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 1.77 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 168.0, 160.6, 107.1, 95.4, 27.2; **HRMS** (ESI) m/z $[M+H]^+$: calcd. for $C_7H_9O_5$: 173.0450, found: 173.0457. Spectra consistent with known data.

***t*-Butyl formylacetate (3)**:[4]

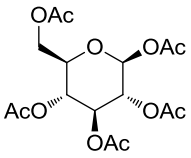


A solution of formyl Meldrum's acid (10 g, 58.1 mmol) and *tert*-butylalcohol (6.6 mL, 69.7 mmol) in dry benzene (100 mL) was refluxed for 90 min. The solvent was evaporated in vacuo at room temperature. Distillation of the residue in 35−60 ^{o}C in 11 torr obtained colourless oil which was immediately stored in −78^{o}C fridge. (5.8 g, 70 % yield); **^{1}H NMR** (400 MHz, $CDCl_3$): mixture of Keto-enol tautomers δ 11.5 (d, J=12.5, 1H, –OH), 9.87 (t, J = 2.4, 1H, –CHO), 7.46 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 1.77 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 168.0, 160.6, 107.1, 95.4, 27.2; **HRMS** (ESI) m/z $[M+Na]^+$: calcd. for $C_7H_{12}O_3Na$: 167.0684, found: 167.0681. Spectra consistent with known data.

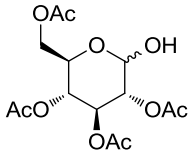
Sugar fragment:[5]



5.17 86% yield **5.18** 88% yield **5.19** 85 % Yield

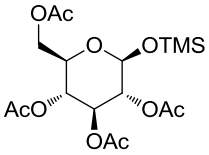


Perchloric acid was added dropwise to a suspension of 0.5 g of glucose in acetic anhydride (36 mL) at 0 ^{o}C. Additional glucose (9.5 g, 55.5 mmol) was added portion wise then the solution was warmed to room temperature and stirred for additional 3 h. Quench and hydrolyzed the excess acetic anhydride by 2 N HCl (100 mL). The reaction mixture was extracted with ethylacetate (250 mL) and washed with water (3x100 mL), ammonium chloride (50 mL) and sodium chloride (50 mL). The organic layer was dried using Na_2SO_4, filtered and concentrated to obtained petaacetyl glucose as white solid which is used for further steps (17.3 g, 80 %).



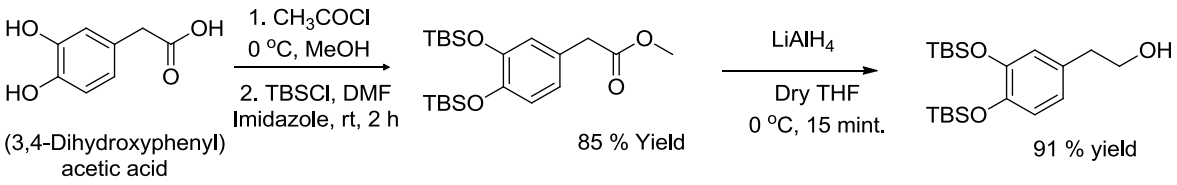
Methyl amine in THF (1M) was added drop wise to a suspension of penta acetyl glucose (3 g, 7.69 mmol), in dry THF (15 mL) to obtained tetraacetyl glucose at 0 ^{o}C. Additionally the reaction mixture was stirred for 3 h. Evaporate the solvent and the residue was purified by column chromatography obtained. tetraacetyl glucose which is immediately used for next steps (2.32 g, 85 %).

l-*O*-(Trimethylsily1)-2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranose:[6]

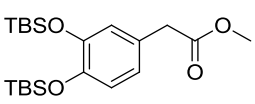


To a stirred solution of tetraacetyl glucose (2 g, 5.7 mmol) in dichloromethane (15 mL) containing triethylamine (0.89 mL, 6.8 mmol) was added chlorotrimethylsilane (0.73 mL, 6.8 mmol) dropwise at room temperature. After being stirred for 2 h, the mixture was filtered through a pad of Celite and worked up to afford a residue that was crystallized to afford silyl derivative of tetraacetyl glucose in 85 % yield as a single anomer: mp 104−105 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.17 (t, J = 9.2 Hz, 1H), 5.04 (t, J = 9.6 Hz, 1H), 4.90 (dd, J_1 = 9.6 Hz, J_2 = 7.6 Hz, 1H), 4.73 (d, J = 7.6 Hz, 1H), 4.20–4.09 (m, 2H), 3.72–3.67 (m, 1H), 2.15 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 0.13 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.6, 170.3, 169.4, 169.3,

95.5, 73.2, 72.7, 71.8, 68.6, 62.2, 20.6 (3C), –0.02 (3C); **HRMS** (ESI) m/z $[M+Na]^+$: calcd. for $C_{17}H_{28}O_{10}SiNa$: 443.1349, found: 443.1359. Spectra consistent with known data.

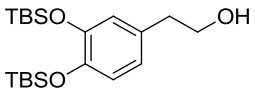


Methyl [3,4-Bis(*tert*-butyldimethylsilyloxy)phenyl]acetate:[7]



At 0 °C acetyl chloride (6 mL) was added dropwise to the solution of (3,4-dihydroxyphenyl)acetic acid (6.51 g, 38.7 mmol) in MeOH (250 mL). After 1 h, the mixture was allowed to warm to room temperature. The progress of the reaction was monitor by TLC which tells complete conversion after 2 h. The reaction mixture was concentrated to dryness, and the residue was redissolved in dry DMF (60 mL). From the reaction mixture, TBDMSCl (14 g, 92.8 mmol) and imidazole (3.8 g, 57 mmol) were added and the mixture was stirred for 2 h. After complete conversion by TLC the reaction mixture was diluted with diethyl ether (200 mL) and washed with water (3x100 mL). The organic layer was dried over Na_2SO_4 and concentrated to obtained crude oil which upon column chromatography to form TBS protected ester . **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.78–6.76 (m, 1H), 6.74 (s, 1H), 6.69 (dd, J_1 = 8.2 Hz, J_2 = 2.1 Hz, 1H), 3.67 (s, 3H), 3.49 (s, 3H), 0.98 (s, 18H), 0.19 (s, 12H), 0.13 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.1, 146.6, 145.9, 126.8, 122.0, 51.8, 40.4, 25.8; Spectra consistent with known data.

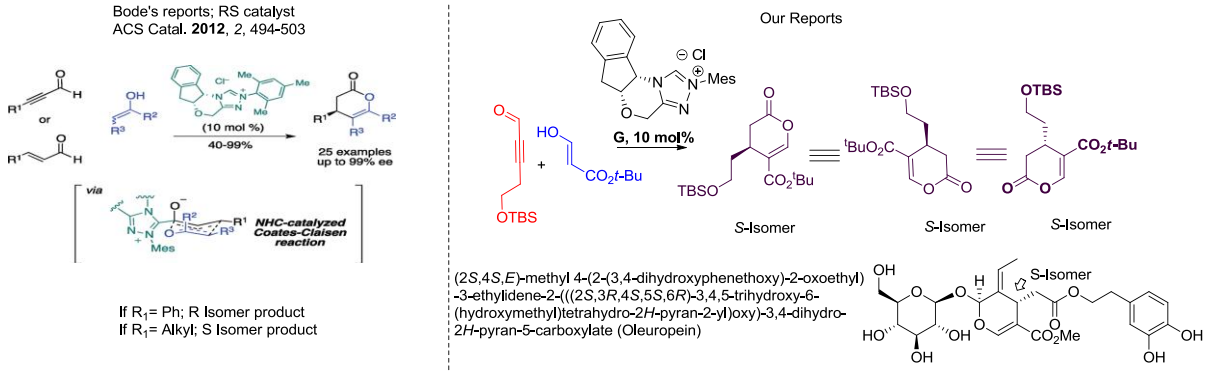
2-[3,4-Bis(*tert*-butyldimethylsilyloxy)phenyl]ethanol:[7]



Methyl[3,4-bis(*tert*-butyldimethylsilyloxy)phenyl]acetate (4.13 g, 10.03 mmol) in dry THF (25 mL) was added dropwise to a cooled (0 °C) suspension of $LiAlH_4$ (400 mg, 10.5 mmol) in THF (25 mL) and stirred for 15 min. TlC analysis revealed complete disappearance of the starting material in this time period. The

reaction was quenched by dropwise addition of methanol and diluted with diethyl ether and subsequently washed with water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to obtained residual oil which is purified through silica gel column chromatography. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.76 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.63 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 3.78 (q, J = 4.2 Hz, 1H), 2.73 (t, J = 6.5 Hz, 1H), 1.45 (s, 1H), 0.98 (s, 18H), 0.19 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.7, 145.4, 131.2, 121.8, 121.8, 121.0, 63.8, 38.4, 25.9, 18.4, −4.0; **HRMS** (ESI) m/z $[M+Na]^+$: calcd. for $C_{20}H_{39}O_3Si_2$: 383.2438, found: 383.2425. Spectra consistent with known data.

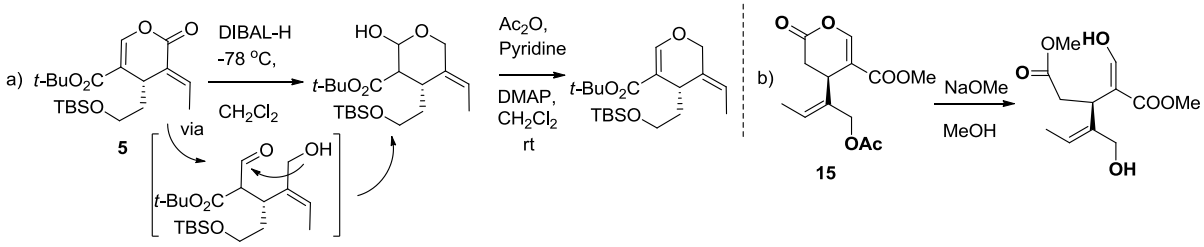
Stereo chemical prediction based on Literature report:



Supporting reactions:

a) DIBAL-H reduction of **5**:

b) Acetyl deprotection of **15**:



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2. H. F. Sneddon, M. J. Gaunt and S. V. Ley, *Org. Lett.* 2003, **5**, 1147.
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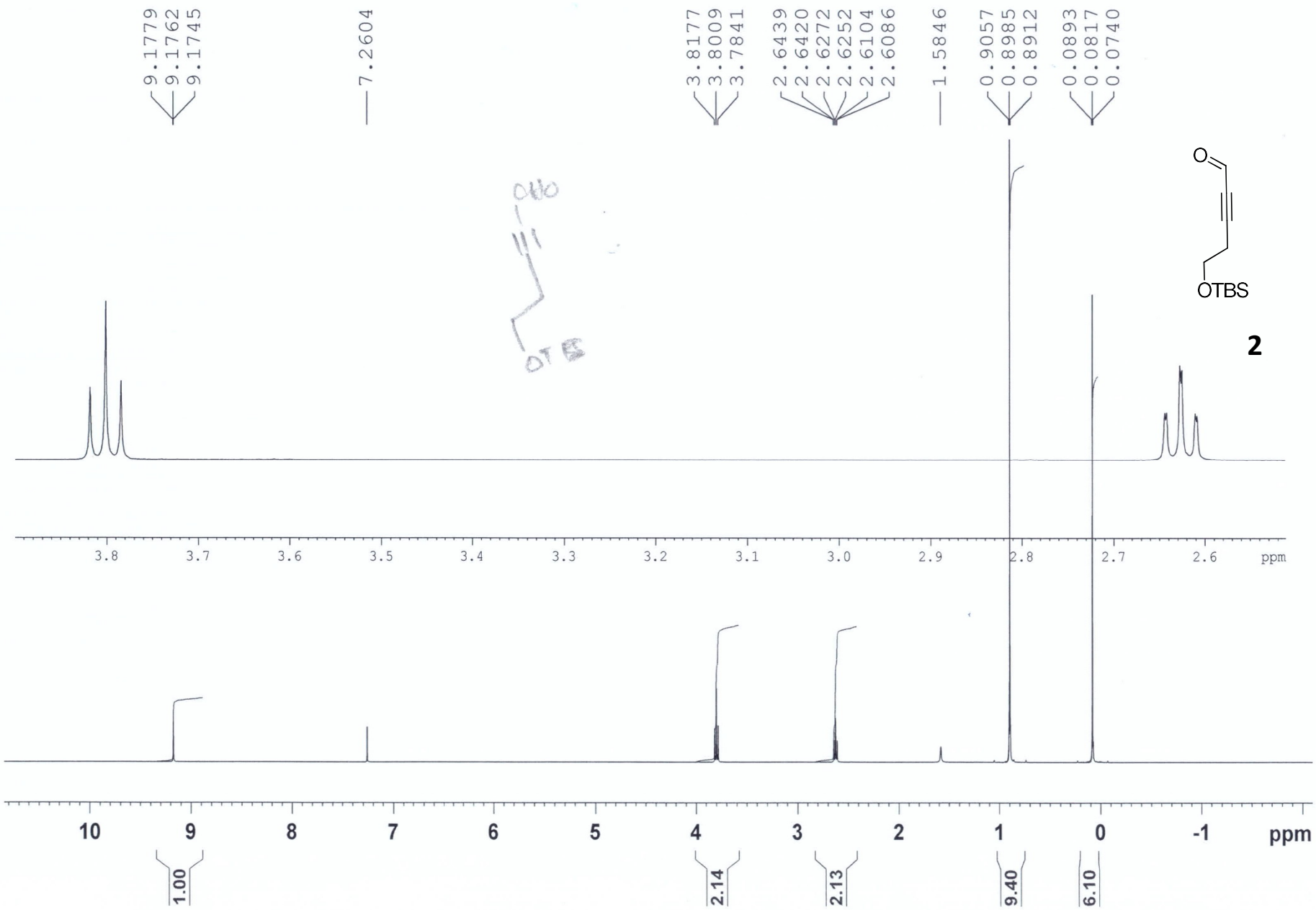
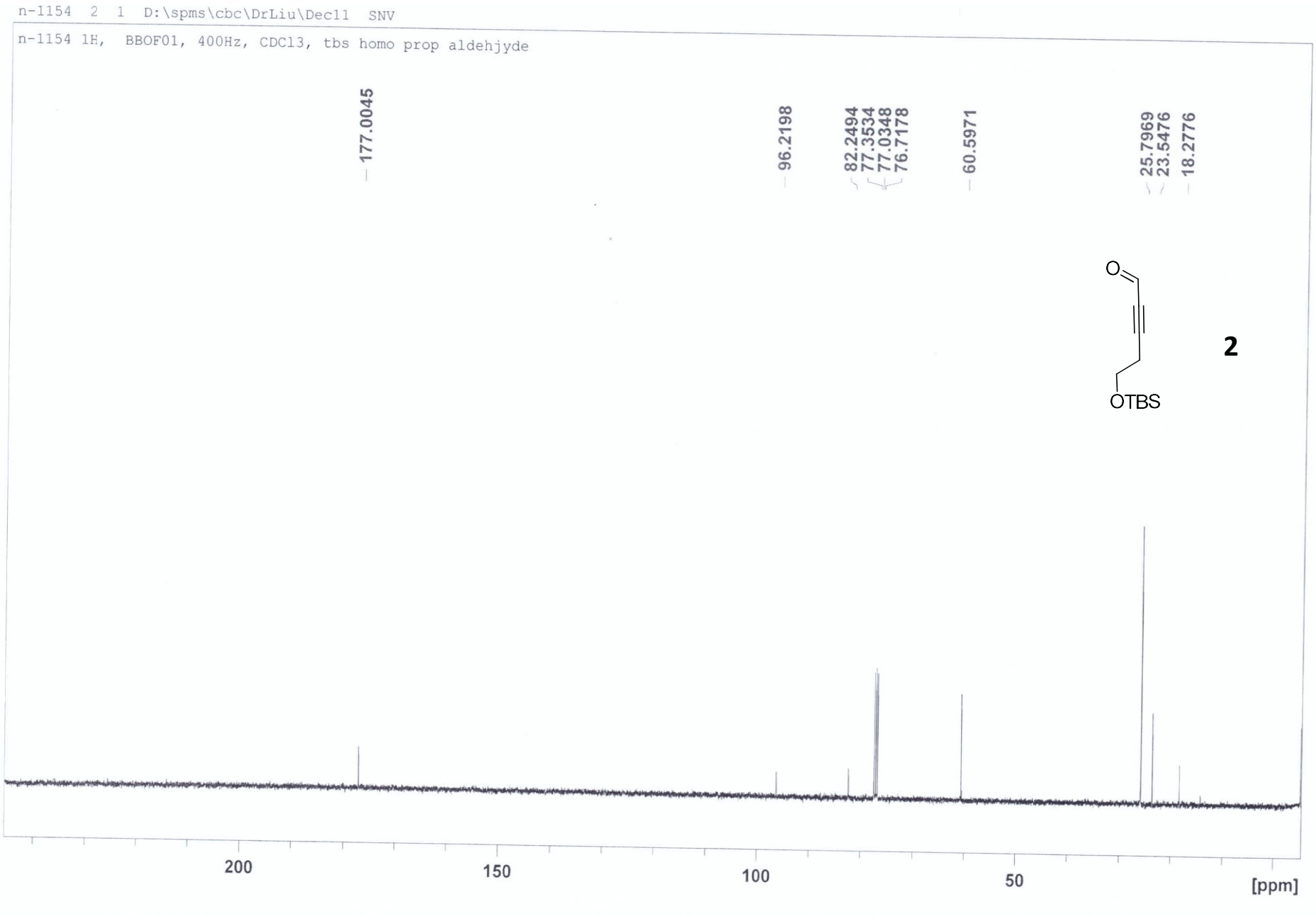
6. P. Allevi, M. Anastasia, P. Ciuffreda, E. Bigatti and P. *J.* Macdonald, *Org. Chem.* 1993, **58**, 4175.
7. H. I. Duynstee, M. C. de Koning, H. Ovaa, G. A. van der Marel and J. H. v. Boom, *Eur. J. Org. Chem.* 1999, 2623.

n-2018 400MHz, CDCl3, bbf4 o1,otbs formyl alkyne

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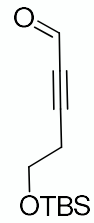
Elemental Composition Report



2

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
159 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-32 H: 0-34 O: 0-7 S: 0-5 Si: 0-1

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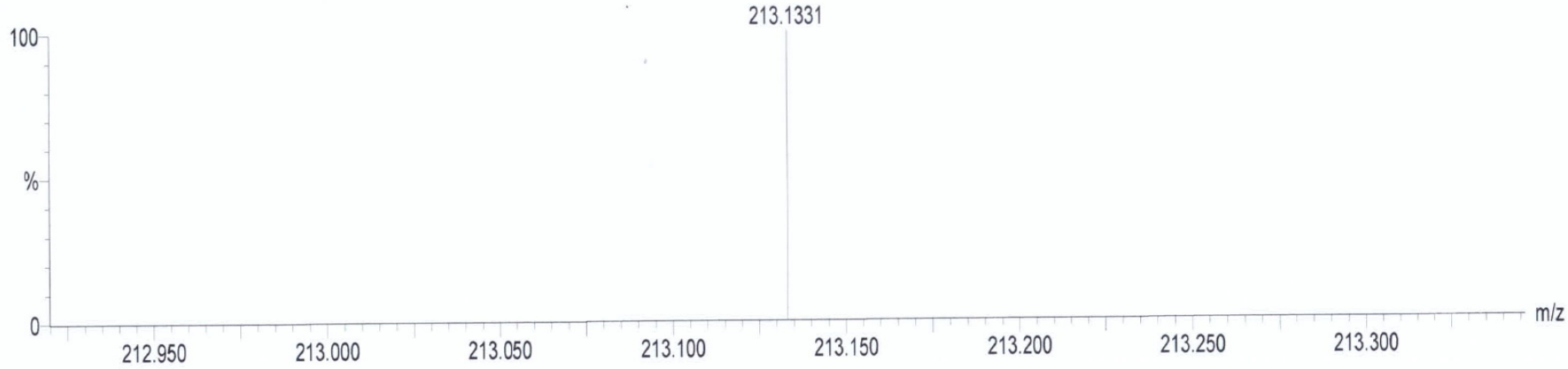
1: TOF MS ES+
7.58e+002



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Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
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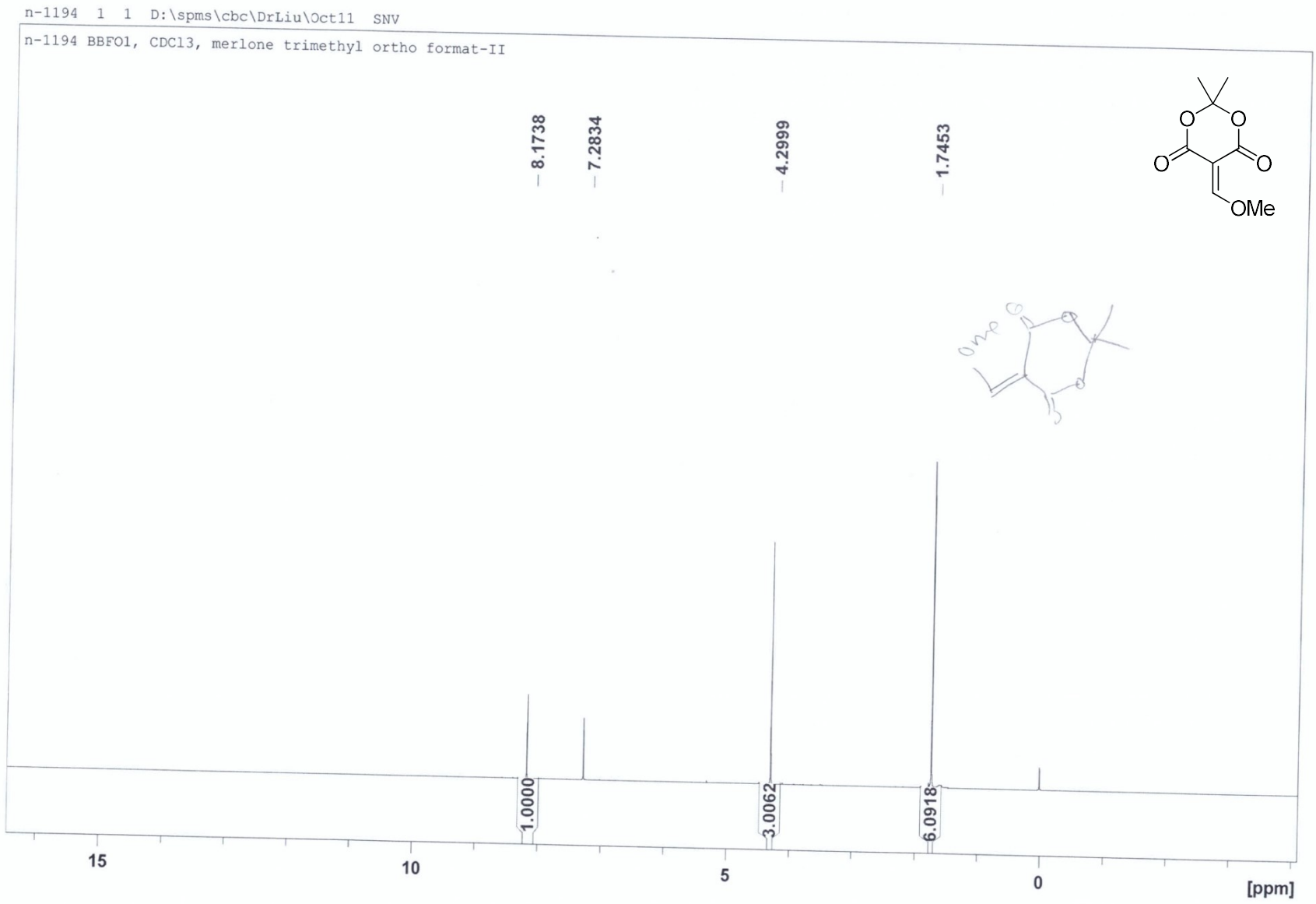
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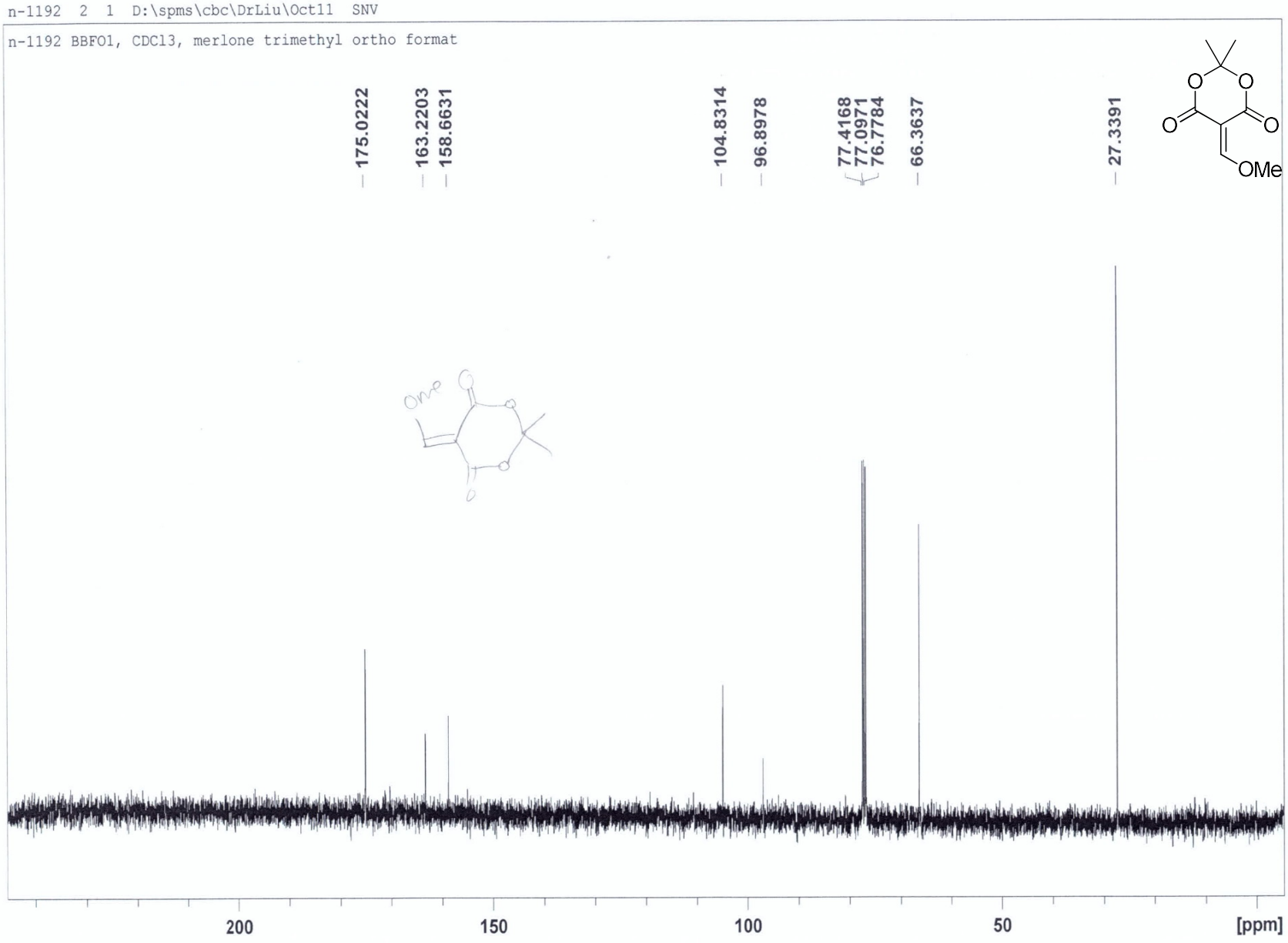
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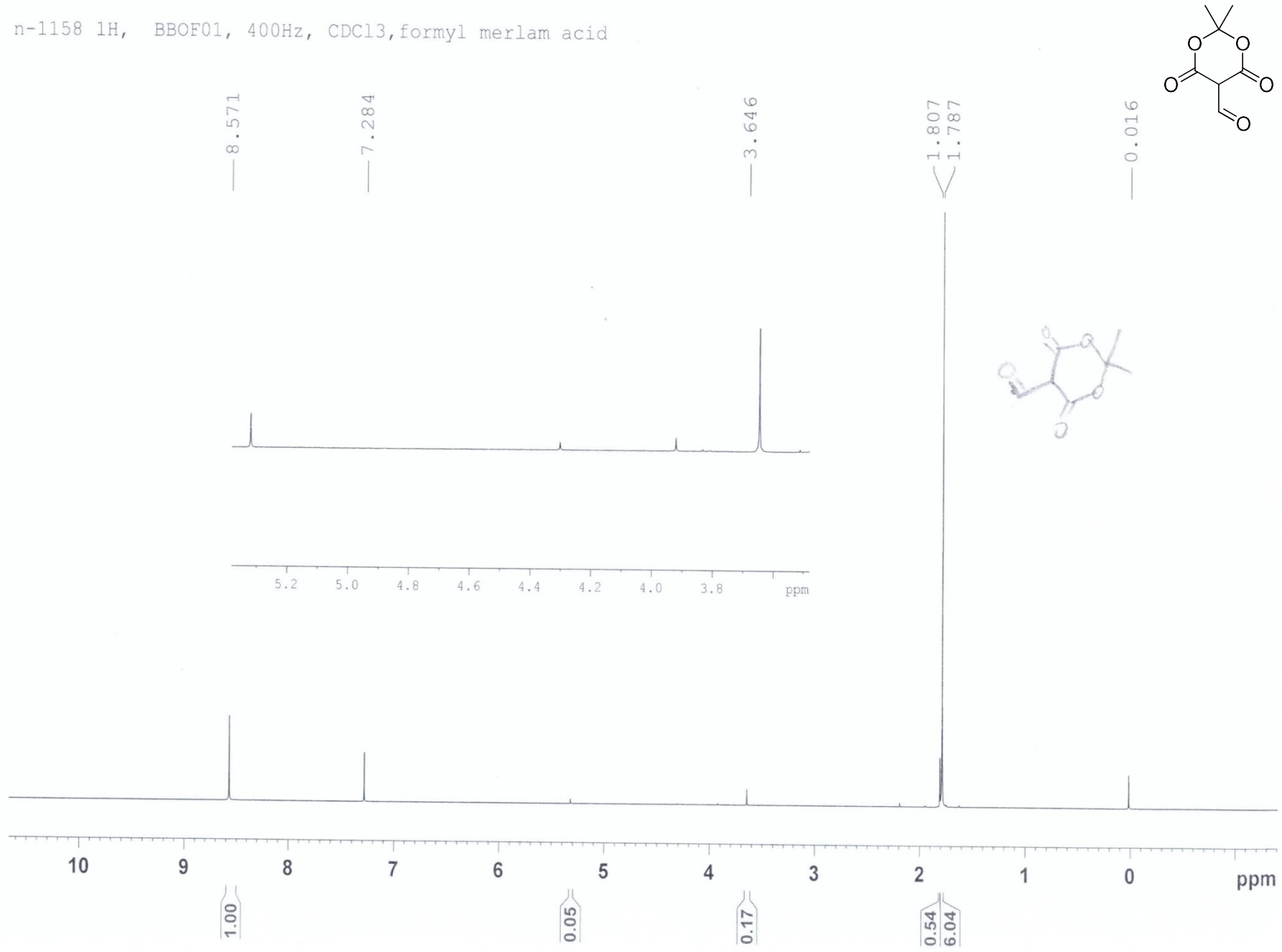
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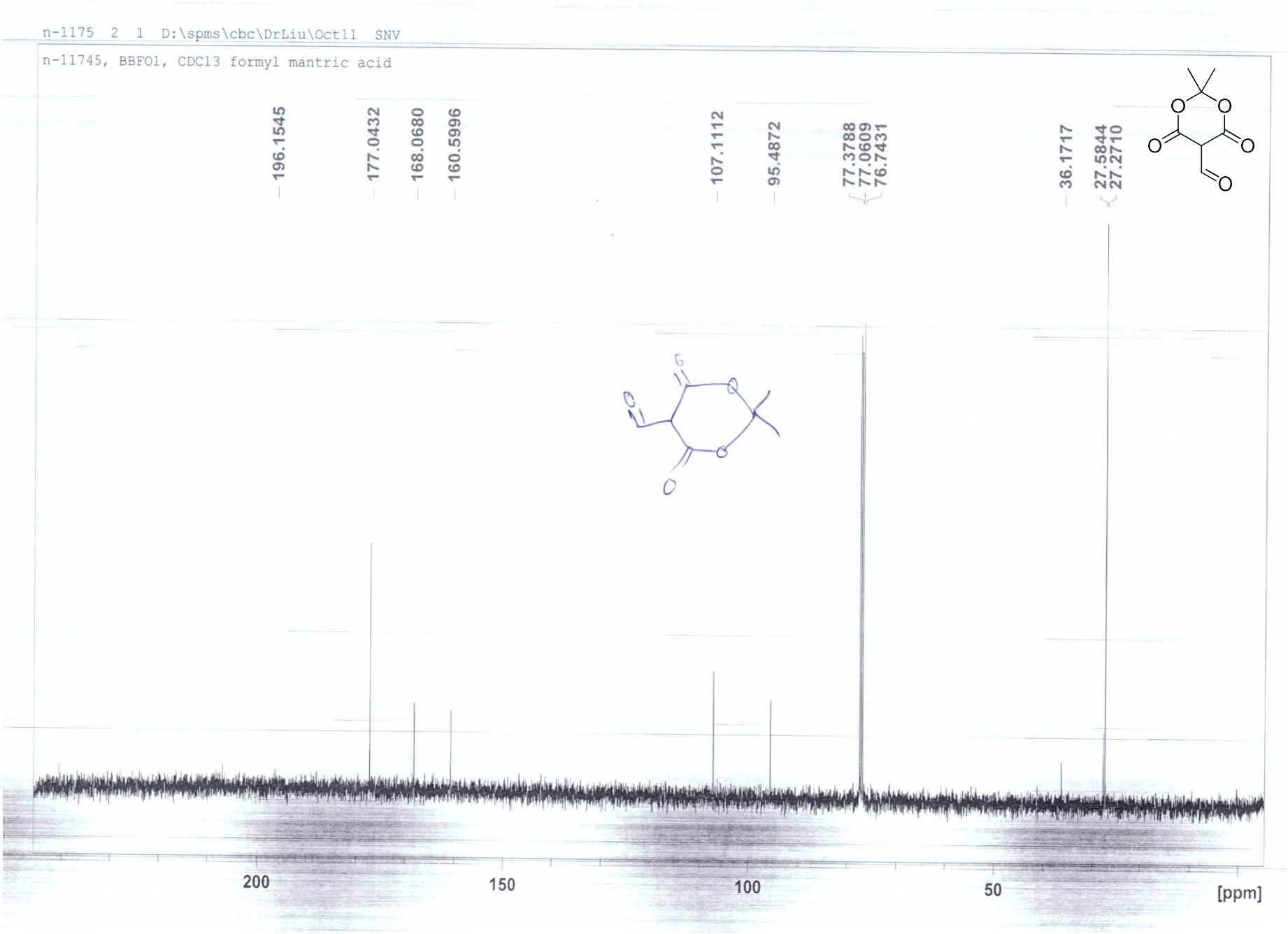
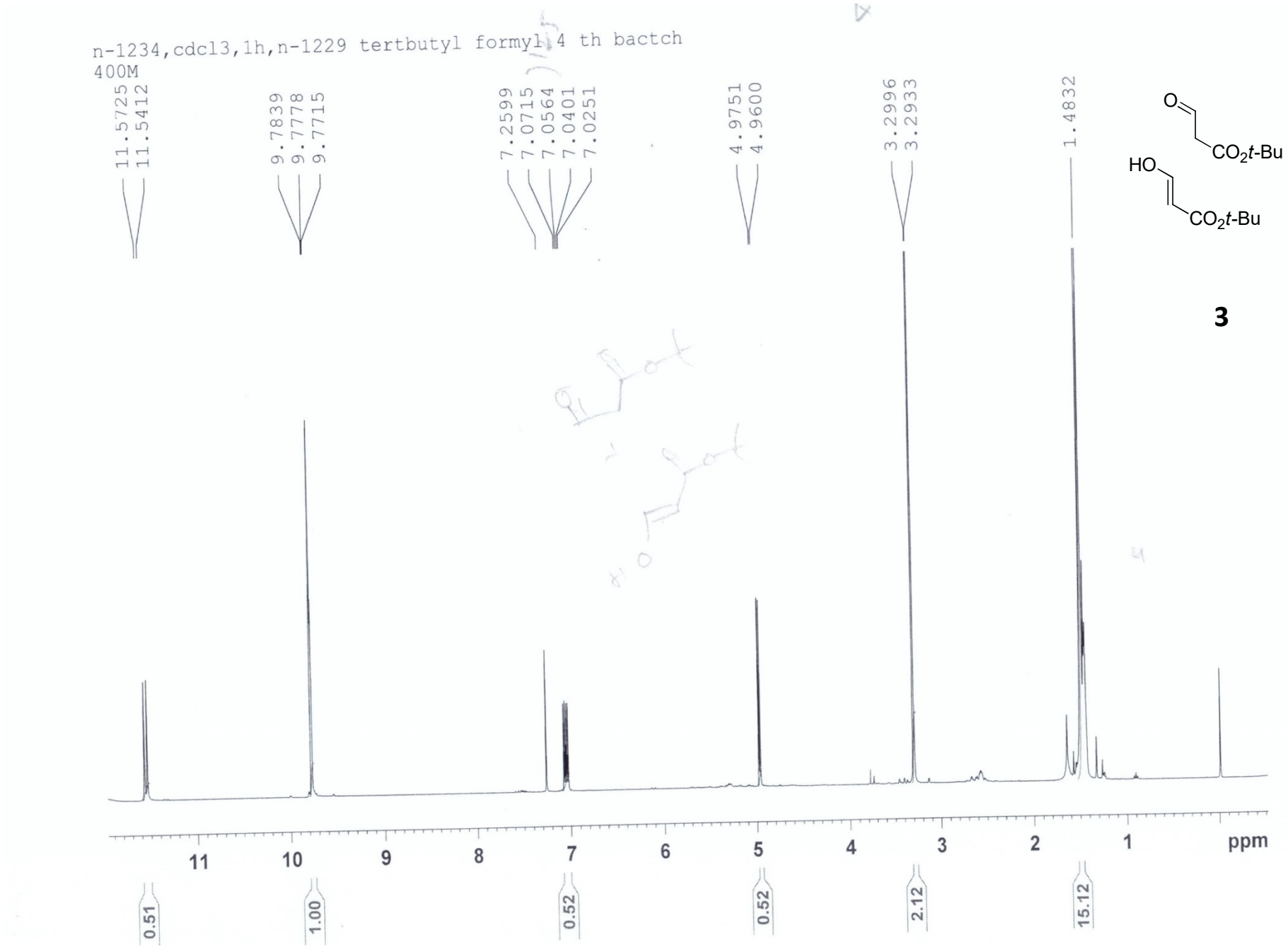
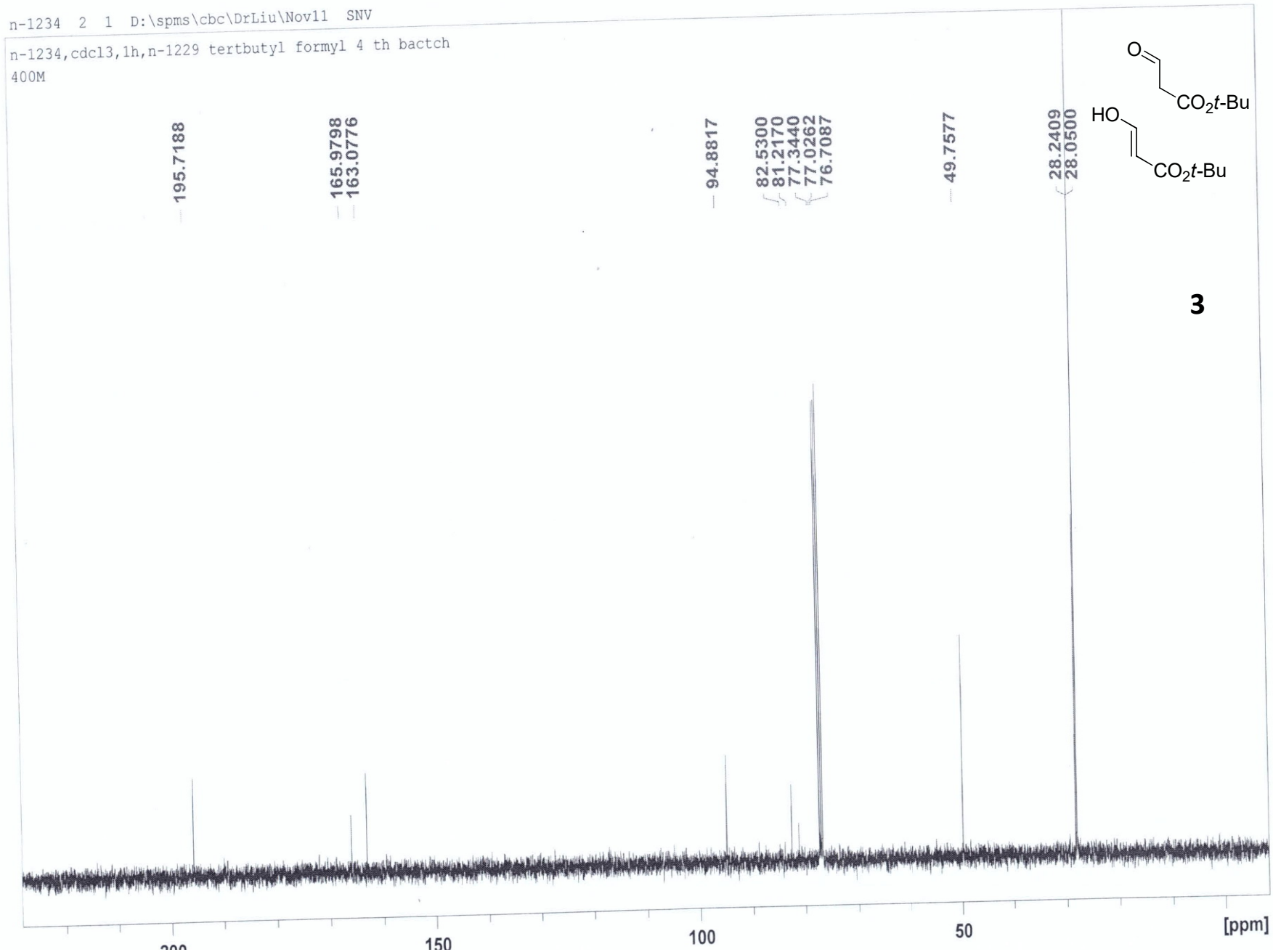
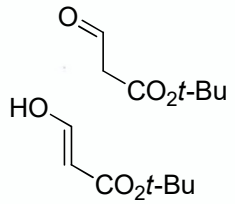
0.54
6.04


n-1175 2 1 D:\spms\cbc\DrLiu\Oct11 SNV
n-11745, BBFO1, CDCl3 formyl mantric acid
196.1545
177.0432
168.0680
160.5996
107.1112
95.4872
77.3788
77.0609
76.7431
36.1717
27.5844
27.2710
200
150
100
50
[ppm]


n-1234,cdcl3,1h,n-1229 tertbutyl formyl 4 th bactch
400M
11.5725
11.5412
9.7839
9.7778
9.7715
7.2599
7.0715
7.0564
7.0401
7.0251
4.9751
4.9600
3.2996
3.2933
1.4832
O
CO2t-Bu
HO
CO2t-Bu
3
11
10
9
8
7
6
5
4
3
2
1
ppm
0.51
1.00
0.52
0.52
2.12
15.12


n-1234 2 1 D:\spms\cbc\DrLiu\Nov11 SNV
n-1234,cdcl3,1h,n-1229 tertbutyl formyl 4 th bactch
400M
195.7188
165.9798
163.0776
94.8817
82.5300
81.2170
77.3440
77.0262
76.7087
49.7577
28.2409
28.0500
O
CO2t-Bu
HO
CO2t-Bu
3
150
100
50
[ppm]

Elemental Composition Report



Single Mass Analysis

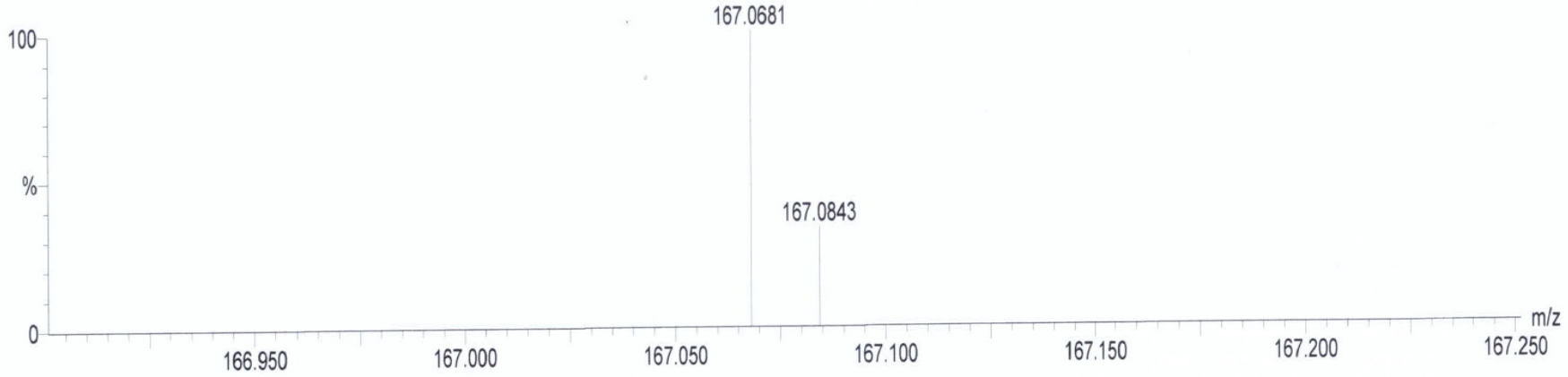
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-7 H: 0-13 O: 0-7 S: 0-5 Na: 1-1

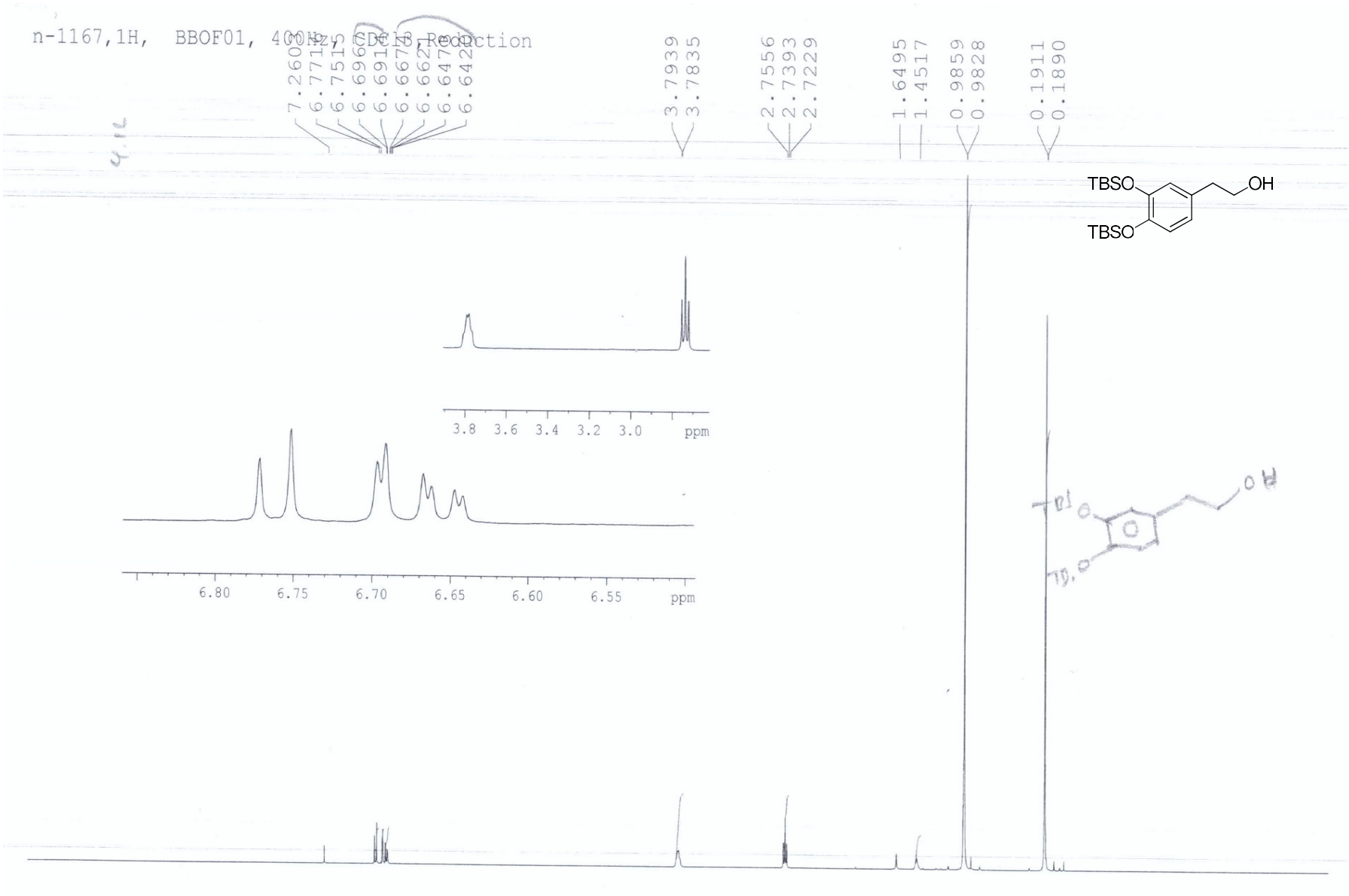
3

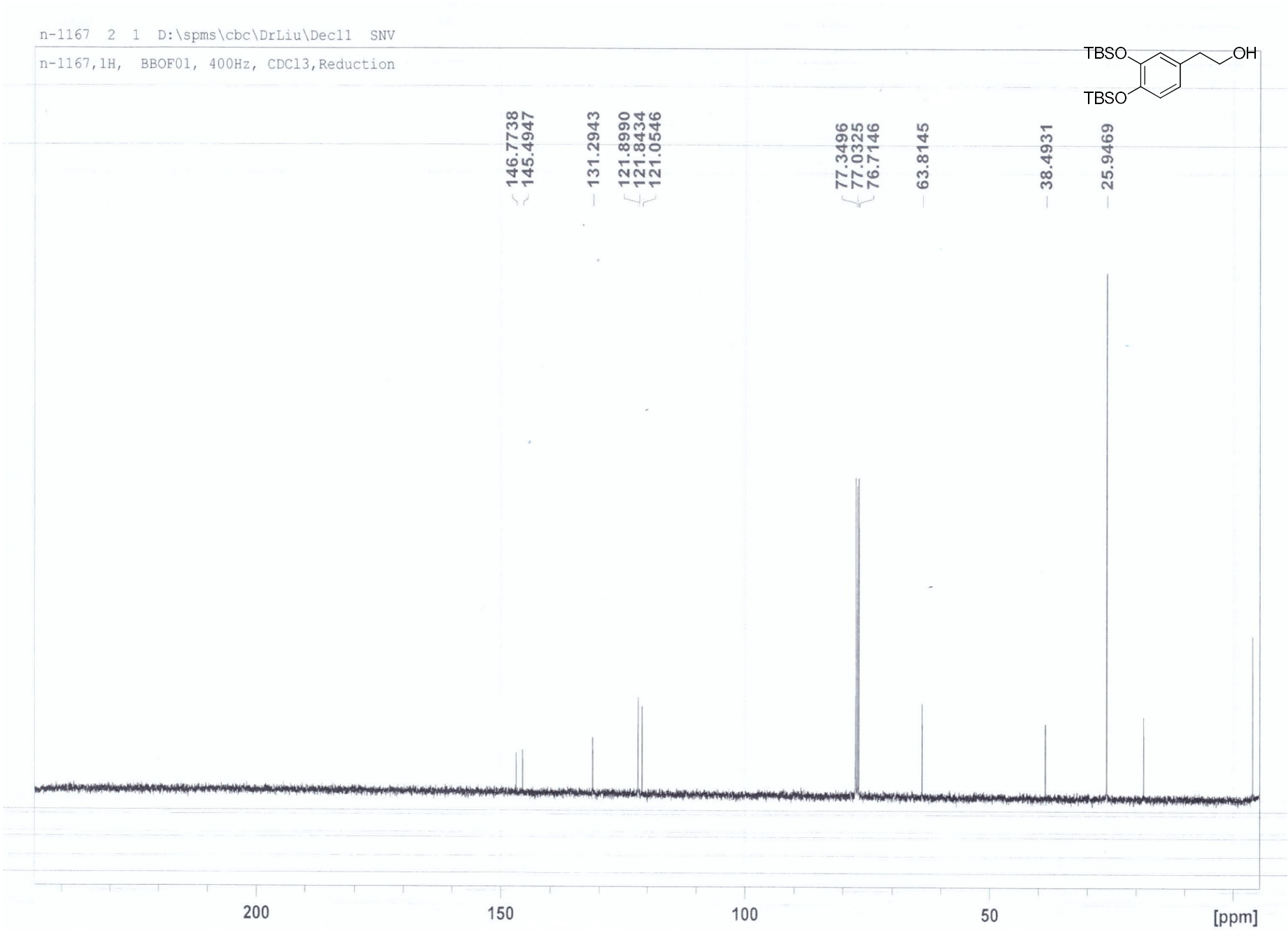
C7H12O3
SNV-2-13 9 (0.220)

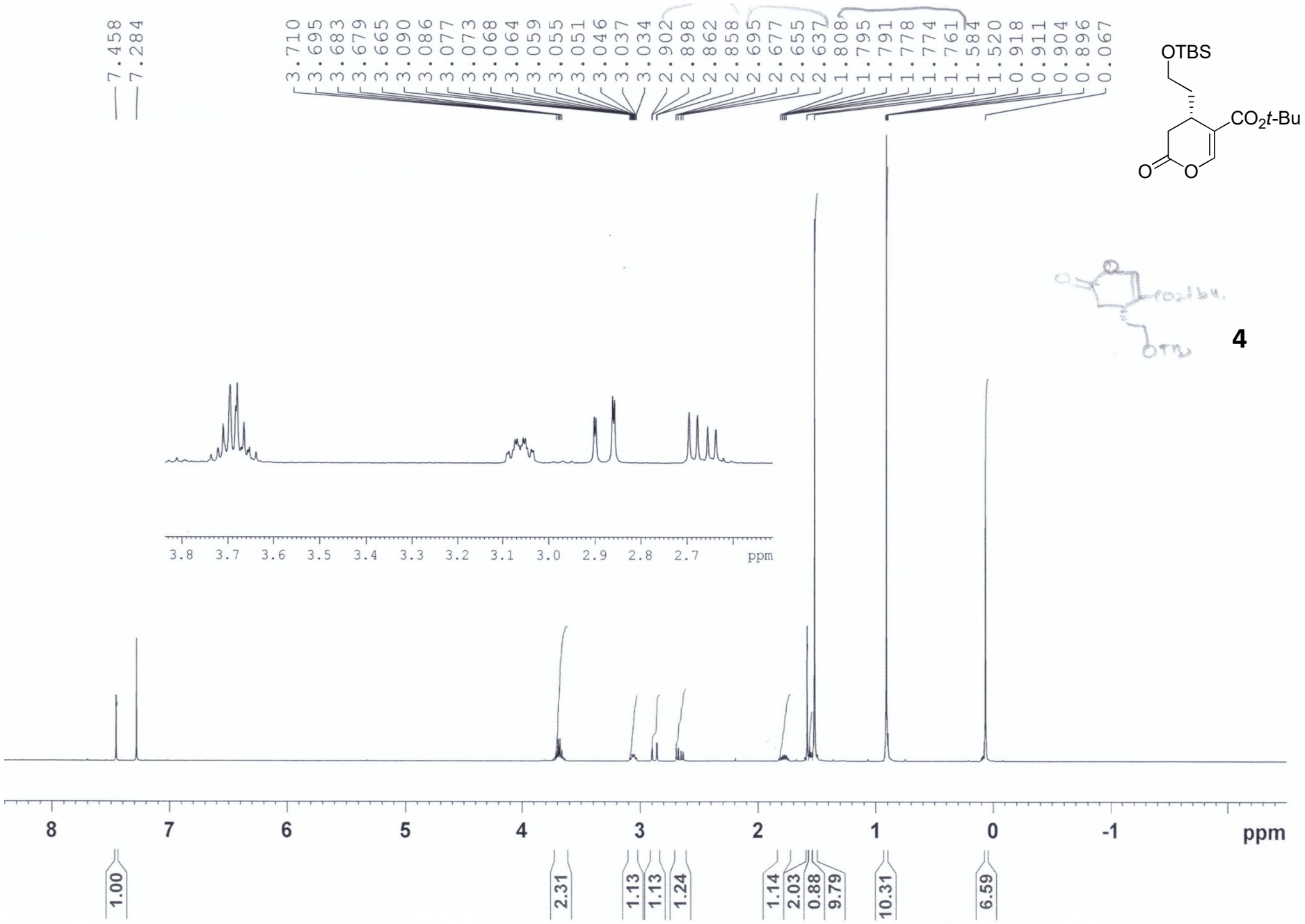
1: TOF MS ES+
3.04e+000

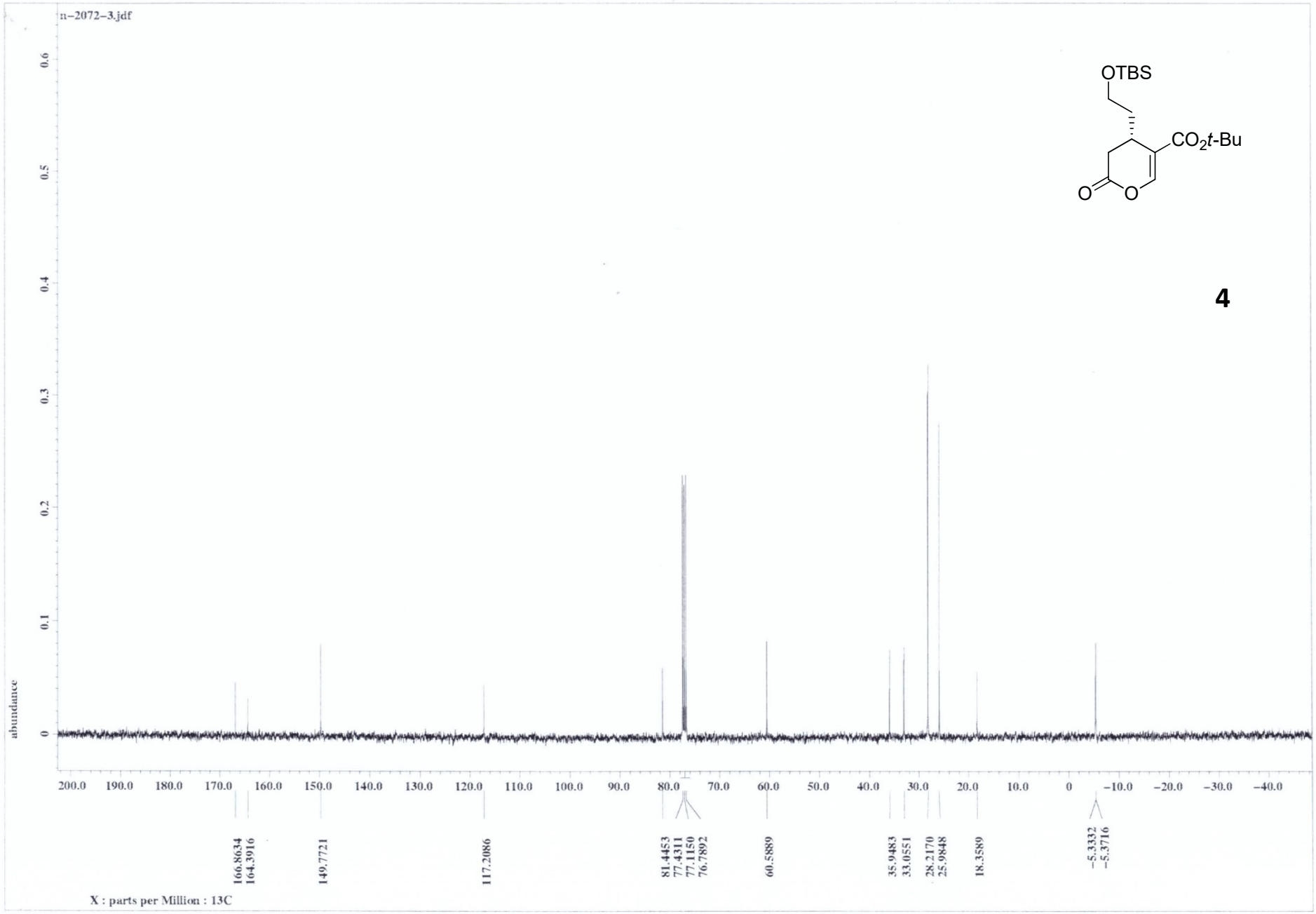


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
167.0681	167.0684	-0.3	-1.8	1.5	13.7	0.0	C7 H12 O3 Na


n-1167,1H, BBOF01, 400MHz, CDCl3, Reduction
7.2603
6.7715
6.7515
6.6966
6.6914
6.6673
6.6621
6.6478
6.6420
3.7939
3.7835
2.7556
2.7393
2.7229
1.6495
1.4517
0.9859
0.9828
0.1911
0.1890
TBSO
TBSO
OH
3.8 3.6 3.4 3.2 3.0 ppm
6.80 6.75 6.70 6.65 6.60 6.55 ppm


n-1167 2 1 D:\spms\cbc\DrLiu\Dec11 SNV
n-1167,1H, BBOF01, 400Hz, CDCl3,Reduction
TBSO
TBSO
OH
146.7738
145.4947
131.2943
121.8990
121.8434
121.0546
77.3496
77.0325
76.7146
63.8145
38.4931
25.9469
200
150
100
50
[ppm]

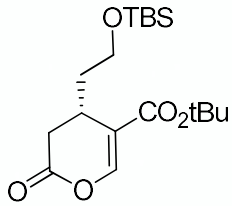

7.458
7.284
3.710
3.695
3.683
3.679
3.665
3.090
3.086
3.077
3.073
3.068
3.064
3.059
3.055
3.051
3.046
3.037
3.034
2.902
2.898
2.862
2.858
2.695
2.677
2.655
2.637
1.808
1.795
1.791
1.778
1.774
1.761
1.584
1.520
0.918
0.911
0.904
0.896
0.067
OTBS
CO2t-Bu
O
O
4
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 ppm
8 7 6 5 4 3 2 1 0 -1 ppm
1.00
2.31
1.13
1.13
1.24
1.14
2.03
0.88
9.79
10.31
6.59

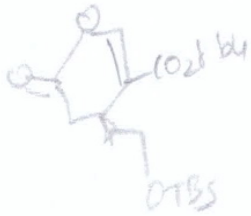

n-2072-3.jdf
OTBS
CO2t-Bu
O
O
4
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
-30.0
-40.0
166.8634
164.3916
149.7721
117.2086
81.4453
77.4311
77.1150
76.7892
60.5889
35.9483
33.0551
28.2170
25.9848
18.3589
-5.3332
-5.3716
X : parts per Million : 13C

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

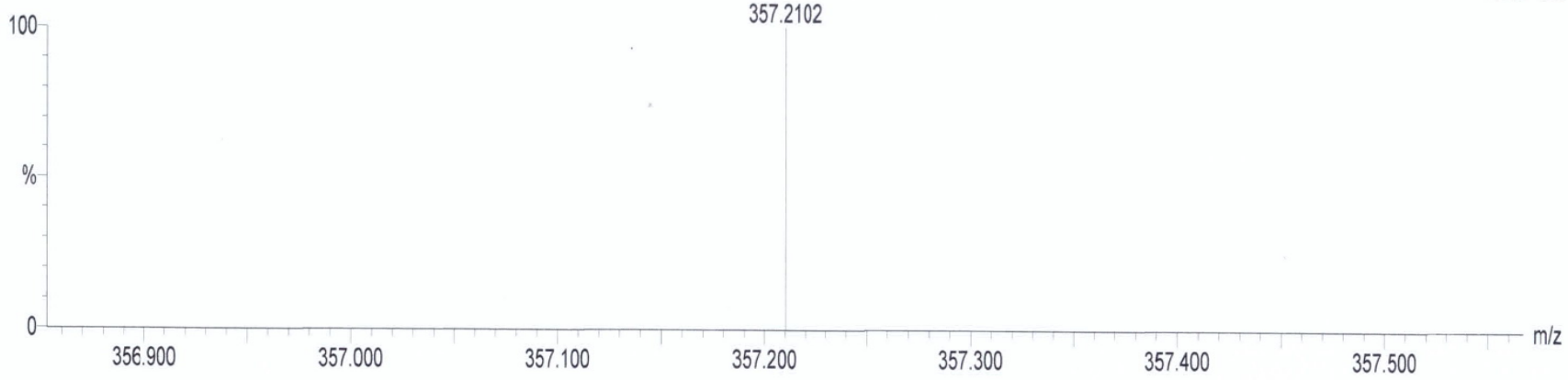




4

Monoisotopic Mass, Even Electron Ions
147 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-39 O: 0-5 Si: 0-1 S: 0-5
C18H32O5Si
SNV-2-21 7 (0.156)

1: TOF MS ES+
1.01e+000

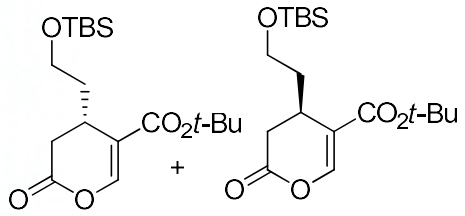


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
357.2102	357.2097	0.5	1.4	3.5	13.4	0.0	C18 H33 O5 Si

==== Shimadzu LCsolution Analysis Report ====

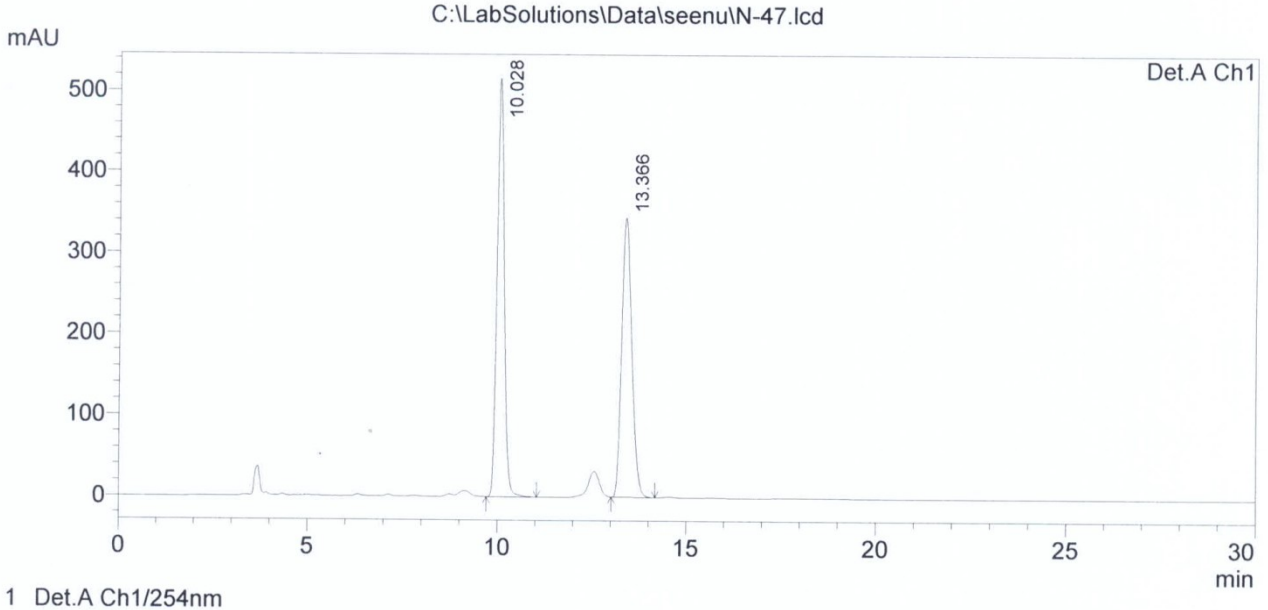
C:\LabSolutions\Data\seenu\N-47.lcd

Acquired by	: Admin
Sample Name	: N-47
Sample ID	: N-47, IC,achiral, rt,toluene
Tray#	: 1
Vail #	: 100
Injection Volume	: 1 uL
Data File Name	: N-47.lcd
Method File Name	: IPA2%-30min254nm-5.lcm
Batch File Name	: 03-03-2012.lcb
Report File Name	: Default.lcr
Data Acquired	: 3/5/2012 5:16:29 PM
Data Processed	: 3/5/2012 6:18:25 PM



4

<Chromatogram>



1 Det.A Ch1/254nm

PeakTable

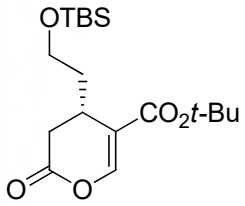
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.028	6934795	516509	51.945	60.028
2	13.366	6415356	343937	48.055	39.972
Total		13350151	860446	100.000	100.000

==== Shimadzu LCsolution Analysis Report ====

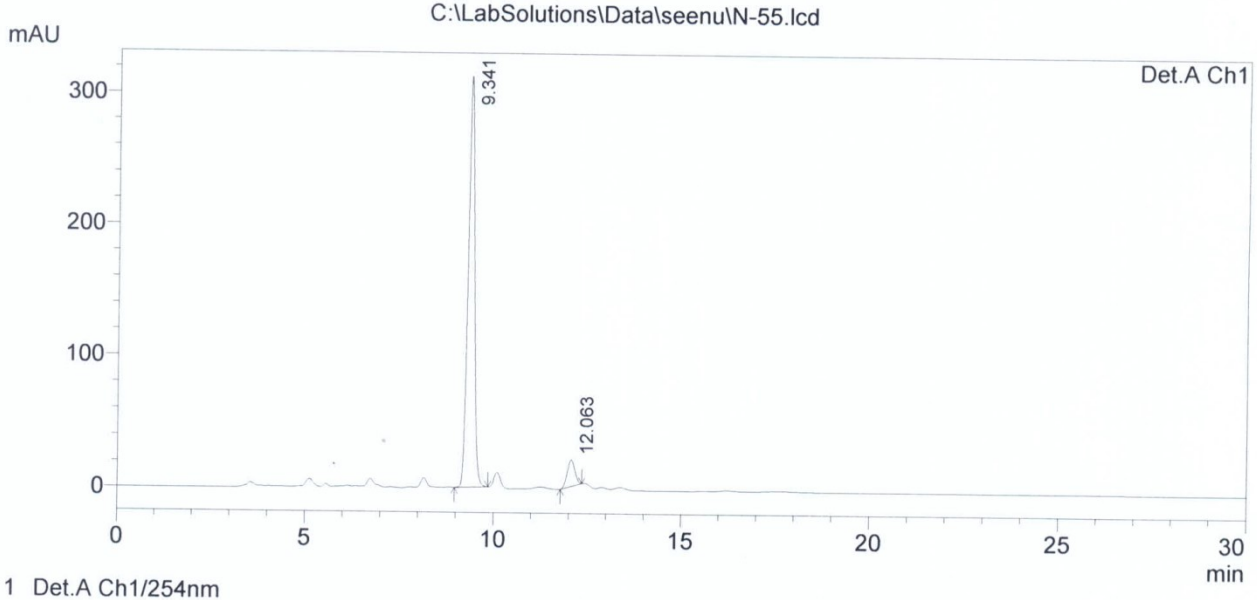
C:\LabSolutions\Data\seenu\N-55.lcd

Acquired by	: Admin
Sample Name	: N-55
Sample ID	: N-55, IC,rs, 40oC,0.1 eq toluen
Tray#	: 1
Vail #	: 102
Injection Volume	: 1 uL
Data File Name	: N-55.lcd
Method File Name	: IPA2%-30min254nm-5.lcm
Batch File Name	: 03-03-2012.lcb
Report File Name	: Default.lcr
Data Acquired	: 3/23/2012 12:01:30 PM
Data Processed	: 3/23/2012 2:52:21 PM



4

<Chromatogram>

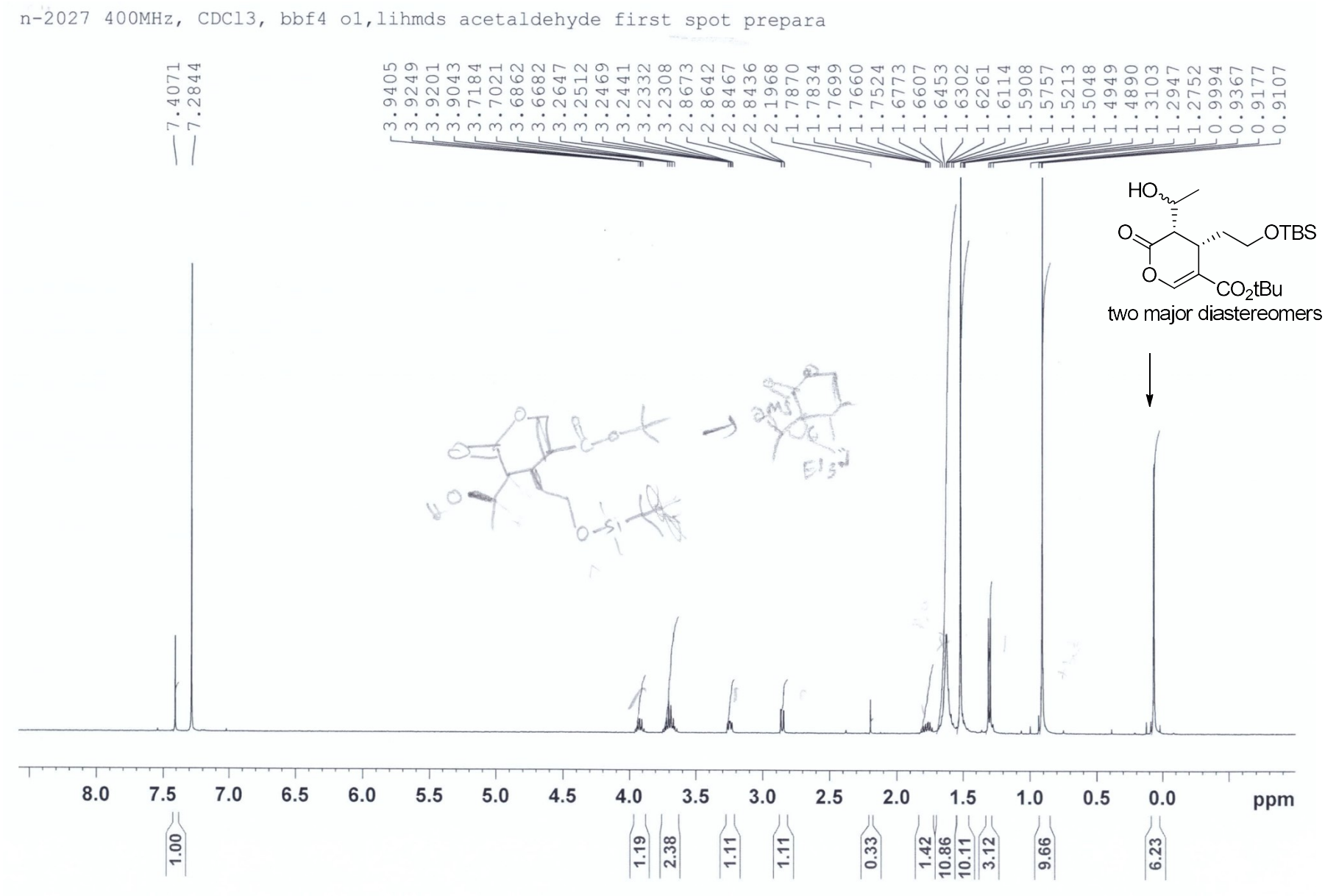


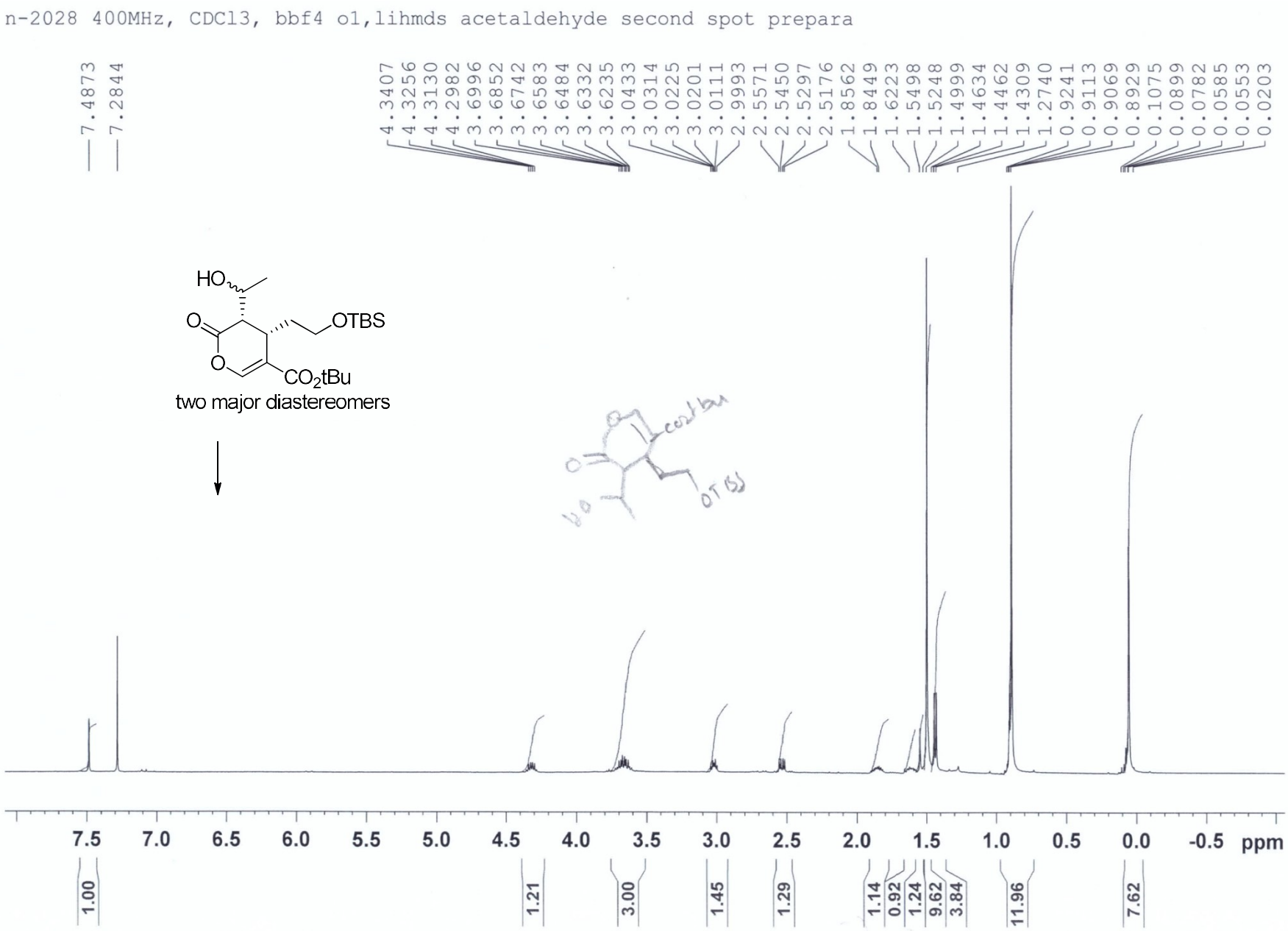
1 Det.A Ch1/254nm

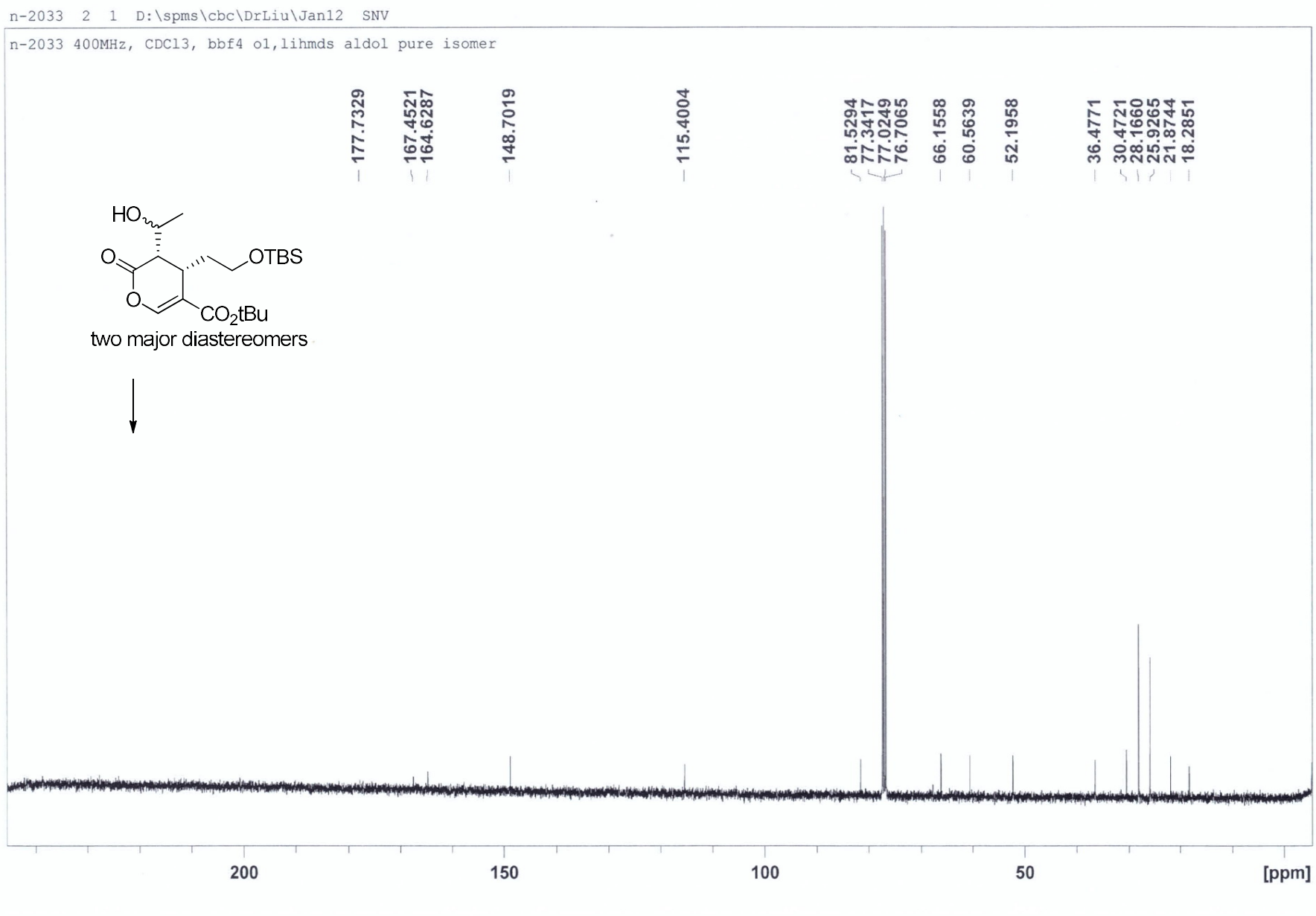
PeakTable

Detector A Ch1 254nm

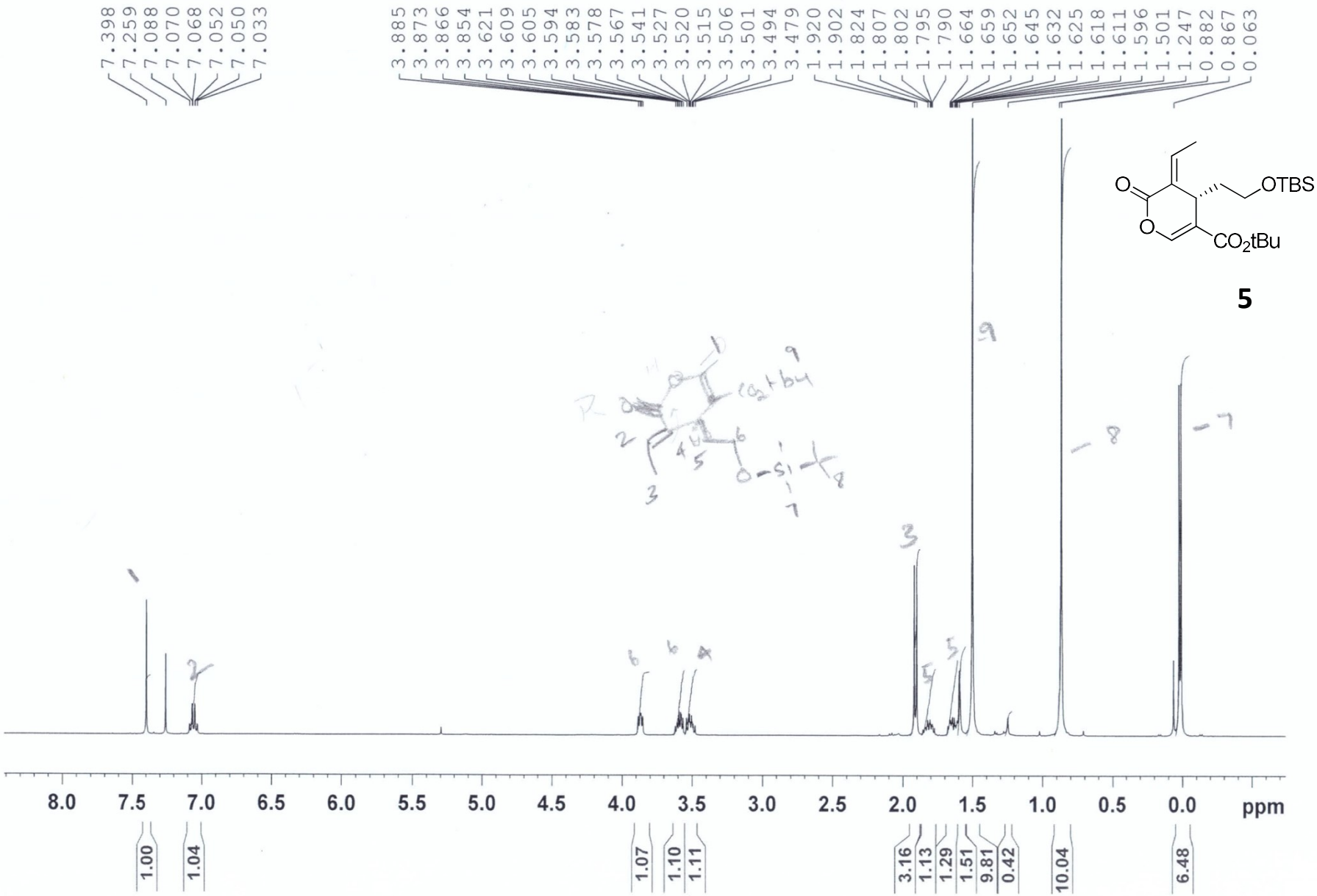
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.341	3782003	312605	92.886	93.878
2	12.063	289670	20386	7.114	6.122
Total		4071673	332991	100.000	100.000


n-2027 400MHz, CDCl3, bbf4 o1,lihmds acetaldehyde first spot prepara
7.4071
7.2844
3.9405
3.9249
3.9201
3.9043
3.7184
3.7021
3.6862
3.6682
3.2647
3.2512
3.2469
3.2441
3.2332
3.2308
2.8673
2.8642
2.8467
2.8436
2.1968
1.7870
1.7834
1.7699
1.7660
1.7524
1.6773
1.6607
1.6453
1.6302
1.6261
1.6114
1.5908
1.5757
1.5213
1.5048
1.4949
1.4890
1.3103
1.2947
1.2752
0.9994
0.9367
0.9177
0.9107
HO
O
O
OTBS
CO2tBu
two major diastereomers
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.19
2.38
1.11
1.11
0.33
1.42
10.86
10.11
3.12
9.66
6.23

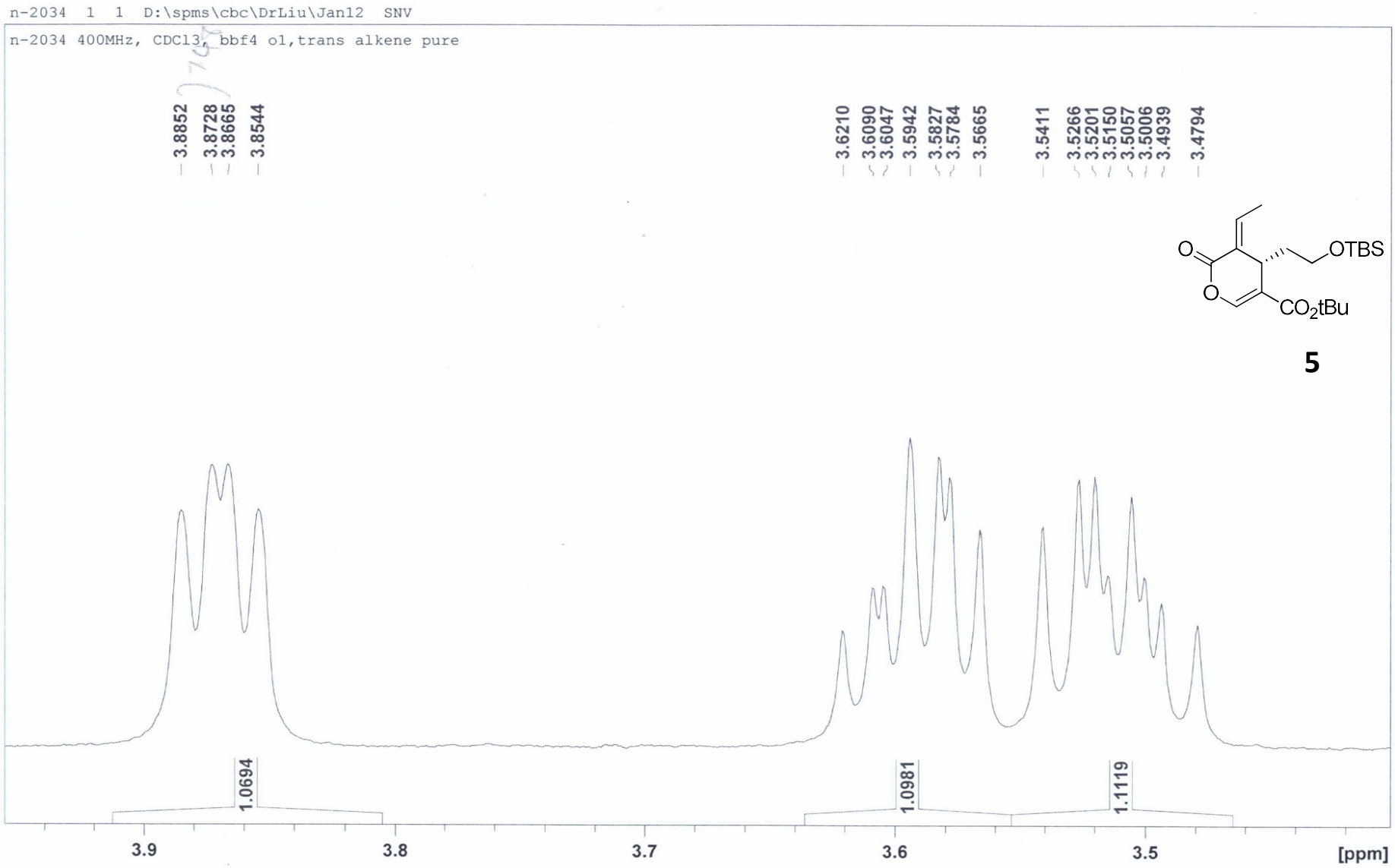

n-2028 400MHz, CDCl3, bbf4 o1,lihmds acetaldehyde second spot prepara
7.4873
7.2844
4.3407
4.3256
4.3130
4.2982
3.6996
3.6852
3.6742
3.6583
3.6484
3.6332
3.6235
3.0433
3.0314
3.0225
3.0201
3.0111
2.9993
2.5571
2.5450
2.5297
2.5176
1.8562
1.8449
1.6223
1.5498
1.5248
1.4999
1.4634
1.4462
1.4309
1.2740
0.9241
0.9113
0.9069
0.8929
0.1075
0.0899
0.0782
0.0585
0.0553
0.0203
HO
O
OTBS
O
CO2tBu
two major diastereomers
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.00
1.21
3.00
1.45
1.29
1.14
0.92
1.24
9.62
3.84
11.96
7.62


n-2033 2 1 D:\spms\cbc\DrLiu\Jan12 SNV
n-2033 400MHz, CDCl3, bbf4 o1,lihmds aldol pure isomer
177.7329
167.4521
164.6287
148.7019
115.4004
81.5294
77.3417
77.0249
76.7065
66.1558
60.5639
52.1958
36.4771
30.4721
28.1660
25.9265
21.8744
18.2851
HO
O
OTBS
O
CO2tBu
two major diastereomers
200
150
100
50
[ppm]

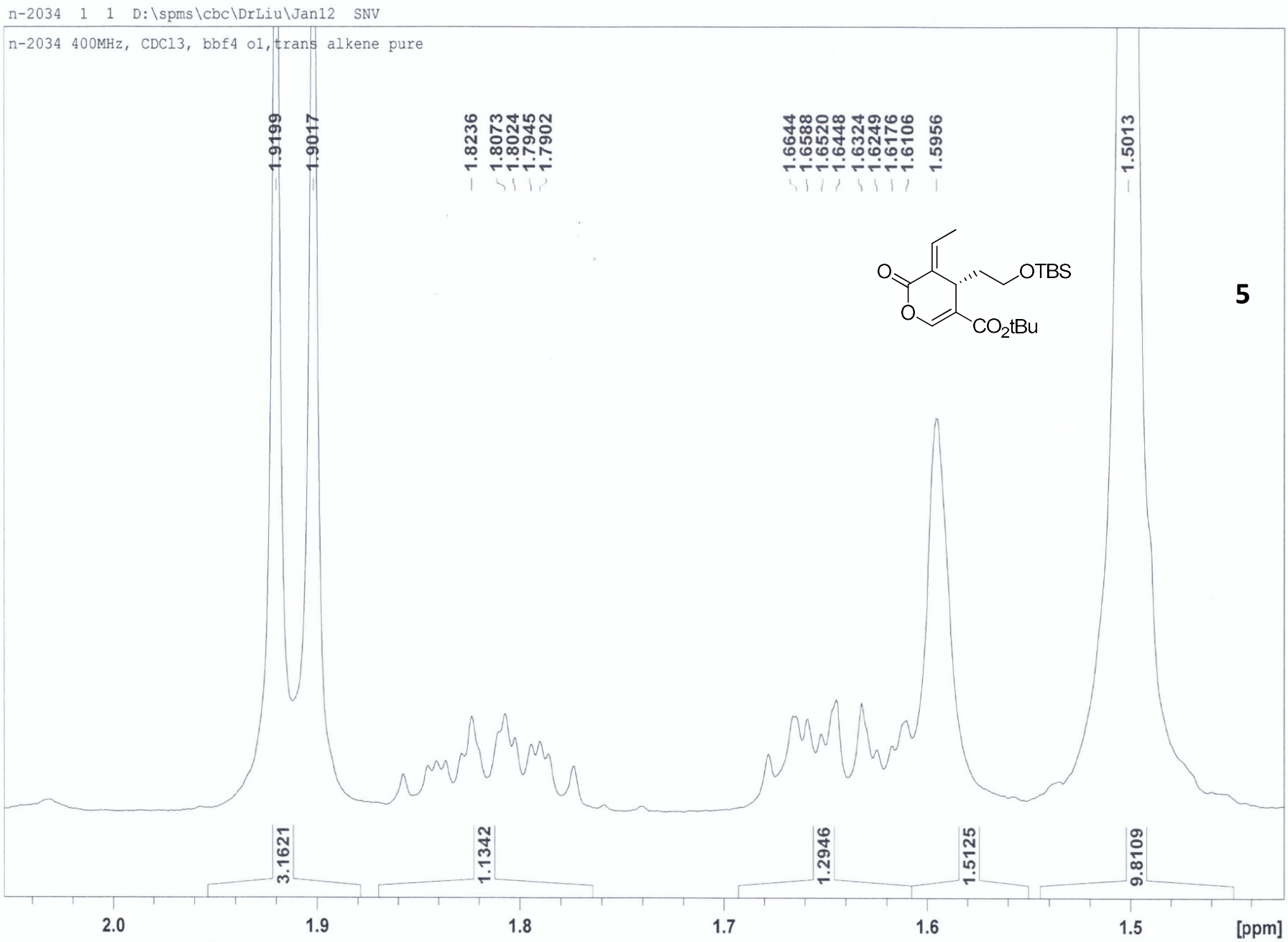
n-2034 400MHz, CDCl3, bbf4 o1,trans alkene pure

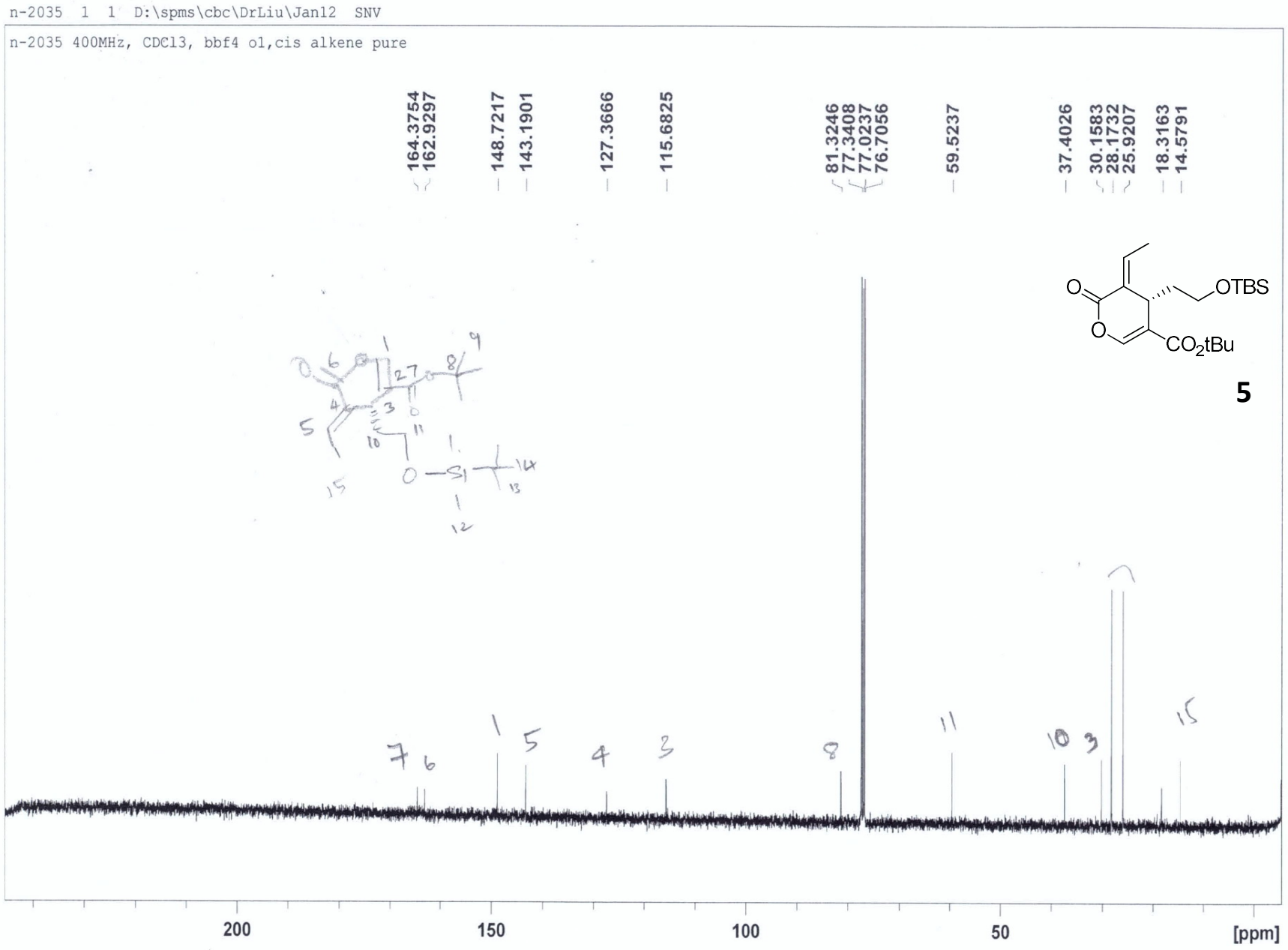


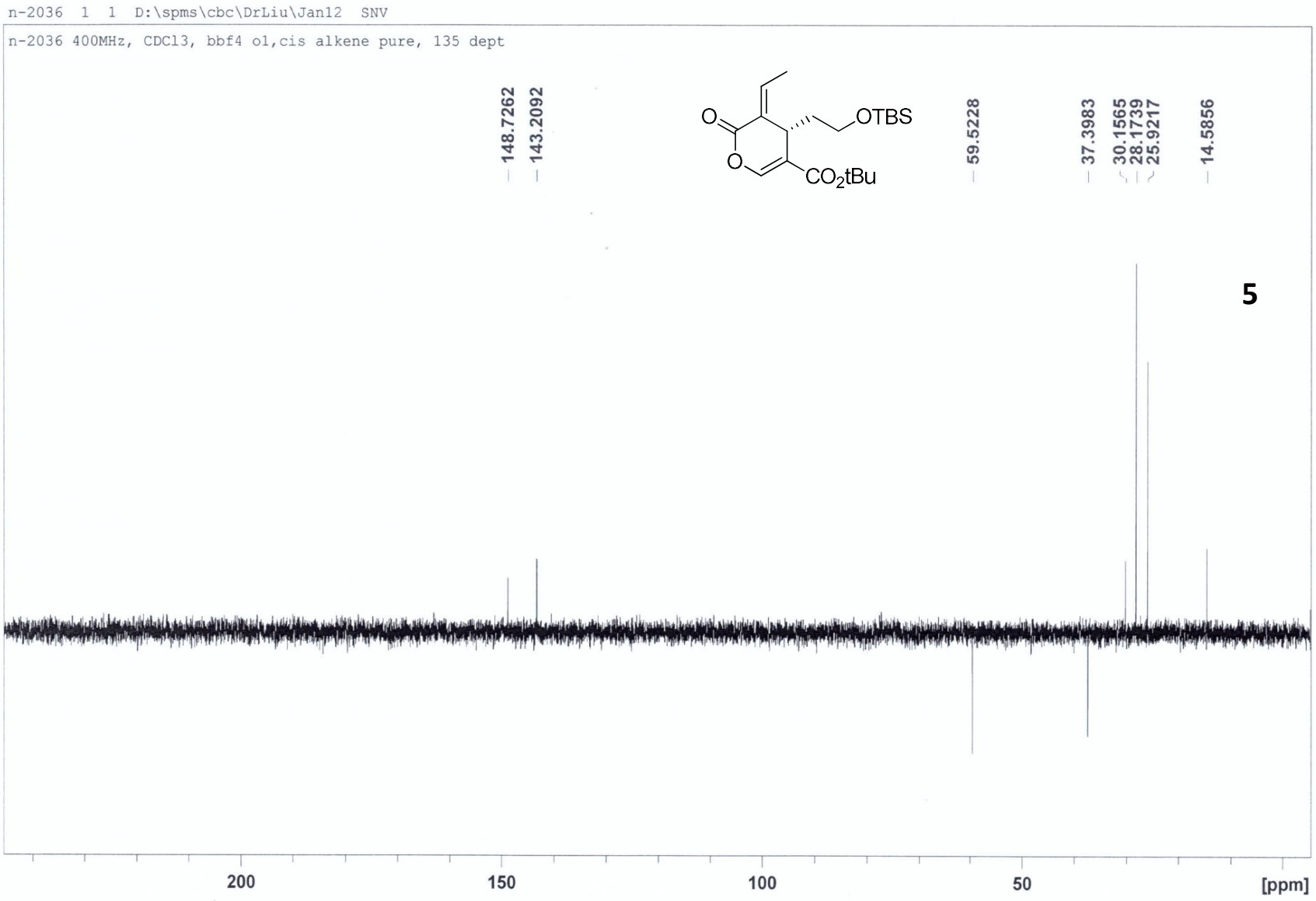
5


n-2034 1 1 D:\spms\cbc\DrLiu\Jan12 SNV
n-2034 400MHz, CDCl3, bbf4 o1,trans alkene pure
3.8852
3.8728
3.8665
3.8544
3.6210
3.6090
3.6047
3.5942
3.5827
3.5784
3.5665
3.5411
3.5266
3.5201
3.5150
3.5057
3.5006
3.4939
3.4794
O
O
OTBS
CO2tBu
1.0694
1.0981
1.1119
3.9
3.8
3.7
3.6
3.5
[ppm]

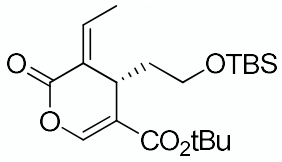
5


n-2034 1 1 D:\spms\cbc\DrLiu\Jan12 SNV
n-2034 400MHz, CDCl3, bbf4 o1,trans alkene pure
1.9199
1.9017
1.8236
1.8073
1.8024
1.7945
1.7902
1.6644
1.6588
1.6520
1.6448
1.6324
1.6249
1.6176
1.6106
1.5956
1.5013
O
O
OTBS
CO2tBu
5
3.1621
1.1342
1.2946
1.5125
9.8109
2.0
1.9
1.8
1.7
1.6
1.5
[ppm]


n-2035 1 1 D:\spms\cbc\DrLiu\Jan12 SNV
n-2035 400MHz, CDCl3, bbf4 o1,cis alkene pure
164.3754
162.9297
148.7217
143.1901
127.3666
115.6825
81.3246
77.3408
77.0237
76.7056
59.5237
37.4026
30.1583
28.1732
25.9207
18.3163
14.5791
OTBS
CO2tBu
5
200
150
100
50
[ppm]


n-2036 1 1 D:\spms\cbc\DrLiu\Jan12 SNV
n-2036 400MHz, CDCl3, bbf4 o1,cis alkene pure, 135 dept
148.7262
143.2092
59.5228
37.3983
30.1565
28.1739
25.9217
14.5856
OTBS
O
O
CO2tBu
5
200
150
100
50
[ppm]

Elemental Composition Report



5

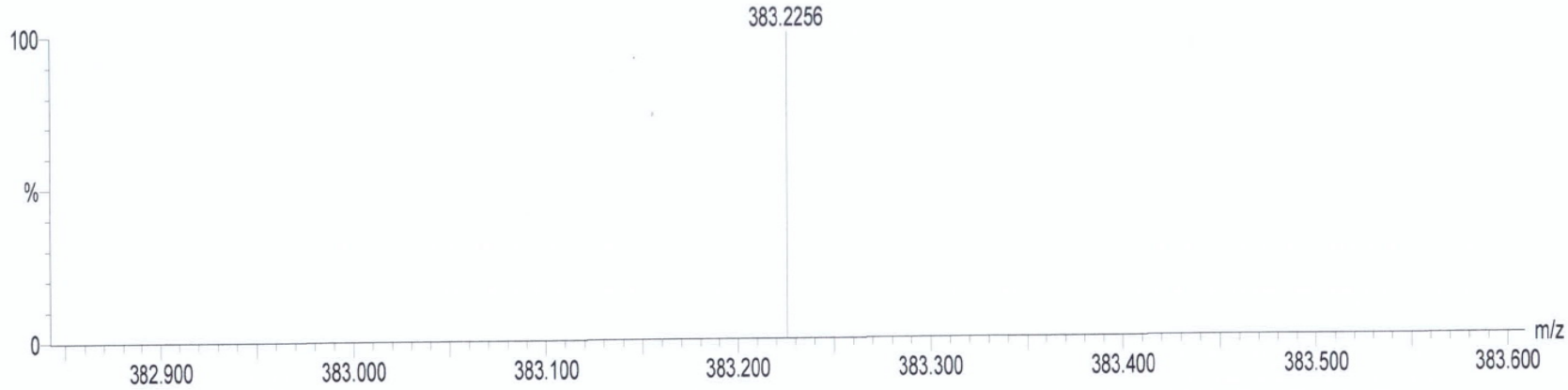
Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

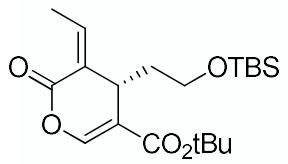
Monoisotopic Mass, Even Electron Ions
167 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-39 O: 0-3 Si: 0-2 S: 0-5

C20H34O5Si
SNV-2-17 4 (0.101)

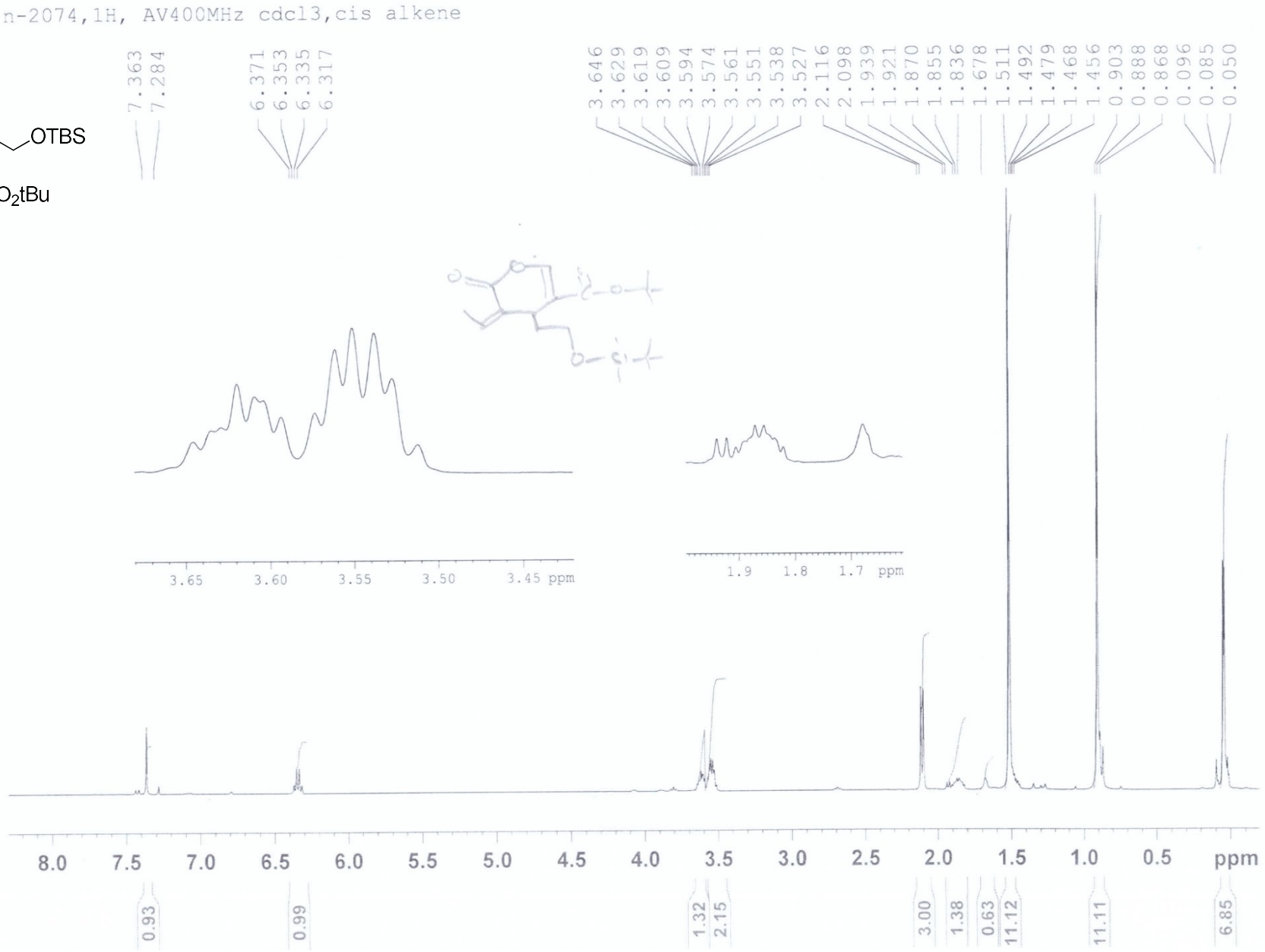
1: TOF MS ES+
2.26e+002

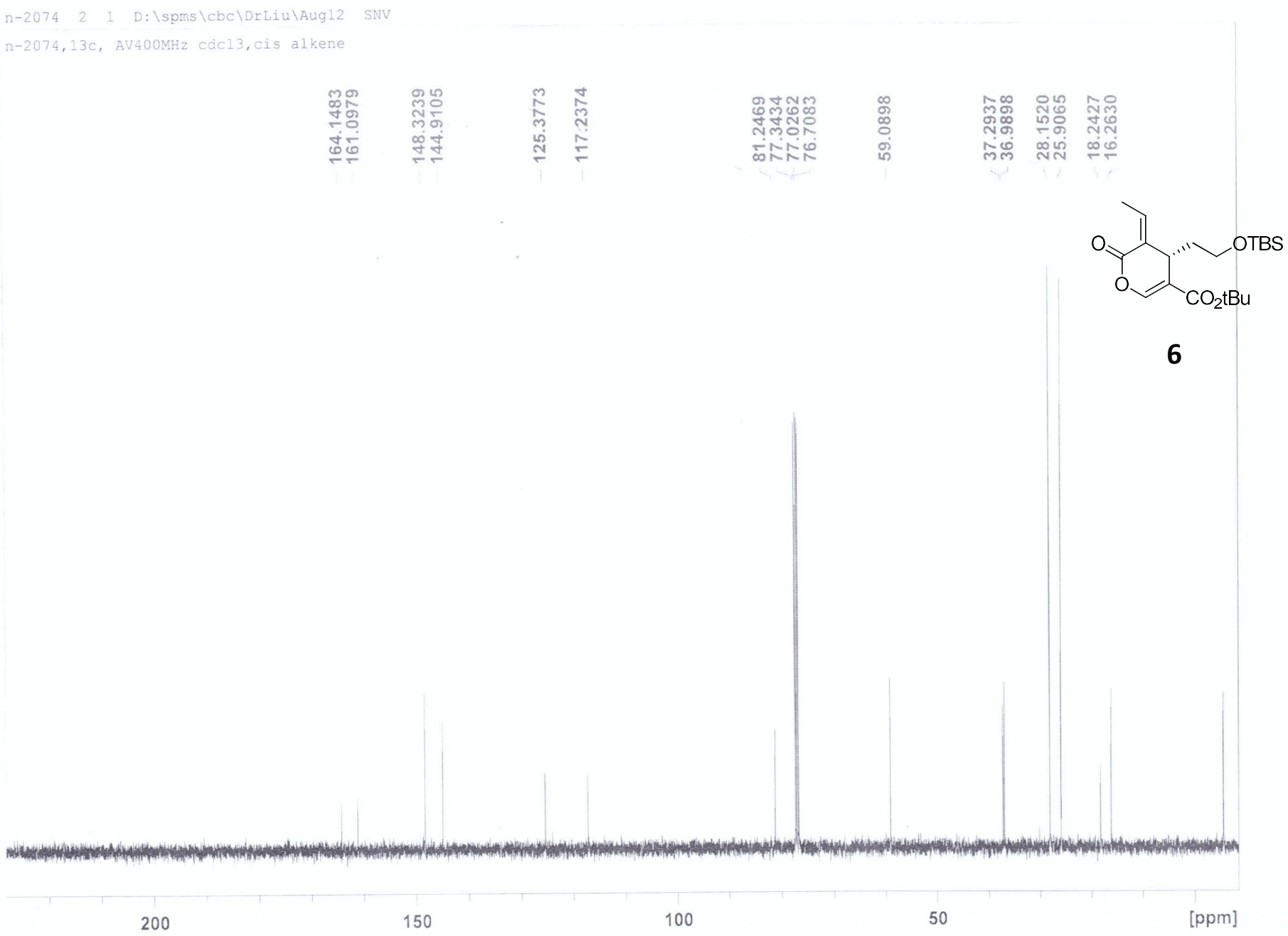


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
383.2256	383.2260	-0.4	-1.0	3.5	20.9	0.0	C20 H39 O Si2 S


O
O
OTBS
CO2tBu

6


n-2074,1H, AV400MHz cdcl3,cis alkene
7.363
7.284
6.371
6.353
6.335
6.317
3.646
3.629
3.619
3.609
3.594
3.574
3.561
3.551
3.538
3.527
2.116
2.098
1.939
1.921
1.870
1.855
1.836
1.678
1.511
1.492
1.479
1.468
1.456
0.903
0.888
0.868
0.096
0.085
0.050
3.65
3.60
3.55
3.50
3.45 ppm
1.9
1.8
1.7 ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.93
0.99
1.32
2.15
3.00
1.38
0.63
11.12
11.11
6.85

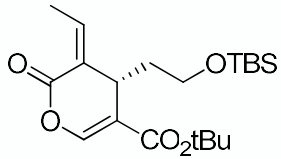

n-2074 2 1 D:\spms\cbc\DrLiu\Aug12 SNV
n-2074,13c, AV400MHz cdcl3,cis alkene
164.1483
161.0979
148.3239
144.9105
125.3773
117.2374
81.2469
77.3434
77.0262
76.7083
59.0898
37.2937
36.9898
28.1520
25.9065
18.2427
16.2630
O
O
OTBS
CO2tBu
200
150
100
50
[ppm]

6

Elemental Composition Report

Single Mass Analysis

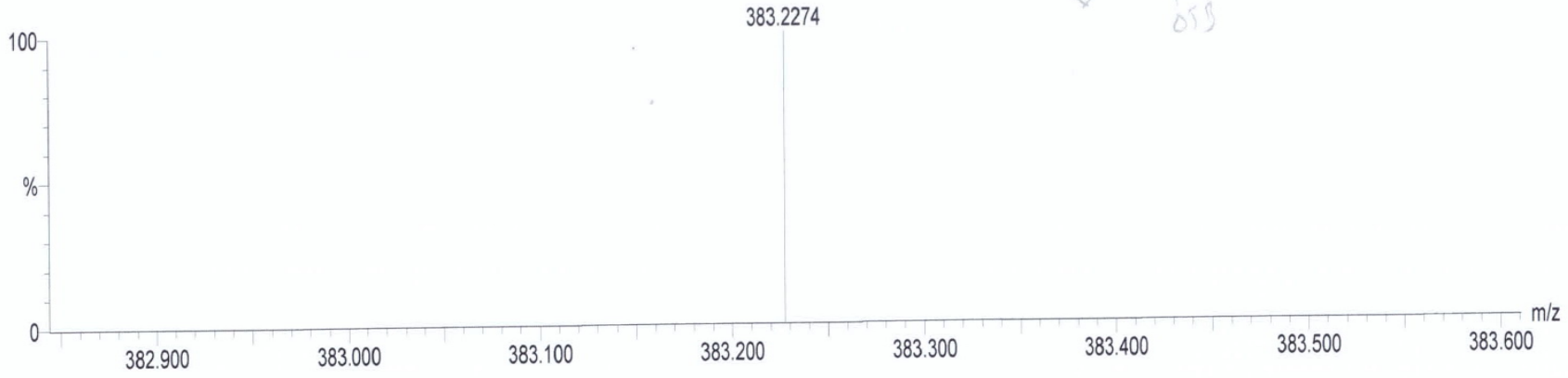
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



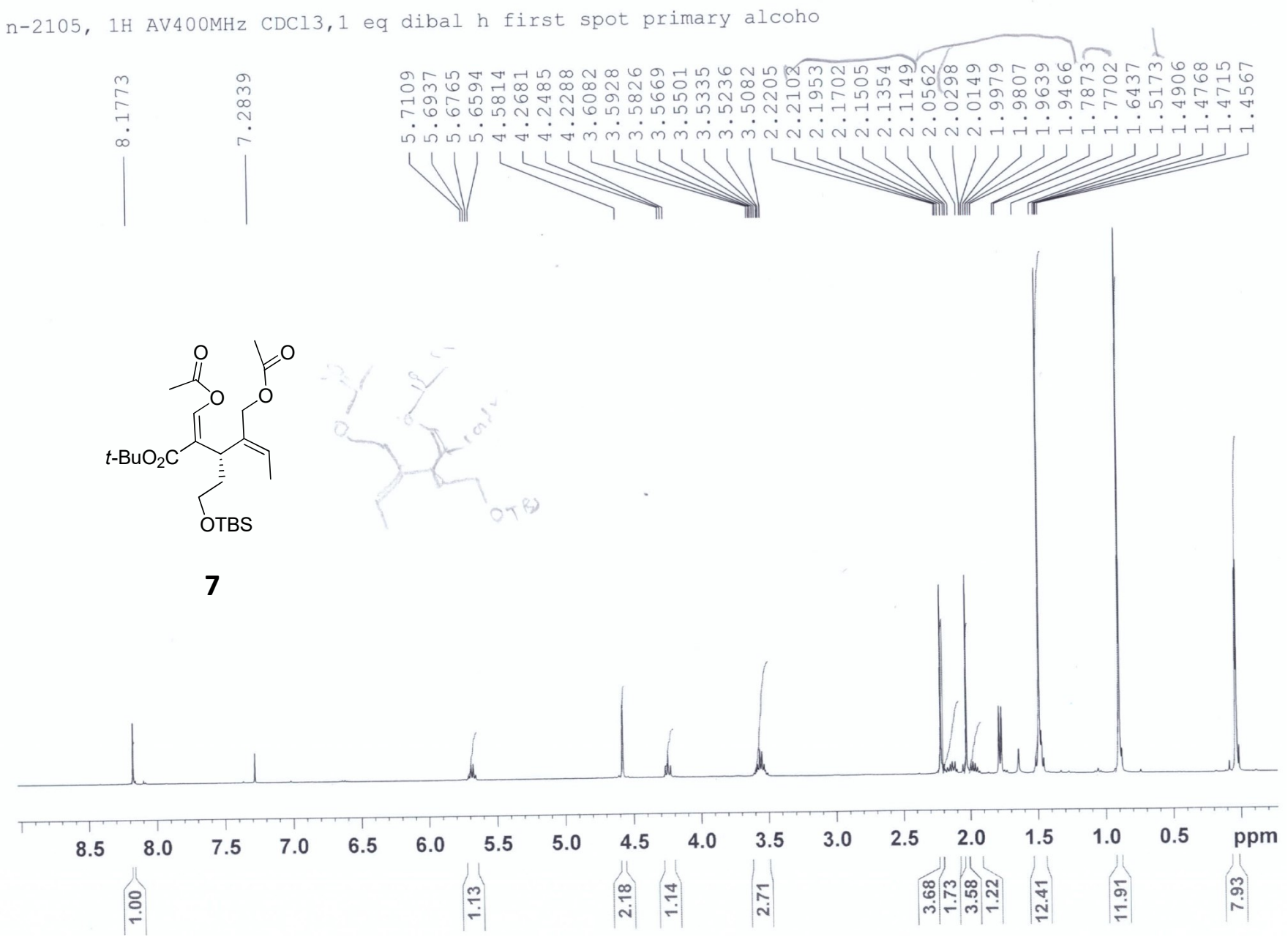
6

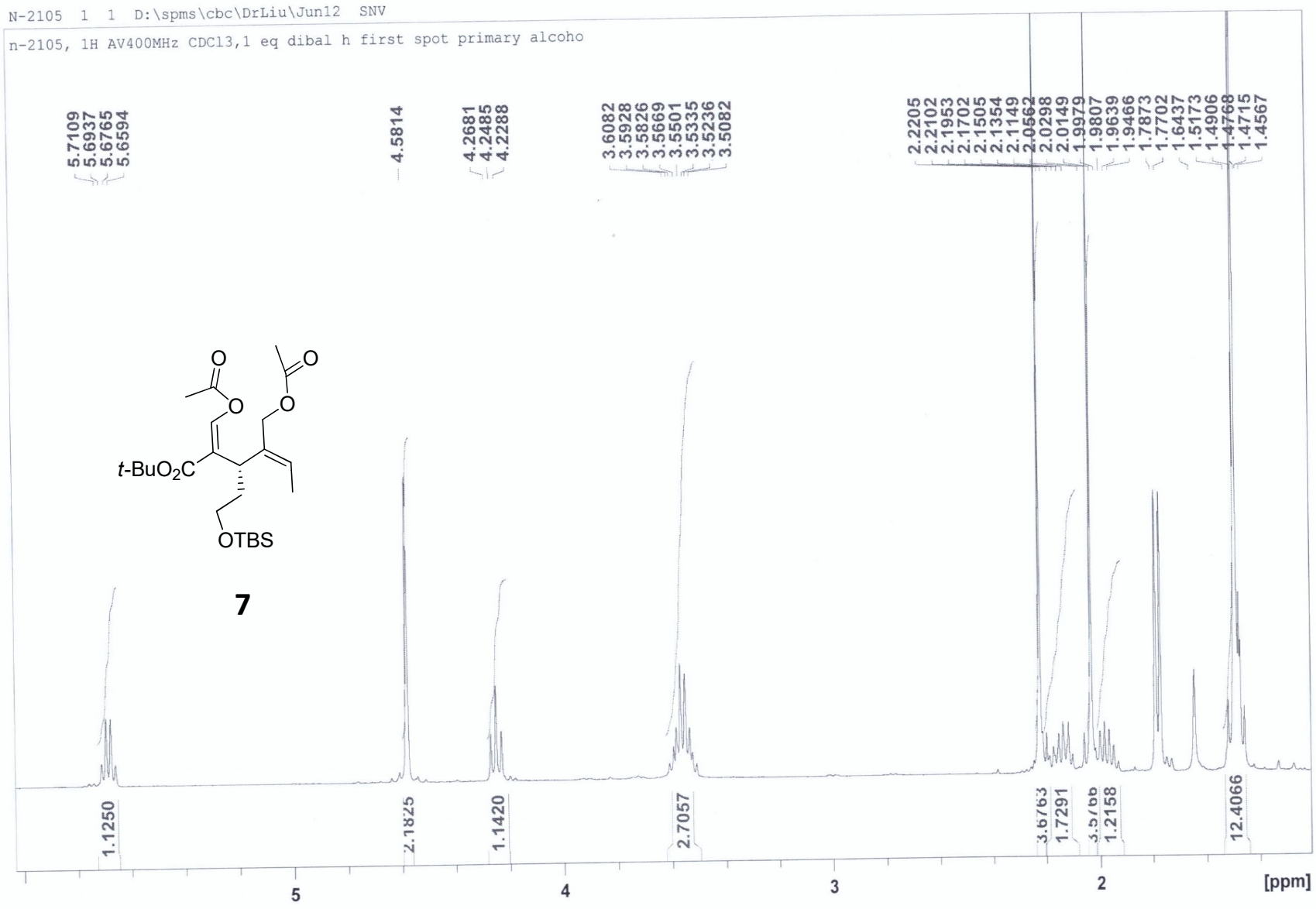
Monoisotopic Mass, Even Electron Ions
167 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-20 H: 0-39 O: 0-3 Si: 0-2 S: 0-5
C20H34O5Si
SNV-2-18 3 (0.082) Cm (3:12)

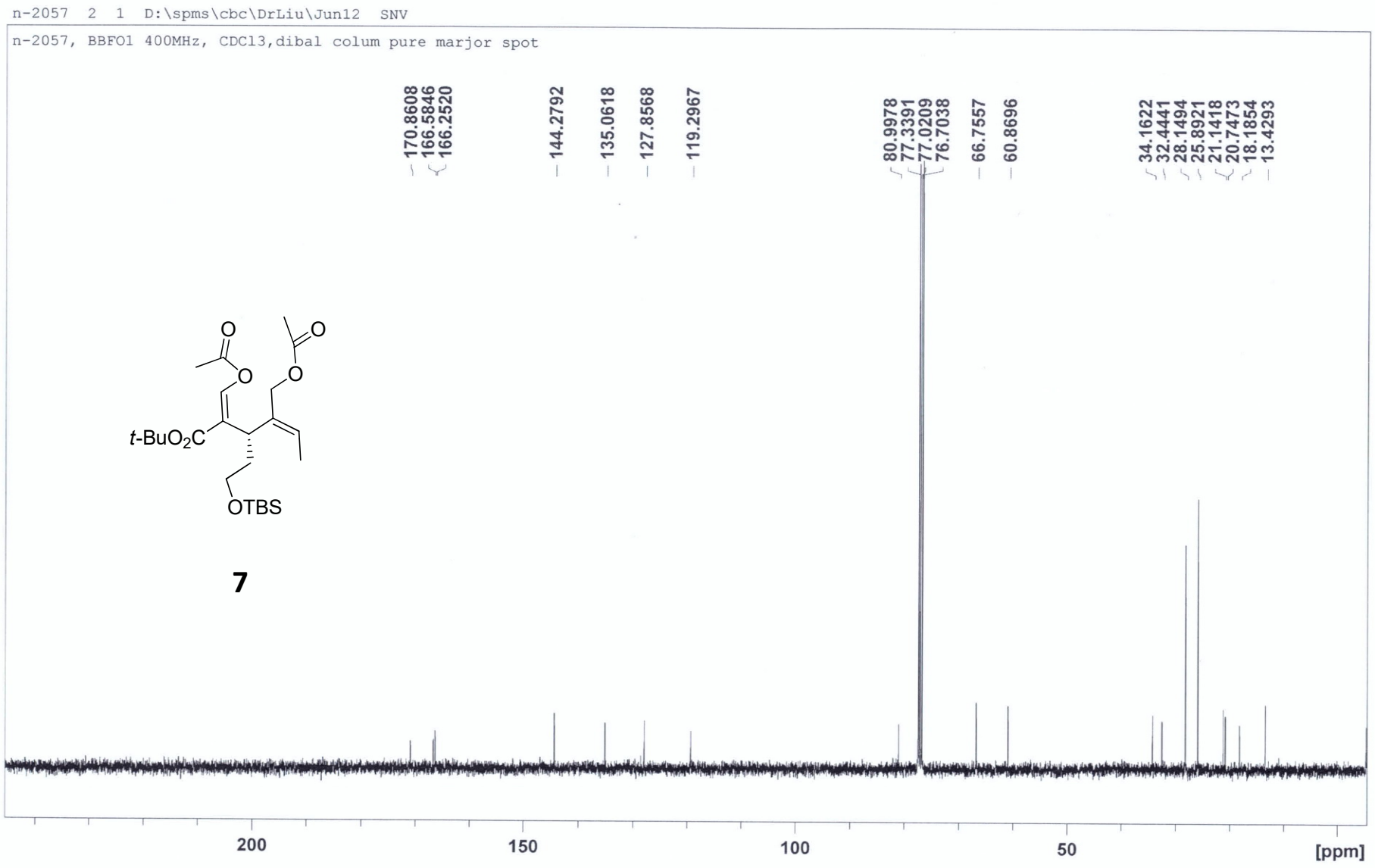
1: TOF MS ES+
6.08e+001



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
383.2274	383.2260	1.4	3.7	3.5	18.0	0.0	C20 H39 O Si2 S


n-2105, 1H AV400MHz CDCl3,1 eq dibal h first spot primary alcoho
8.1773
7.2839
5.7109
5.6937
5.6765
5.6594
4.5814
4.2681
4.2485
4.2288
3.6082
3.5928
3.5826
3.5669
3.5501
3.5335
3.5236
3.5082
2.2205
2.2102
2.1953
2.1702
2.1505
2.1354
2.1149
2.0562
2.0298
2.0149
1.9979
1.9807
1.9639
1.9466
1.7873
1.7702
1.6437
1.5173
1.4906
1.4768
1.4715
1.4567
t-BuO2C
OTBS
7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.13
2.18
1.14
2.71
3.68
1.73
3.58
1.22
12.41
11.91
7.93


N-2105 1 1 D:\spms\cbc\DrLiu\Jun12 SNV
n-2105, 1H AV400MHz CDCl3,1 eq dibal h first spot primary alcoho
5.7109
5.6937
5.6765
5.6594
4.5814
4.2681
4.2485
4.2288
3.6082
3.5928
3.5826
3.5669
3.5501
3.5335
3.5236
3.5082
2.2205
2.2102
2.1953
2.1702
2.1505
2.1354
2.1149
2.0562
2.0298
2.0149
1.9979
1.9807
1.9639
1.9466
1.7873
1.7702
1.6437
1.5173
1.4906
1.4768
1.4715
1.4567
t-BuO2C
OTBS
7
1.1250
2.1825
1.1420
2.7057
3.6763
1.7291
3.5788
1.2158
12.4066
5
4
3
2
[ppm]


n-2057 2 1 D:\spms\cbc\DrLiu\Jun12 SNV
n-2057, BBFO1 400MHz, CDCl3,dibal colum pure marjor spot
170.8608
166.5846
166.2520
144.2792
135.0618
127.8568
119.2967
80.9978
77.3391
77.0209
76.7038
66.7557
60.8696
34.1622
32.4441
28.1494
25.8921
21.1418
20.7473
18.1854
13.4293
t-BuO2C
OTBS
200
150
100
50
[ppm]

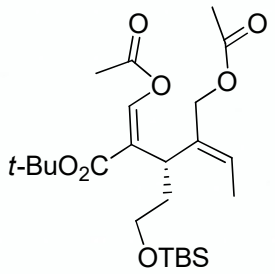
7

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

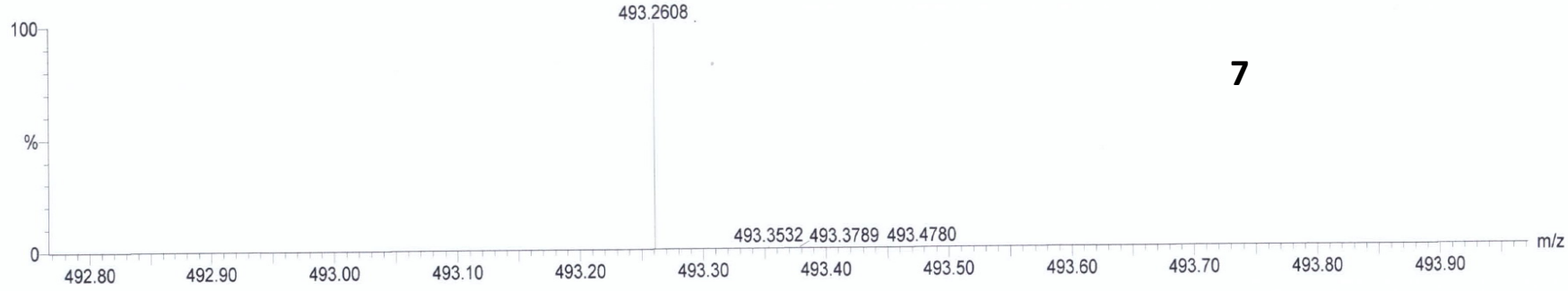
Monoisotopic Mass, Even Electron Ions
330 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-25 H: 0-43 O: 0-7 Si: 0-2 81Br: 0-2 Na: 0-1



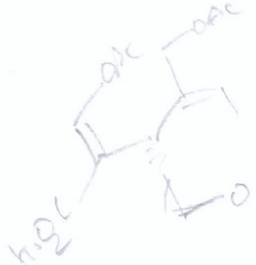
7

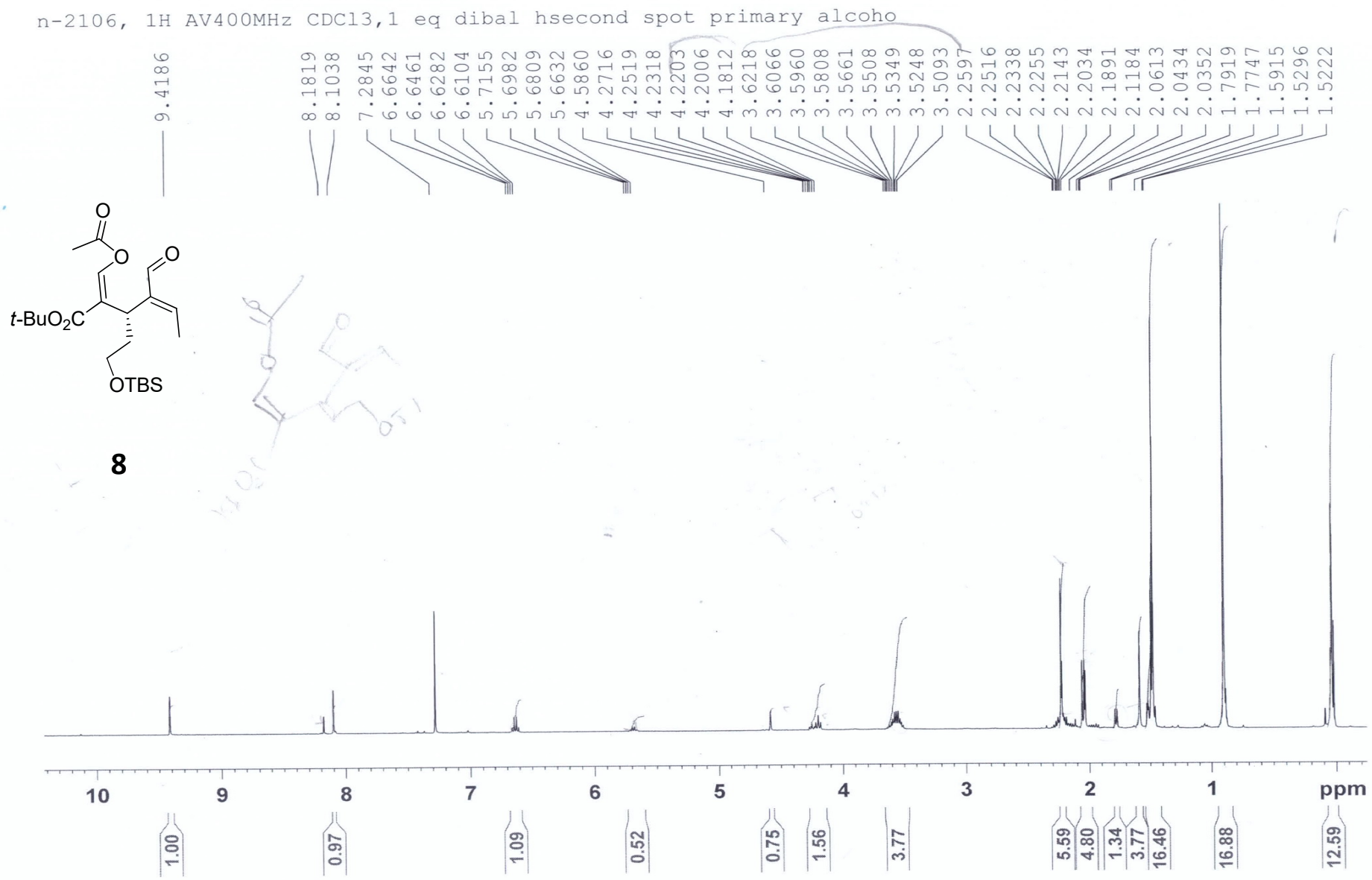
C24H42O7Si
SNV-5-1 3 (0.082) Cm (3:8)

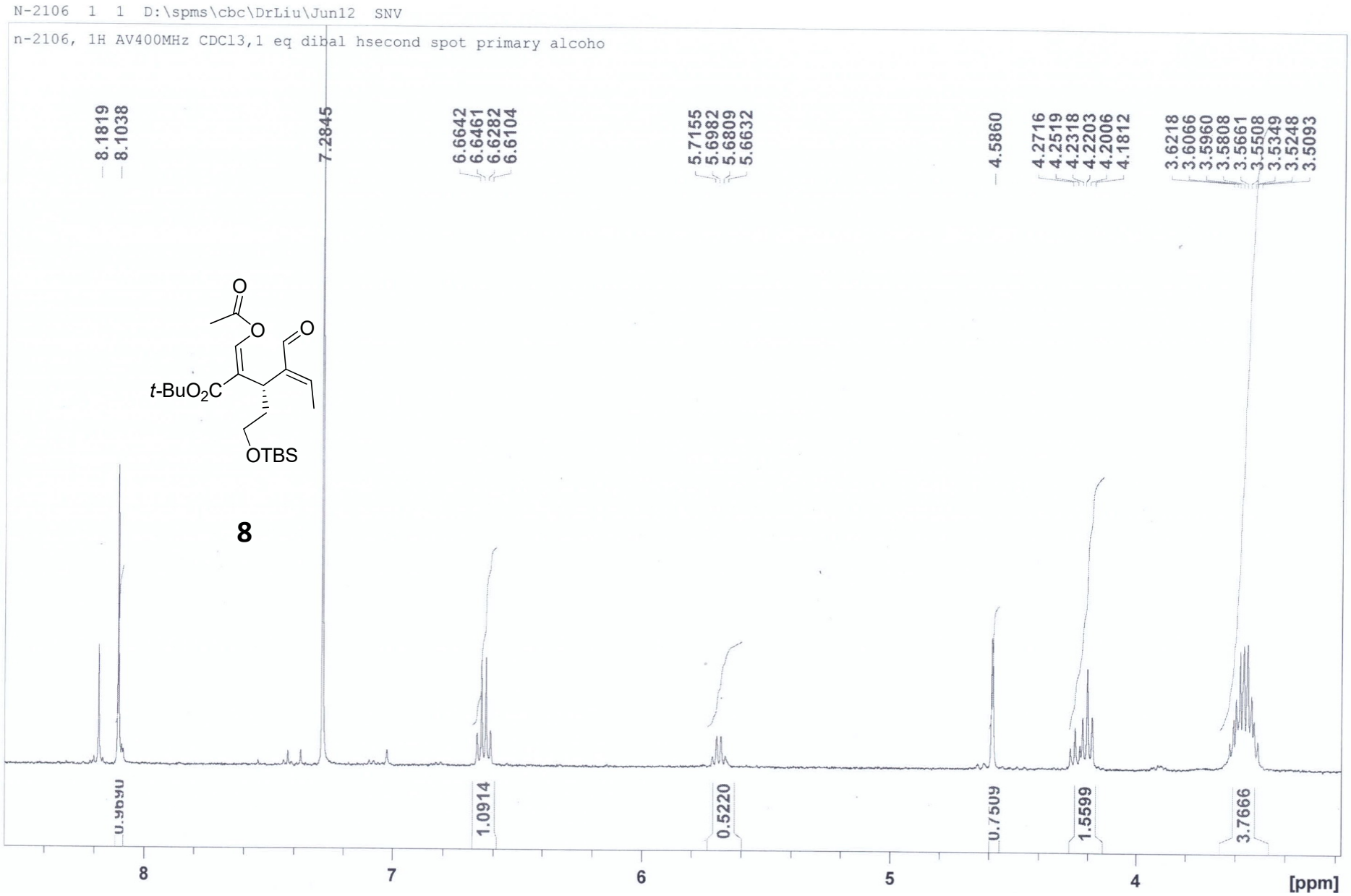
1: TOF MS ES+
5.38e+002

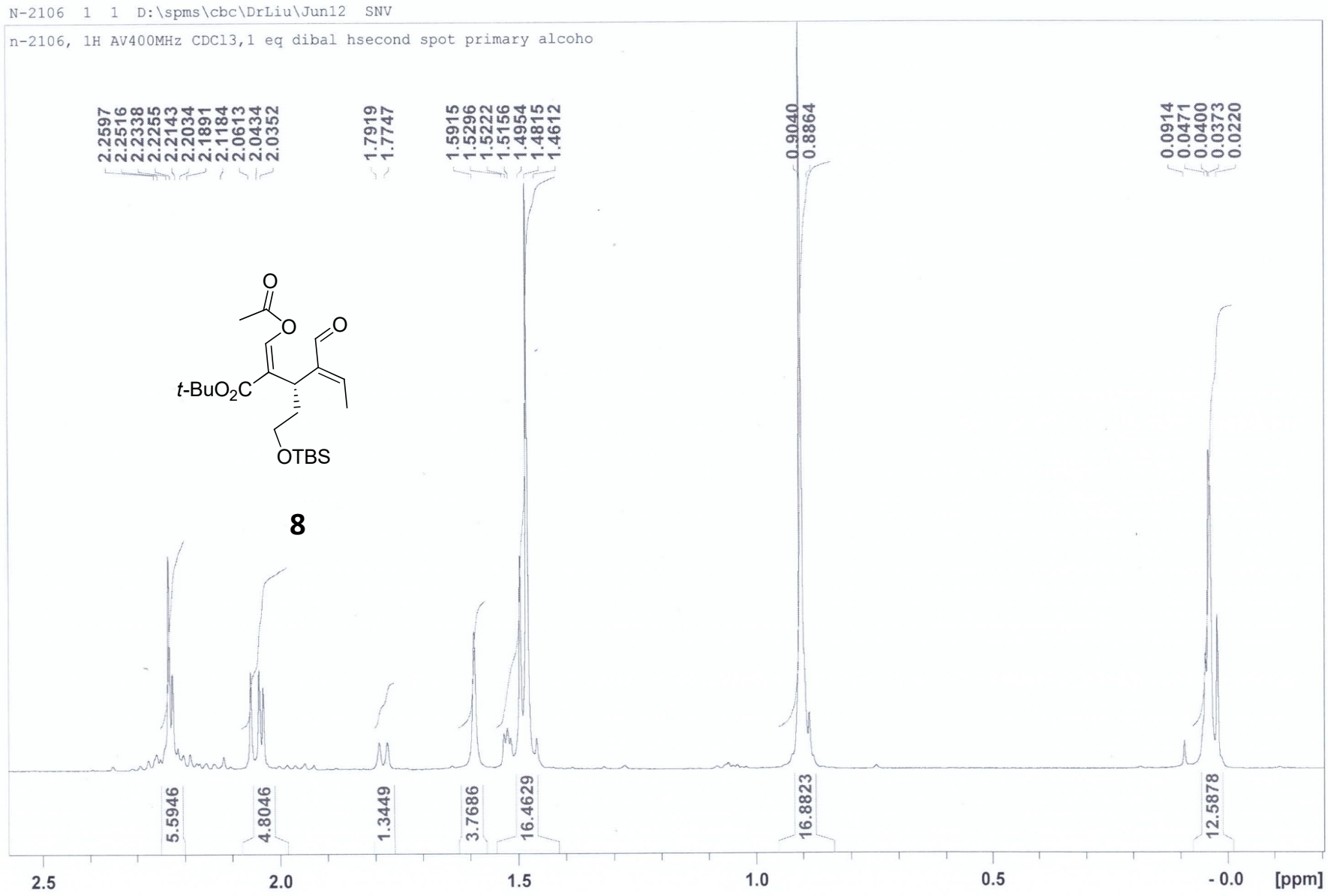


Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
493.2608	493.2598	1.0	2.0	4.5	29.0	0.0	C24 H42 O7 Si Na




n-2106, 1H AV400MHz CDCl3,1 eq dibal hsecond spot primary alcoho
9.4186
8.1819
8.1038
7.2845
6.6642
6.6461
6.6282
6.6104
5.7155
5.6982
5.6809
5.6632
4.5860
4.2716
4.2519
4.2318
4.2203
4.2006
4.1812
3.6218
3.6066
3.5960
3.5808
3.5661
3.5508
3.5349
3.5248
3.5093
2.2597
2.2516
2.2338
2.2255
2.2143
2.2034
2.1891
2.1184
2.0613
2.0434
2.0352
1.7919
1.7747
1.5915
1.5296
1.5222
t-BuO2C
OTBS
8
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.97
1.09
0.52
0.75
1.56
3.77
5.59
4.80
1.34
3.77
16.46
16.88
12.59

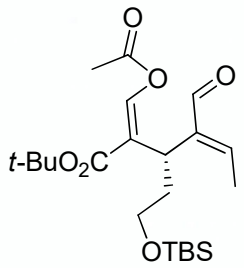

N-2106 1 1 D:\spms\cbc\DrLiu\Jun12 SNV
n-2106, 1H AV400MHz CDCl3,1 eq dibal hsecond spot primary alcoho
8.1819
8.1038
7.2845
6.6642
6.6461
6.6282
6.6104
5.7155
5.6982
5.6809
5.6632
4.5860
4.2716
4.2519
4.2318
4.2203
4.2006
4.1812
3.6218
3.6066
3.5960
3.5808
3.5661
3.5508
3.5349
3.5248
3.5093
t-BuO2C
OTBS
8
1.0914
0.5220
1.5599
3.7666
8
7
6
5
4
[ppm]


N-2106 1 1 D:\spms\cbc\DrLiu\Jun12 SNV
n-2106, 1H AV400MHz CDCl3,1 eq dibal hsecond spot primary alcoho
2.2597
2.2516
2.2338
2.2255
2.2143
2.2034
2.1891
2.1184
2.0613
2.0434
2.0352
1.7919
1.7747
1.5915
1.5296
1.5222
1.5156
1.4954
1.4815
1.4612
0.9040
0.8864
0.0914
0.0471
0.0400
0.0373
0.0220
t-BuO2C
OTBS
8
5.5946
4.8046
1.3449
3.7686
16.4629
16.8823
12.5878
2.5
2.0
1.5
1.0
0.5
- 0.0
[ppm]

Elemental Composition Report

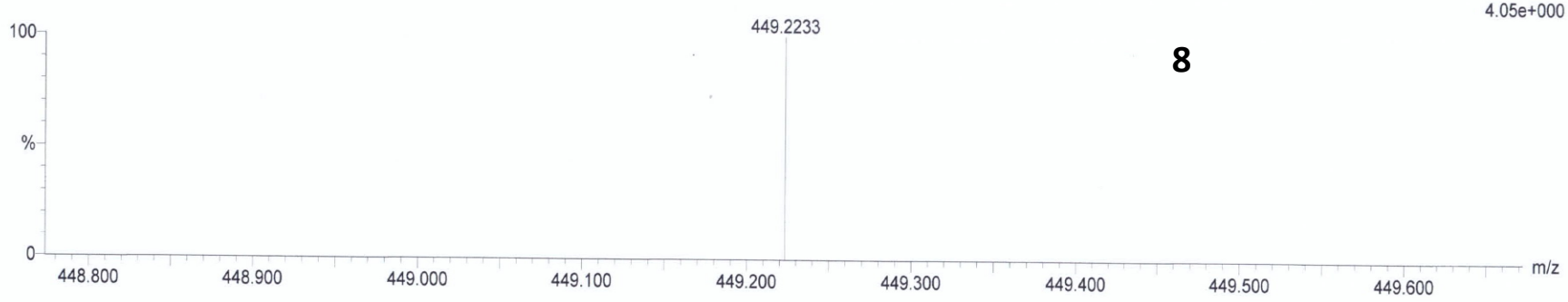
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
176 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-40 H: 0-43 O: 0-7 Na: 0-1 Si: 0-2
C22H38O6Si
SNV-5-2 3 (0.082) Cm (3:9)

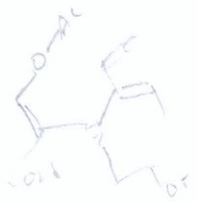


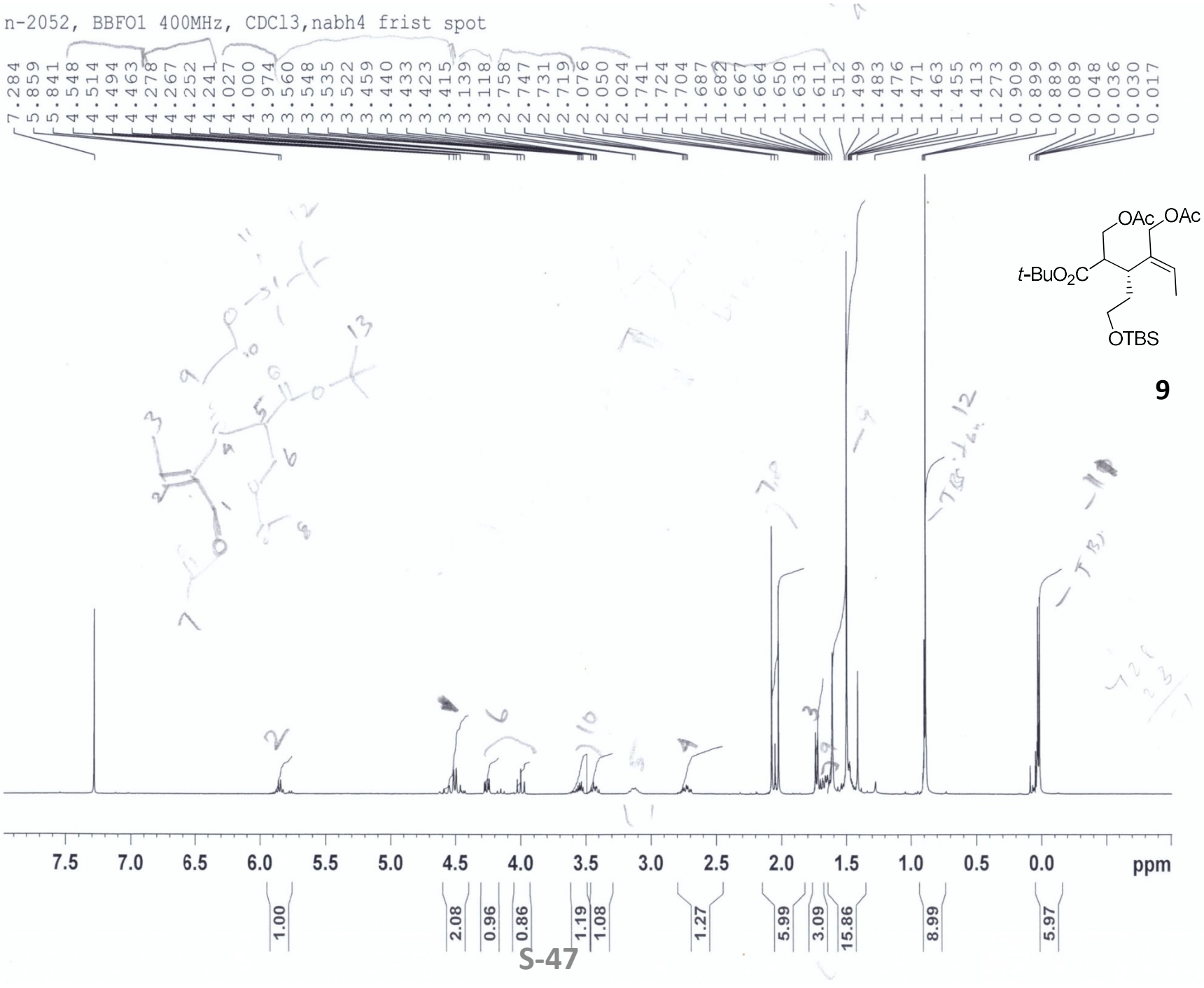
8

1: TOF MS ES+
4.05e+000



Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
449.2233	449.2245	-1.2	-2.7	18.5	12.9	0.0	C33 H30 Na

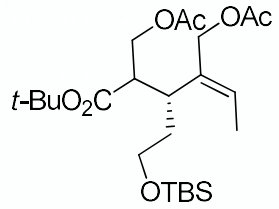



n-2052, BBFO1 400MHz, CDCl3,nabh4 frist spot
7.284
5.859
5.841
4.548
4.514
4.494
4.463
4.278
4.267
4.252
4.241
4.027
4.000
3.974
3.560
3.548
3.535
3.522
3.459
3.440
3.433
3.423
3.415
3.139
3.118
2.758
2.747
2.731
2.719
2.076
2.050
2.024
1.741
1.724
1.704
1.687
1.682
1.667
1.664
1.650
1.631
1.611
1.512
1.499
1.483
1.476
1.471
1.463
1.455
1.413
1.273
0.909
0.899
0.889
0.089
0.048
0.036
0.030
0.017
OAc
OAc
t-BuO2C
OTBS
9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.08
0.96
0.86
1.19
1.08
1.27
5.99
3.09
15.86
8.99
5.97

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

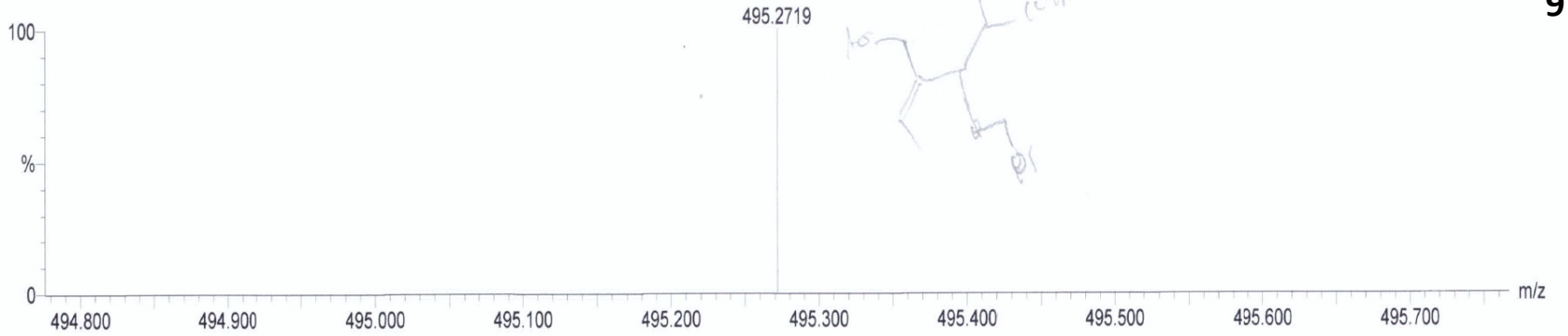


Monoisotopic Mass, Even Electron Ions
90 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-30 H: 0-45 O: 0-7 Na: 0-1 Si: 0-2

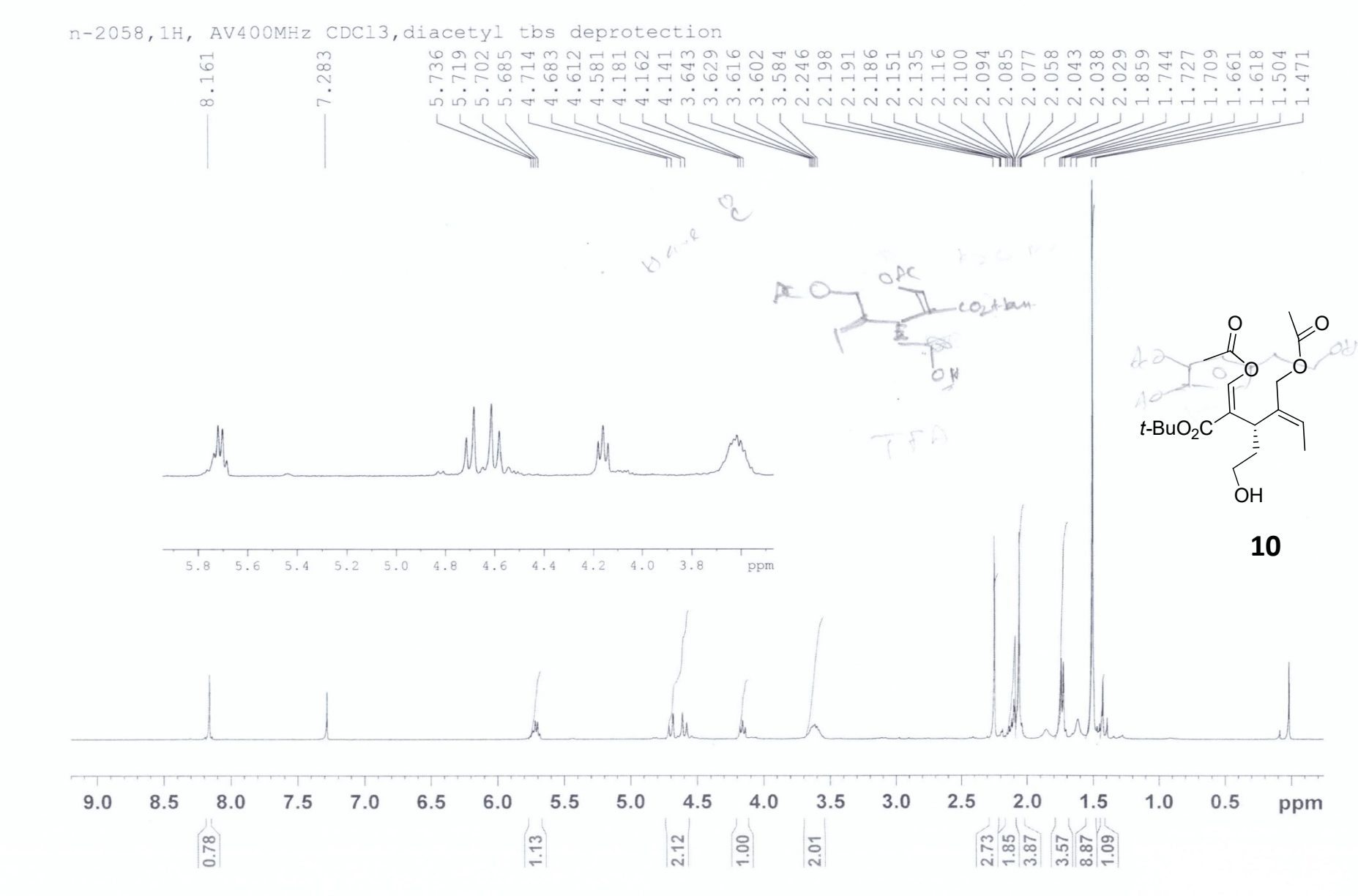
C24H44O7Si
SNV-5-3 4 (0.101)

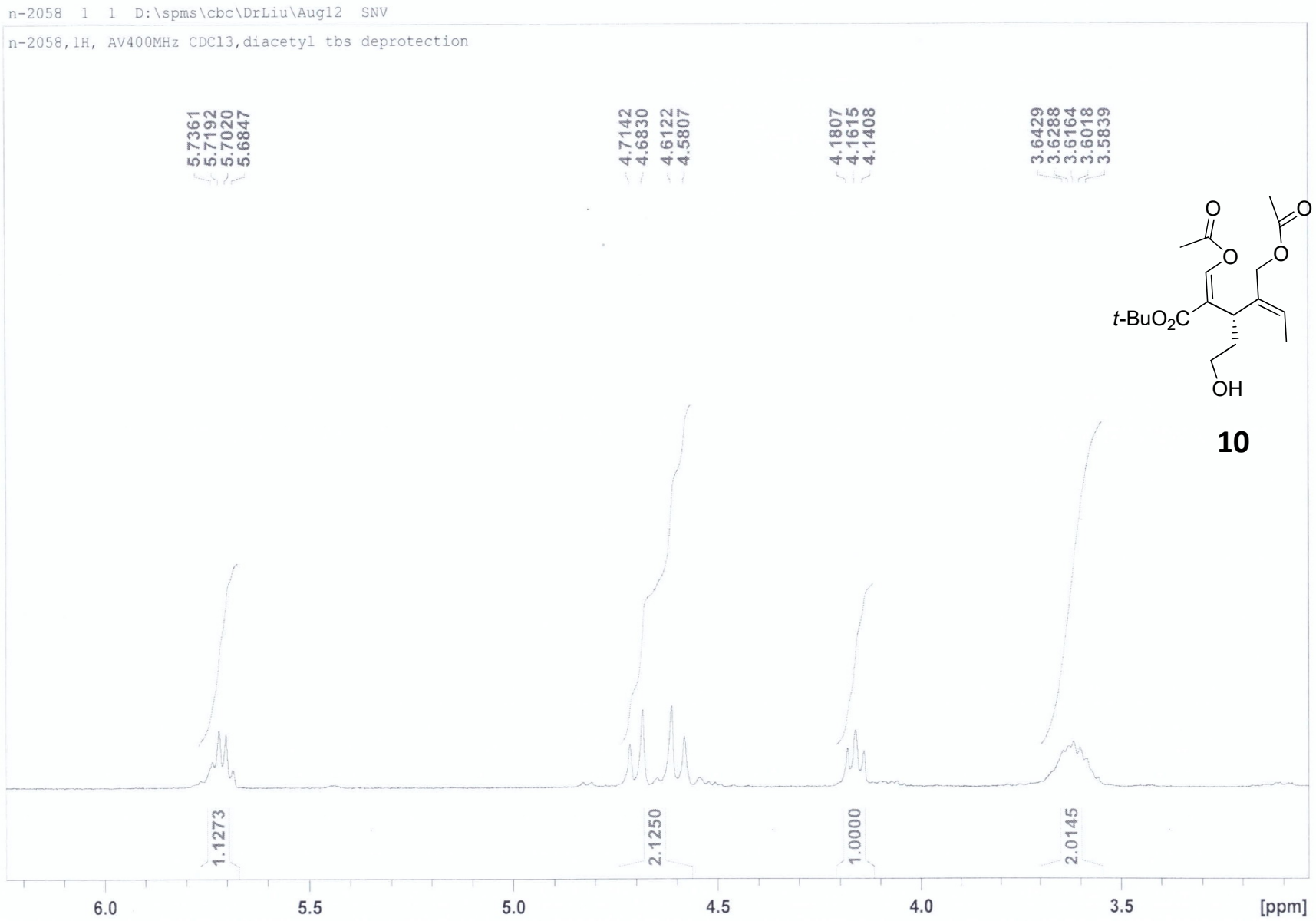
1: TOF MS ES+
8.10e+000

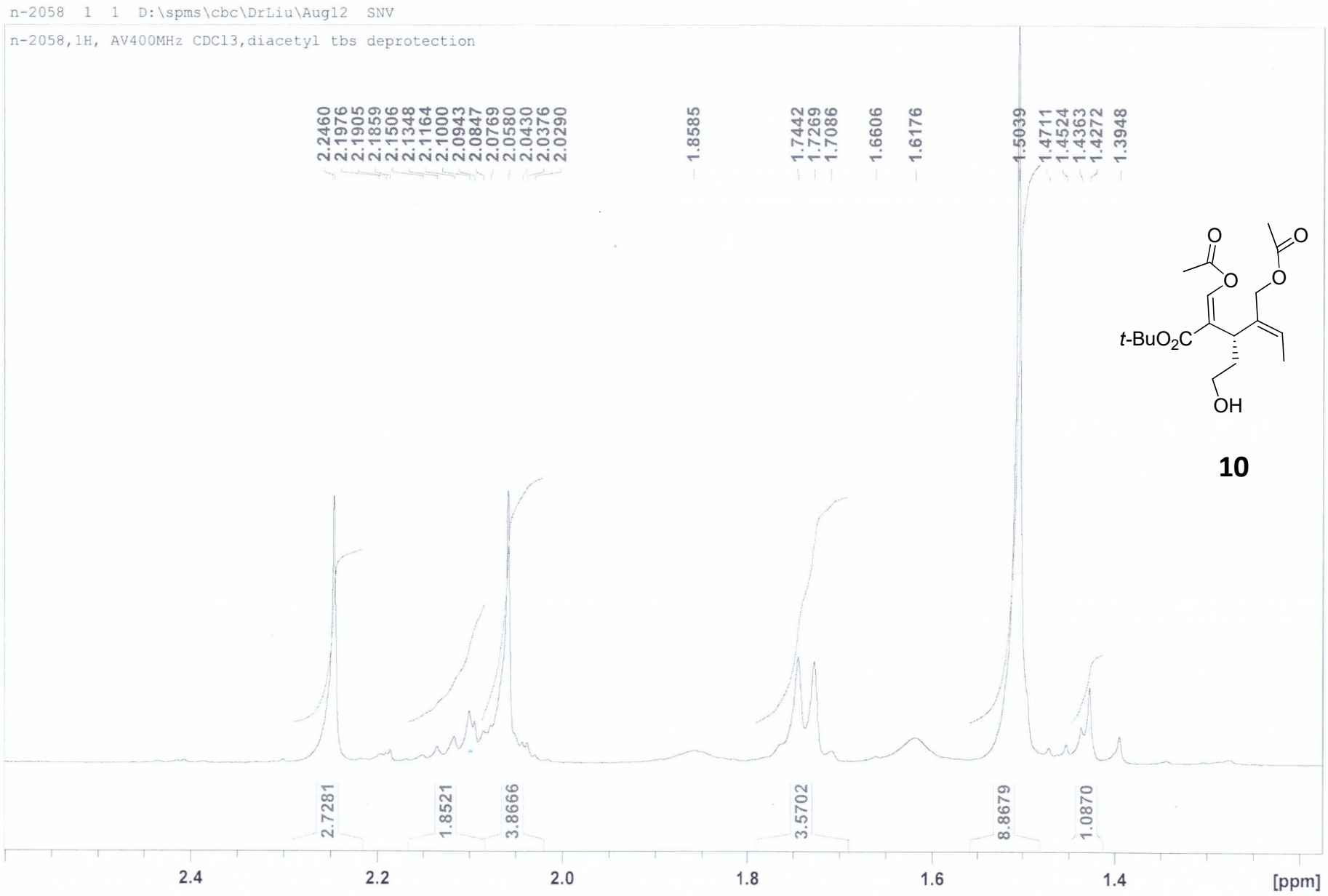
9



Minimum:				-1.5			
Maximum:		5.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
495.2719	495.2723	-0.4	-0.8	8.5	13.1	0.6	C28 H40 O6 Na
	495.2727	-0.8	-1.6	7.5	13.3	0.8	C27 H44 O3 Na Si2

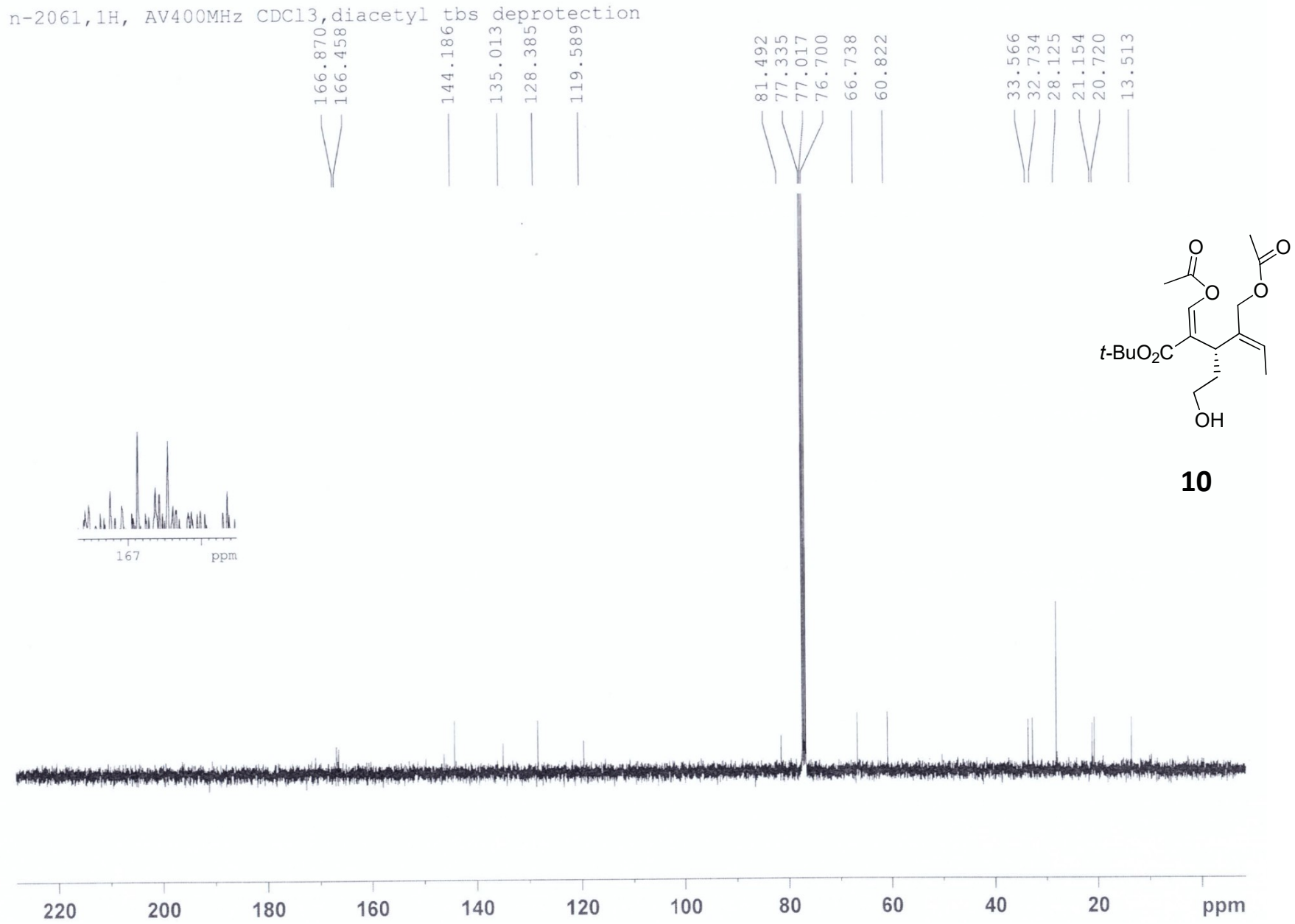

n-2058,1H, AV400MHz CDCl3,diacetyl tbs deprotection
8.161
7.283
5.736
5.719
5.702
5.685
4.714
4.683
4.612
4.581
4.181
4.162
4.141
3.643
3.629
3.616
3.602
3.584
2.246
2.198
2.191
2.186
2.151
2.135
2.116
2.100
2.094
2.085
2.077
2.058
2.043
2.038
2.029
1.859
1.744
1.727
1.709
1.661
1.618
1.504
1.471
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 ppm
t-BuO2C
OH
10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.78
1.13
2.12
1.00
2.01
2.73
1.85
3.87
3.57
8.87
1.09


n-2058 1 1 D:\spms\cbc\DrLiu\Aug12 SNV
n-2058,1H, AV400MHz CDCl3,diacetyl tbs deprotection
5.7361
5.7192
5.7020
5.6847
4.7142
4.6830
4.6122
4.5807
4.1807
4.1615
4.1408
3.6429
3.6288
3.6164
3.6018
3.5839
1.1273
2.1250
1.0000
2.0145
6.0
5.5
5.0
4.5
4.0
3.5
[ppm]
t-BuO2C
OH
10


n-2058 1 1 D:\spms\cbc\DrLiu\Aug12 SNV
n-2058,1H, AV400MHz CDCl3,diacetyl tbs deprotection
2.2460
2.1976
2.1905
2.1859
2.1506
2.1348
2.1164
2.1000
2.0943
2.0847
2.0769
2.0580
2.0430
2.0376
2.0290
1.8585
1.7442
1.7269
1.7086
1.6606
1.6176
1.5039
1.4711
1.4524
1.4363
1.4272
1.3948
2.7281
1.8521
3.8666
3.5702
8.8679
1.0870
2.4
2.2
2.0
1.8
1.6
1.4
[ppm]

O
O
O
O
t-BuO2C
OH

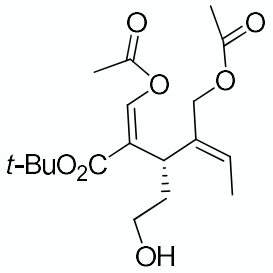
10


n-2061,1H, AV400MHz CDCl3,diacetyl tbs deprotection
166.870
166.458
144.186
135.013
128.385
119.589
81.492
77.335
77.017
76.700
66.738
60.822
33.566
32.734
28.125
21.154
20.720
13.513
167
ppm
t-BuO2C
OH
10
220
200
180
160
140
120
100
80
60
40
20
ppm

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

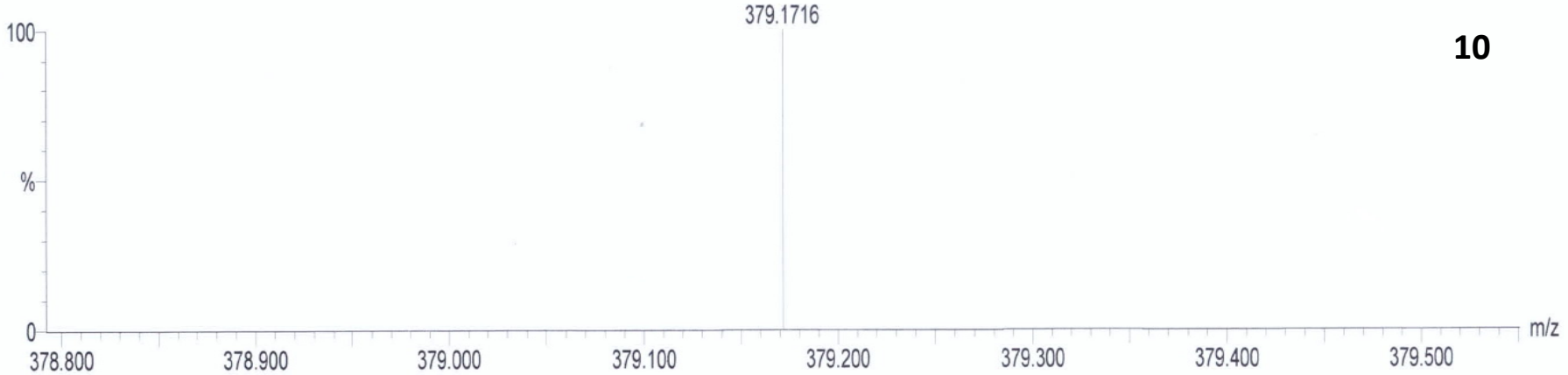


Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-28 O: 0-7 Na: 0-1

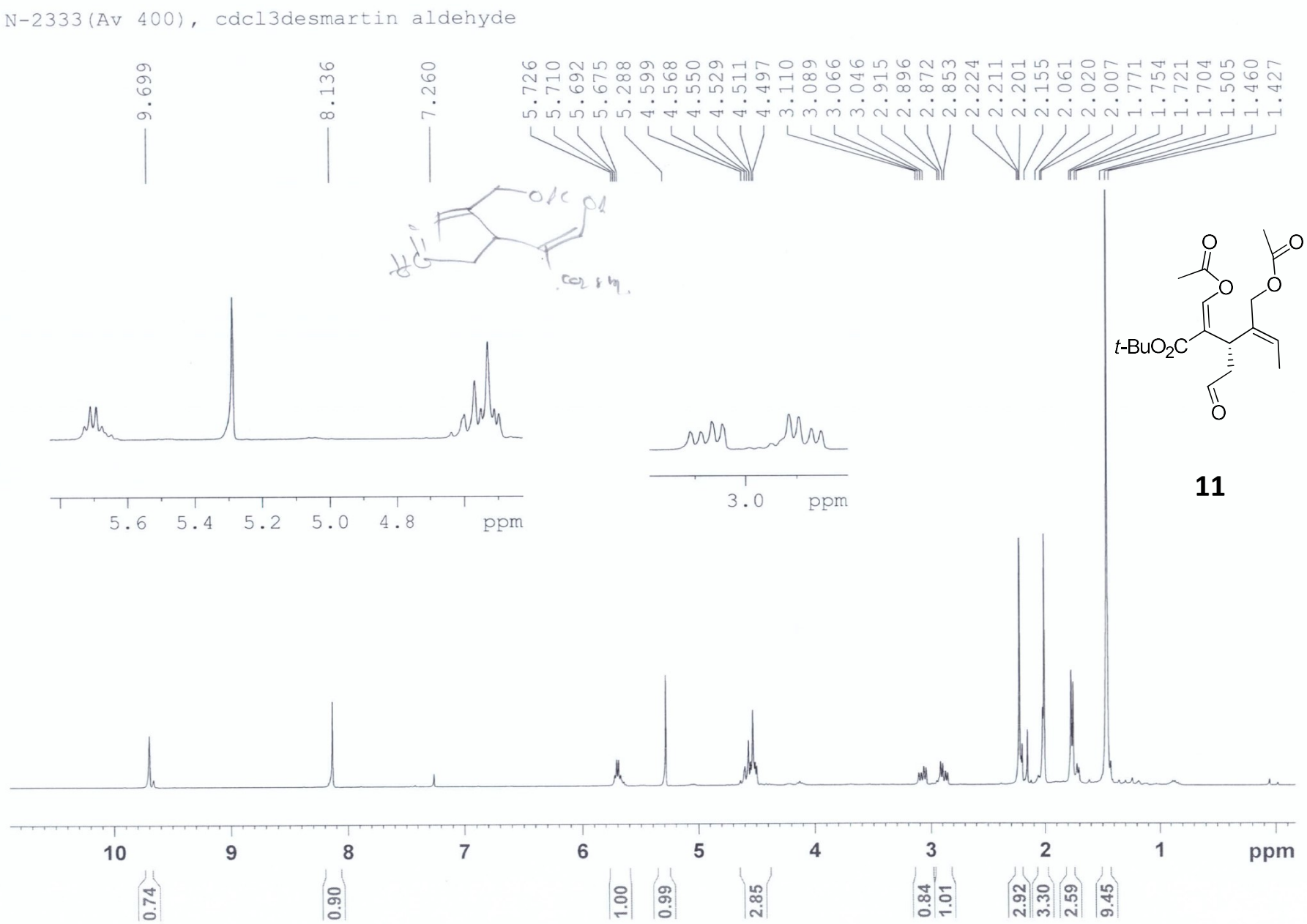
C18H28O7
SNV-100 1 (0.045)

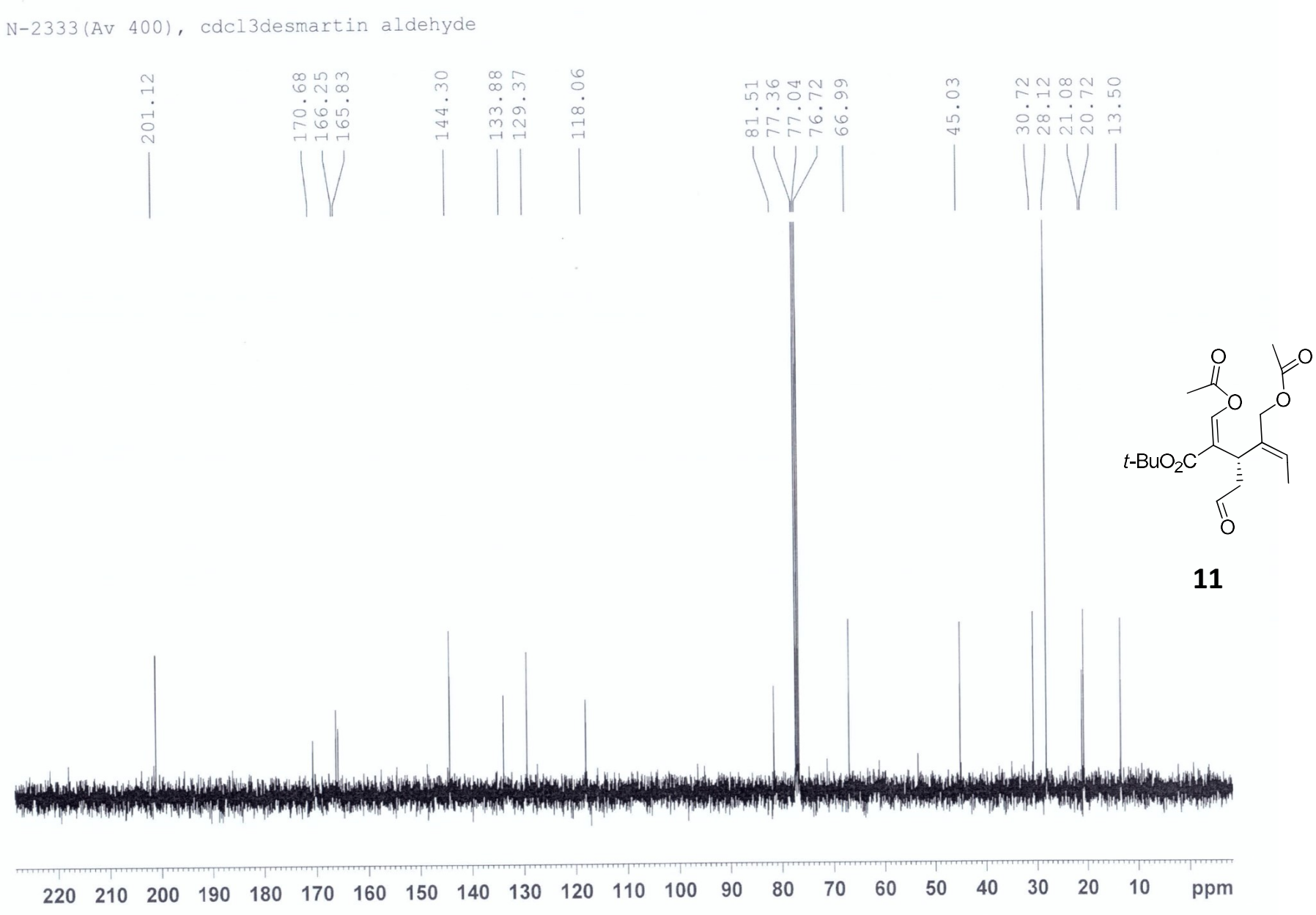
1: TOF MS ES+
1.01e+000

10



Minimum:				-1.5			
Maximum:		5.0	20.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
379.1716	379.1733	-1.7	-4.5	4.5	12.2	0.0	C18 H28 O7 Na


N-2333(Av 400), cdcl3desmartin aldehyde
9.699
8.136
7.260
5.726
5.710
5.692
5.675
5.288
4.599
4.568
4.550
4.529
4.511
4.497
3.110
3.089
3.066
3.046
2.915
2.896
2.872
2.853
2.224
2.211
2.201
2.155
2.061
2.020
2.007
1.771
1.754
1.721
1.704
1.505
1.460
1.427
5.6 5.4 5.2 5.0 4.8 ppm
3.0 ppm
t-BuO2C
11
10 9 8 7 6 5 4 3 2 1 ppm
0.74
0.90
1.00
0.99
2.85
0.84
1.01
2.92
3.30
2.59
9.45


N-2333(Av 400), cdcl3desmartin aldehyde
201.12
170.68
166.25
165.83
144.30
133.88
129.37
118.06
81.51
77.36
77.04
76.72
66.99
45.03
30.72
28.12
21.08
20.72
13.50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

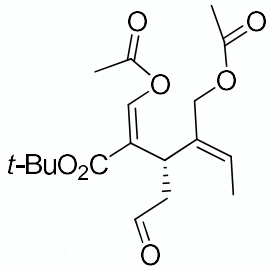
t-BuO2C

11

Elemental Composition Report

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

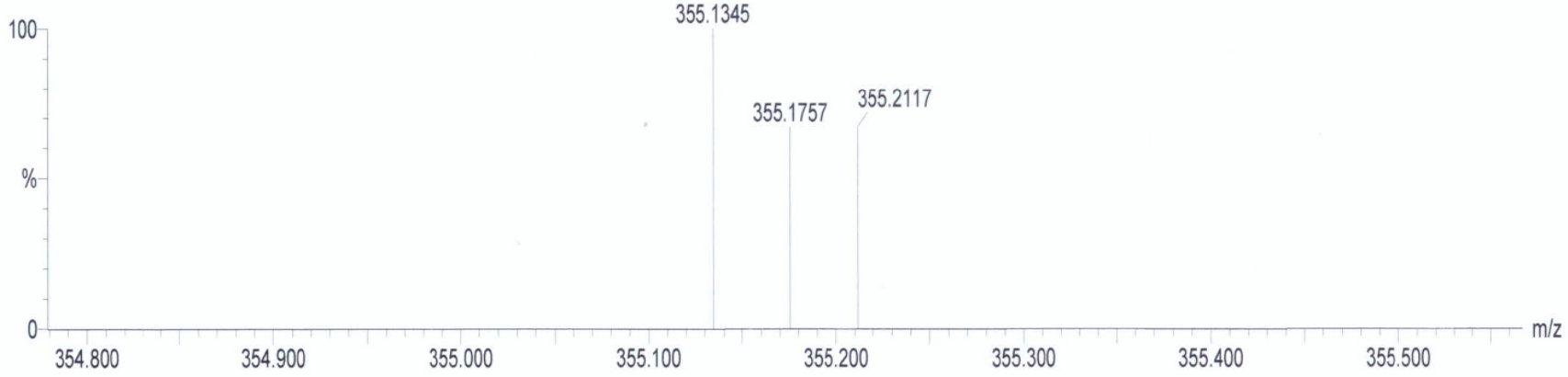


11

Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18 H: 0-27 O: 0-7 Na: 0-1

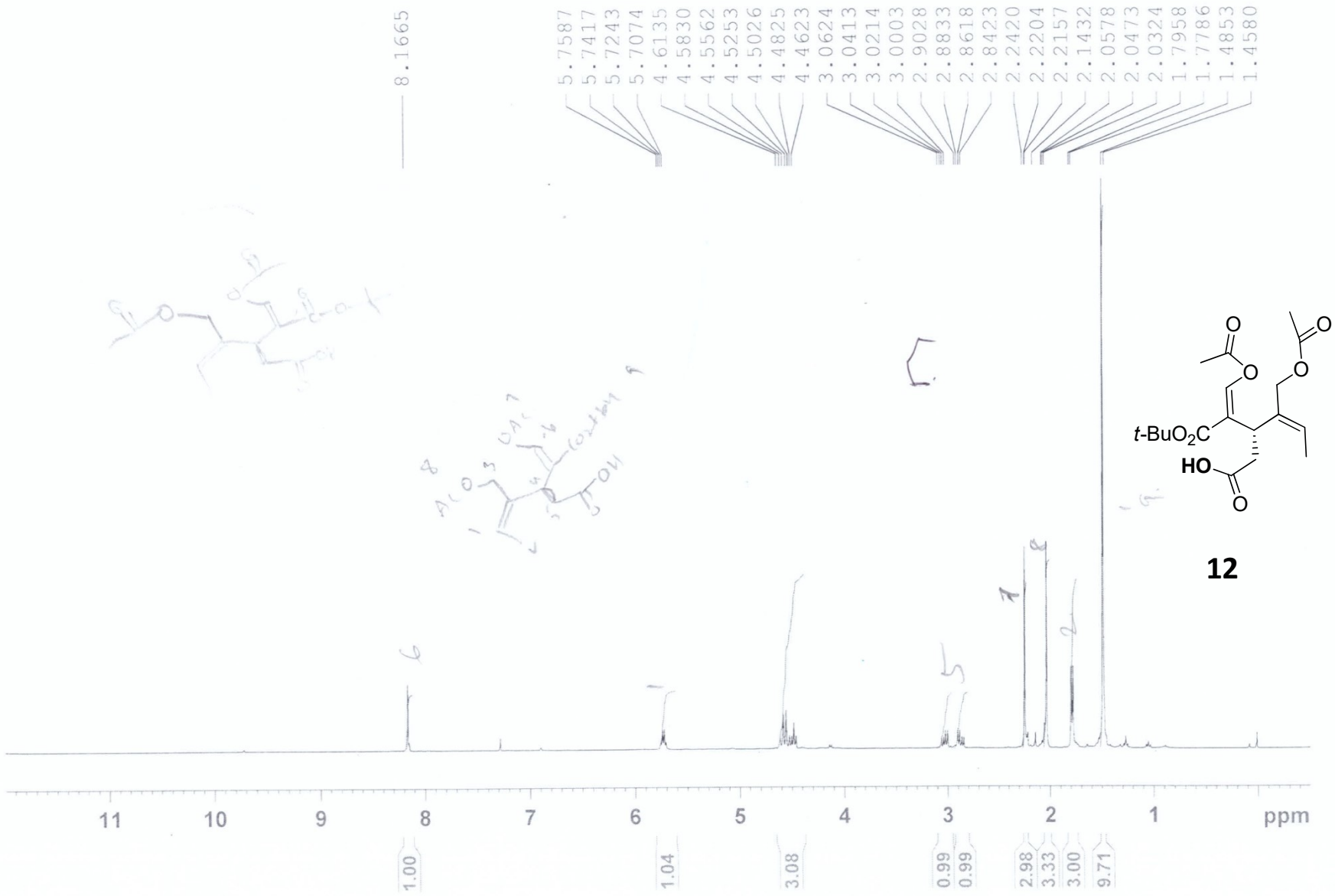
C18H26O7
SNV-101 7 (0.156) Cm (7:9)

1: TOF MS ES+
3.04e+000

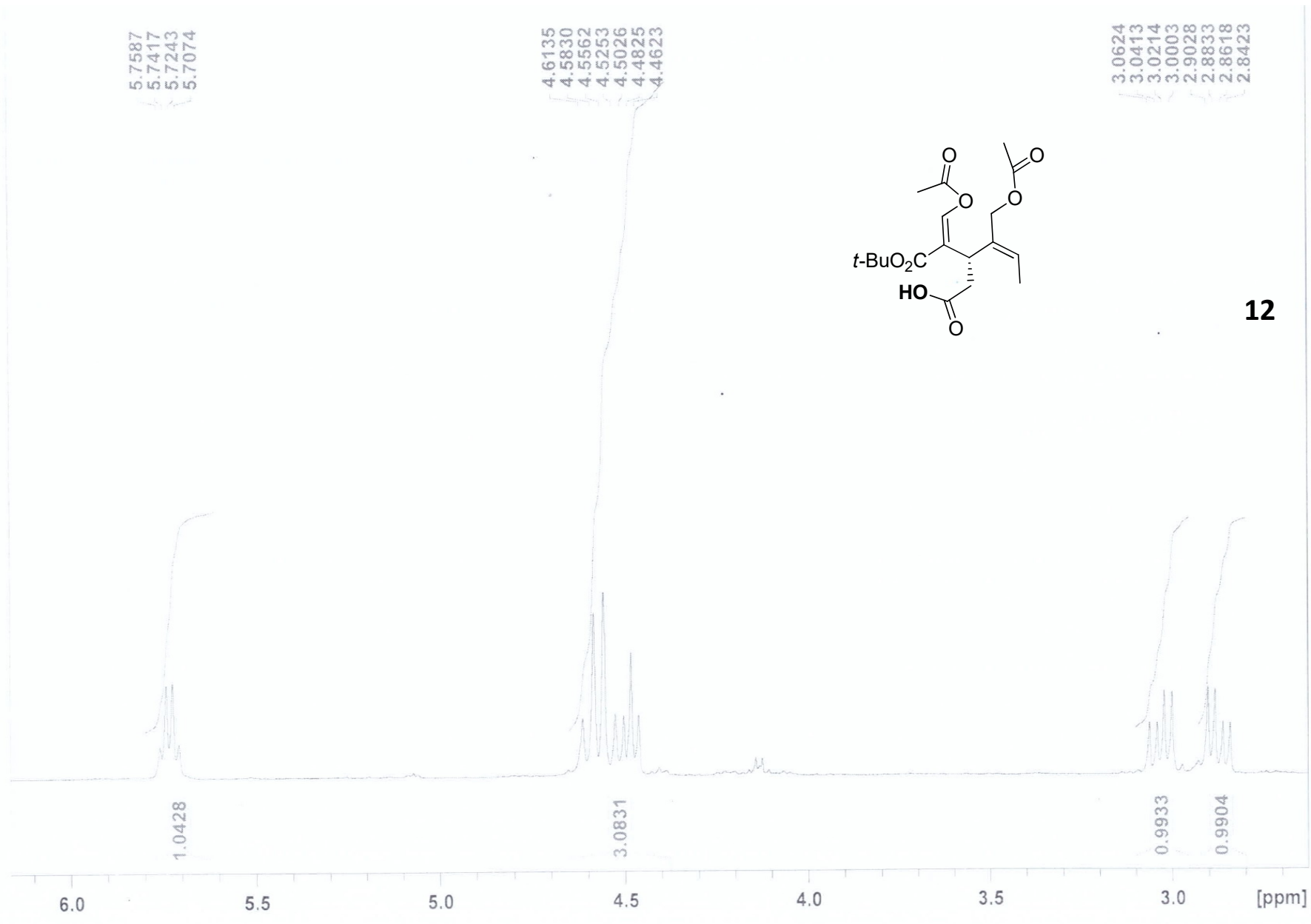


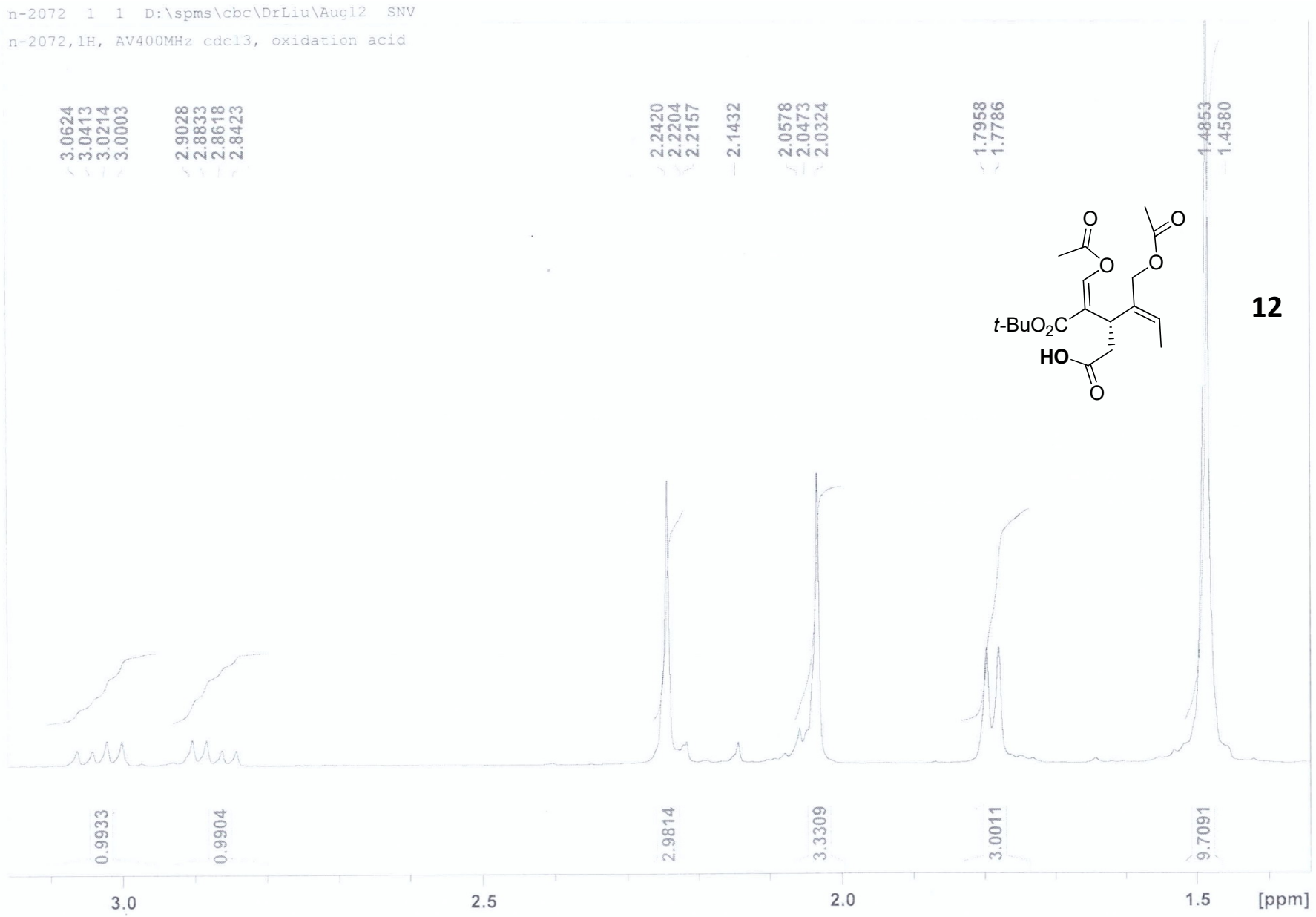
Minimum:				-1.5			
Maximum:		5.0	20.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
355.1757	355.1757	0.0	0.0	5.5	13.9	0.0	C18 H27 O7

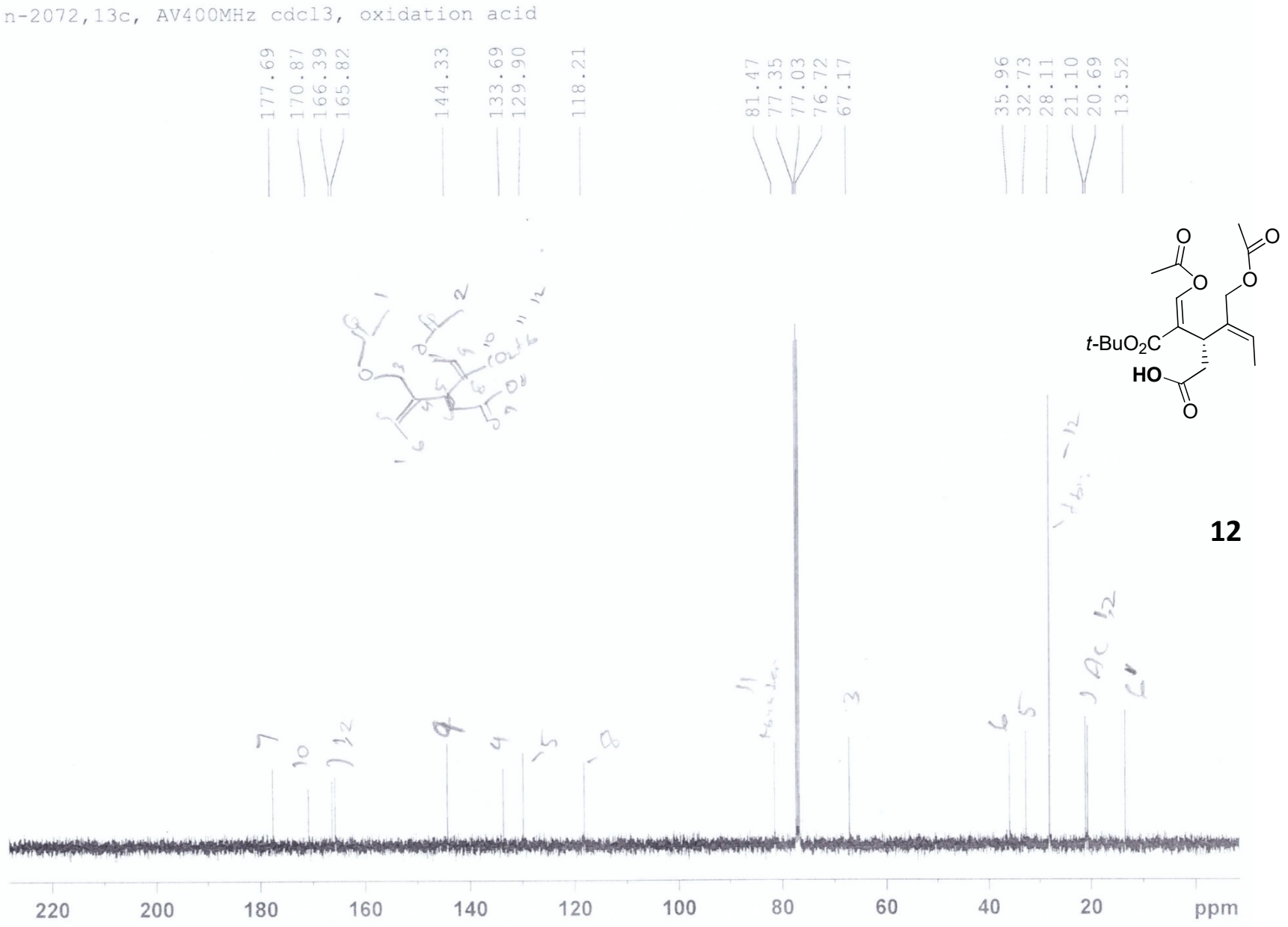
n-2072,1H, AV400MHz cdcl3, oxidation acid



12


5.7587
5.7417
5.7243
5.7074
4.6135
4.5830
4.5562
4.5253
4.5026
4.4825
4.4623
3.0624
3.0413
3.0214
3.0003
2.9028
2.8833
2.8618
2.8423
t-BuO2C
HO
O
O
O
O
12
1.0428
3.0831
0.9933
0.9904
6.0
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]


n-2072 1 1 D:\spms\cbc\DrLiu\Aug12 SNV
n-2072,1H, AV400MHz cdcl3, oxidation acid
3.0624
3.0413
3.0214
3.0003
2.9028
2.8833
2.8618
2.8423
2.2420
2.2204
2.2157
2.1432
2.0578
2.0473
2.0324
1.7958
1.7786
1.4853
1.4580
t-BuO2C
HO
12
0.9933
0.9904
2.9814
3.3309
3.0011
9.7091
3.0
2.5
2.0
1.5
[ppm]


n-2072,13c, AV400MHz cdcl3, oxidation acid
177.69
170.87
166.39
165.82
144.33
133.69
129.90
118.21
81.47
77.35
77.03
76.72
67.17
35.96
32.73
28.11
21.10
20.69
13.52
t-BuO2C
HO
O
220
200
180
160
140
120
100
80
60
40
20
ppm

12

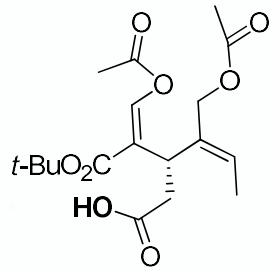
Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

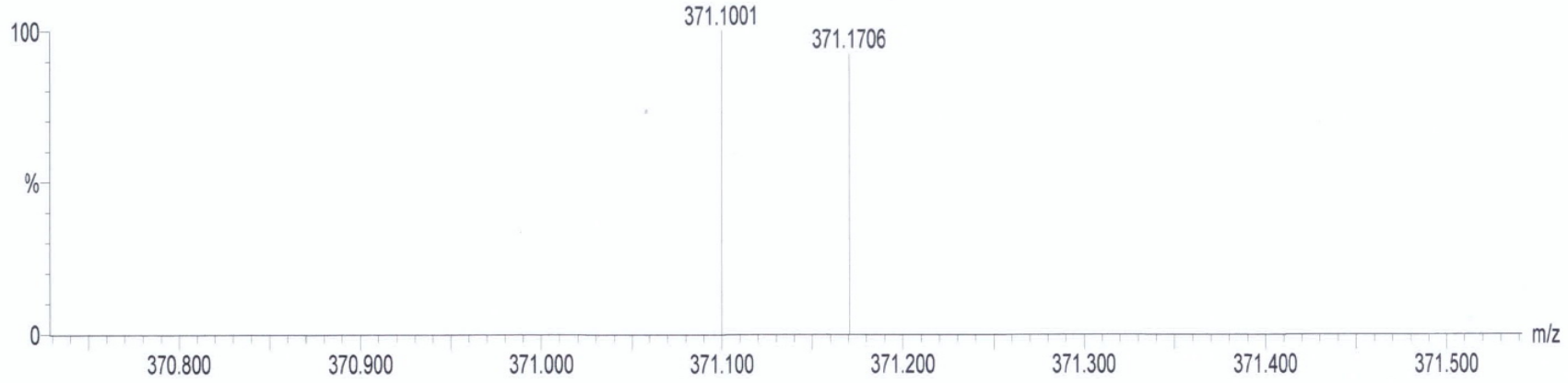
Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26 H: 0-28 O: 0-10

C18H26O8
snv-102 5 (0.119)



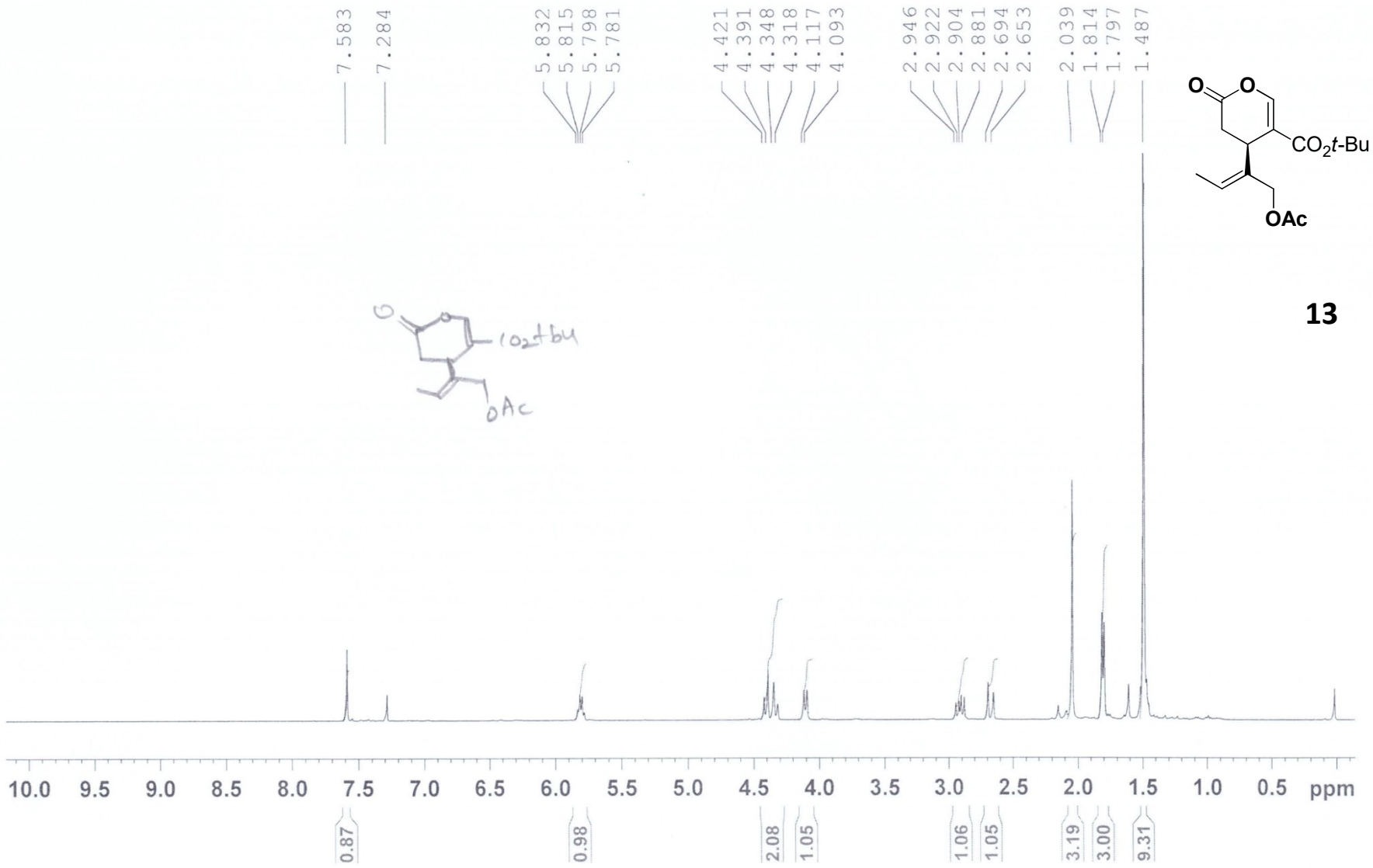
12

1: TOF MS ES+
5.49e+000

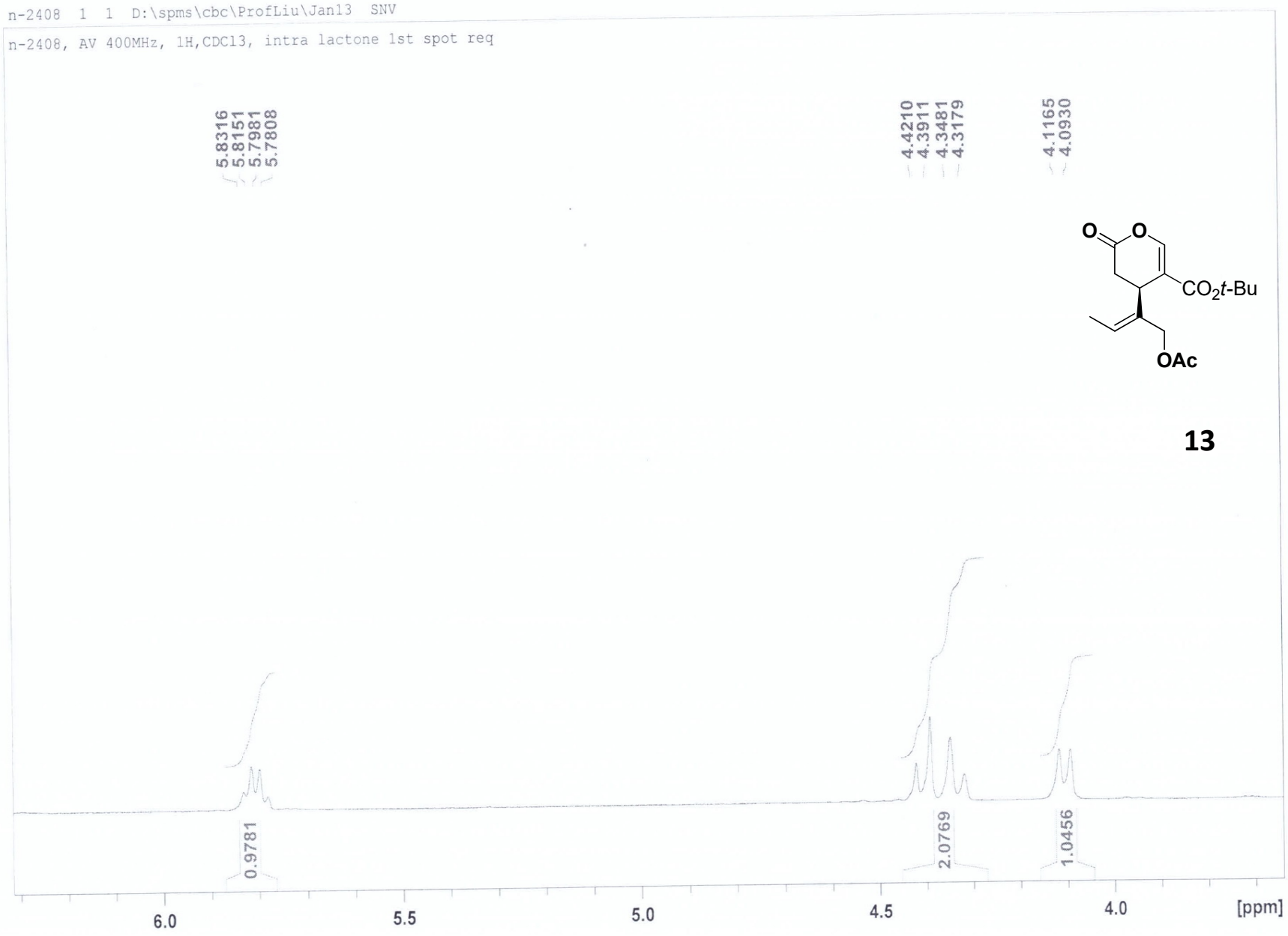


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
371.1706	371.1706	0.0	0.0	5.5	12.6	0.0	C18 H27 O8

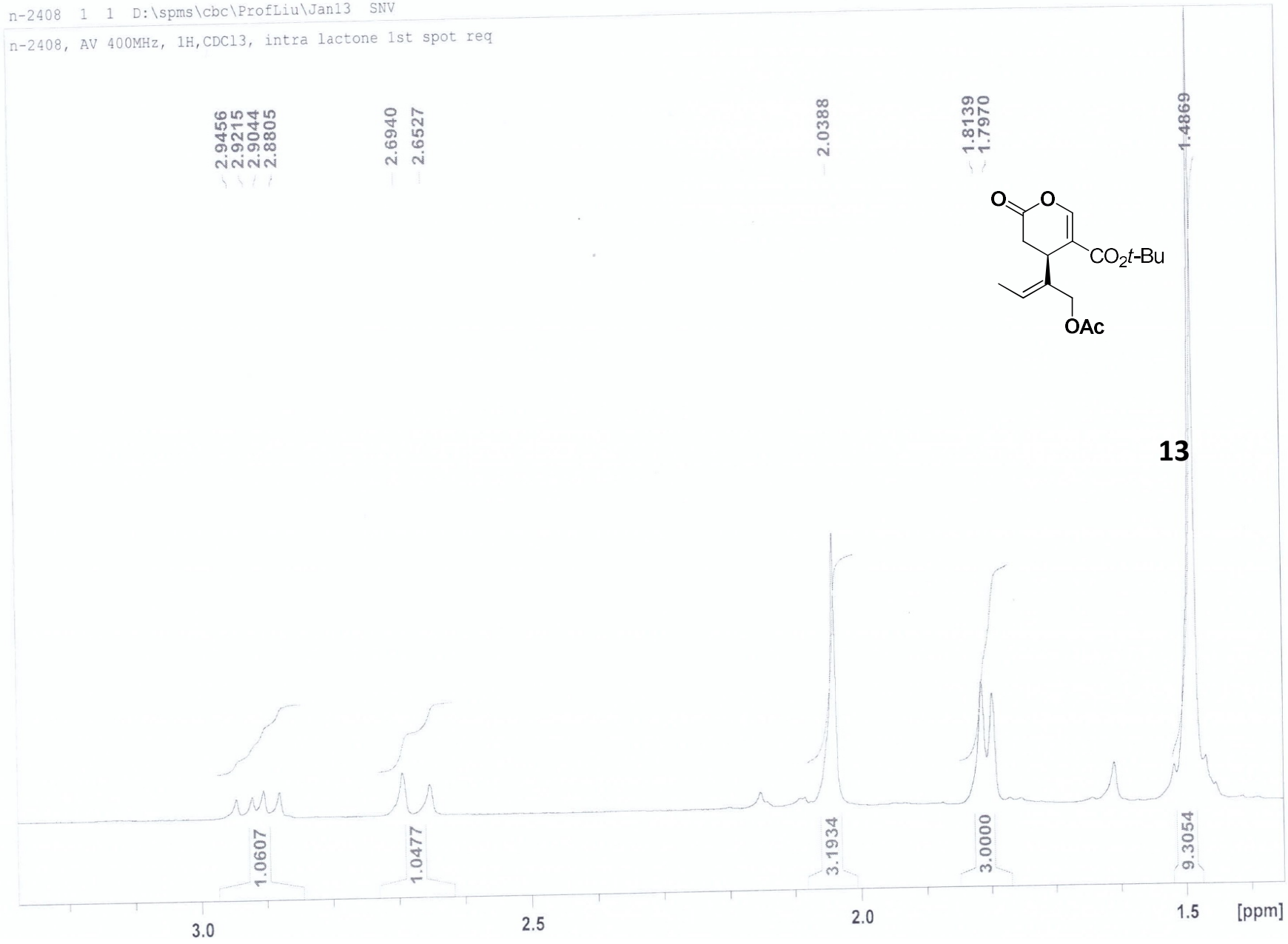
n-2408, AV 400MHz, 1H,CDCl3, intra lactone 1st spot req

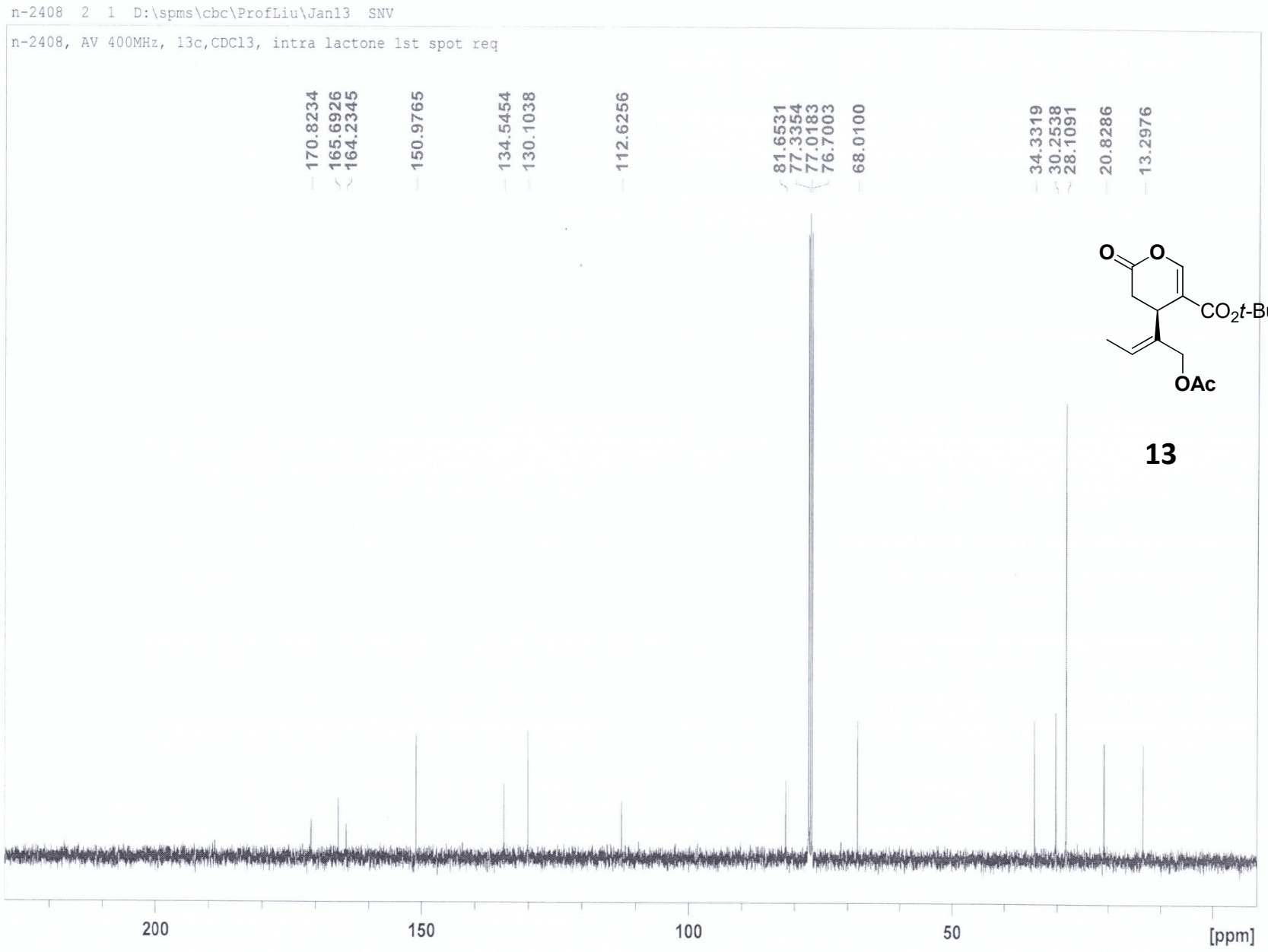


13

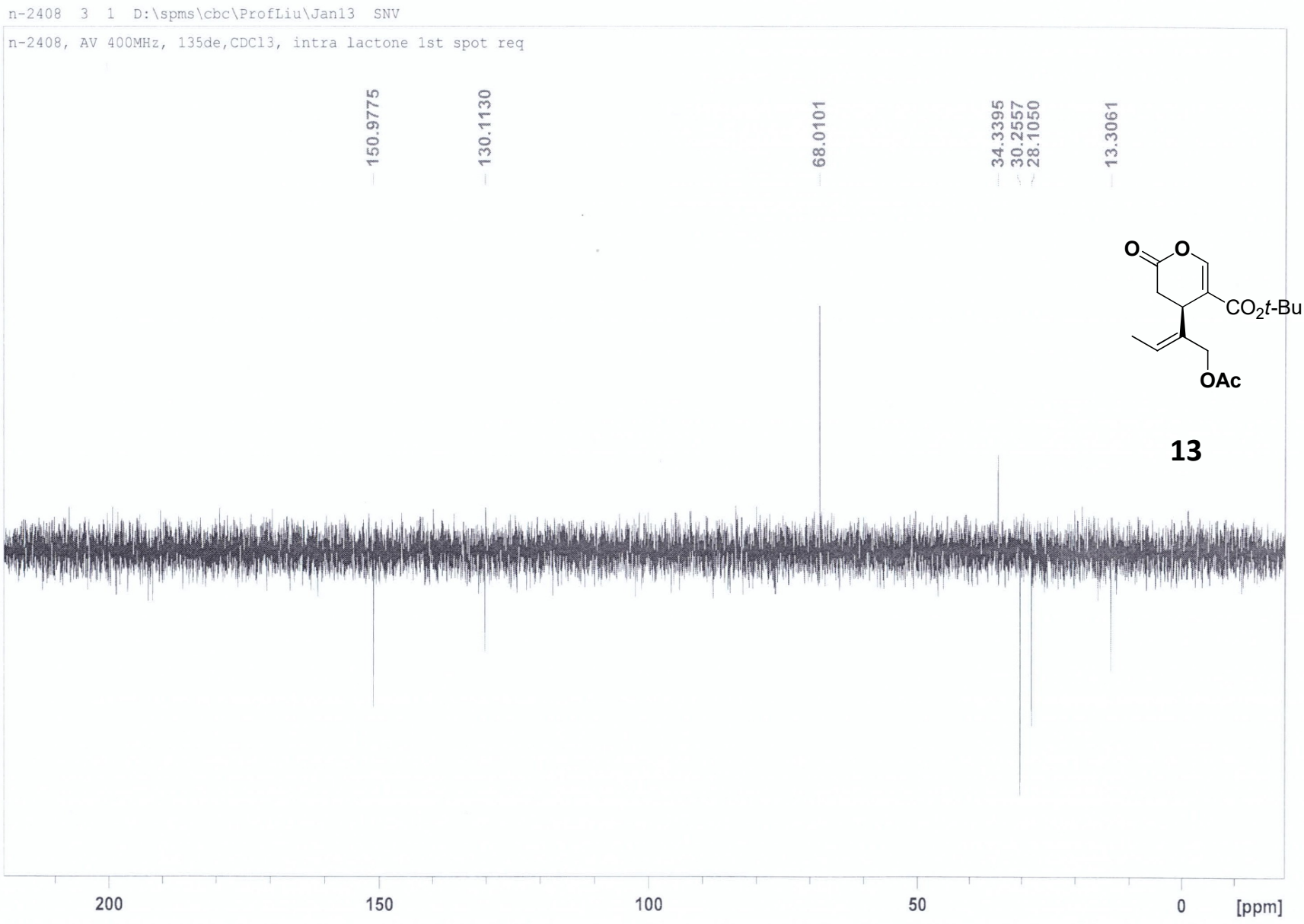

n-2408 1 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2408, AV 400MHz, 1H,CDCl3, intra lactone 1st spot req
5.8316
5.8151
5.7981
5.7808
4.4210
4.3911
4.3481
4.3179
4.1165
4.0930
O
O
CO2t-Bu
OAc
0.9781
2.0769
1.0456
6.0
5.5
5.0
4.5
4.0
[ppm]

13


n-2408 1 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2408, AV 400MHz, 1H,CDCl3, intra lactone 1st spot req
2.9456
2.9215
2.9044
2.8805
2.6940
2.6527
2.0388
1.8139
1.7970
1.4869
O
O
CO2t-Bu
OAc
13
1.0607
1.0477
3.1934
3.0000
9.3054
3.0
2.5
2.0
1.5
[ppm]


n-2408 2 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2408, AV 400MHz, 13c,CDCl3, intra lactone 1st spot req
170.8234
165.6926
164.2345
150.9765
134.5454
130.1038
112.6256
81.6531
77.3354
77.0183
76.7003
68.0100
34.3319
30.2538
28.1091
20.8286
13.2976
O
O
CO2t-Bu
OAc
200
150
100
50
[ppm]

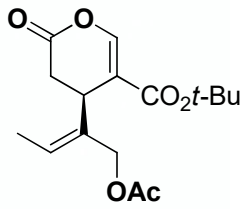
13


n-2408 3 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2408, AV 400MHz, 135de,CDCl3, intra lactone 1st spot req
150.9775
130.1130
68.0101
34.3395
30.2557
28.1050
13.3061
O
O
CO2t-Bu
OAc
13
200
150
100
50
0
[ppm]

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

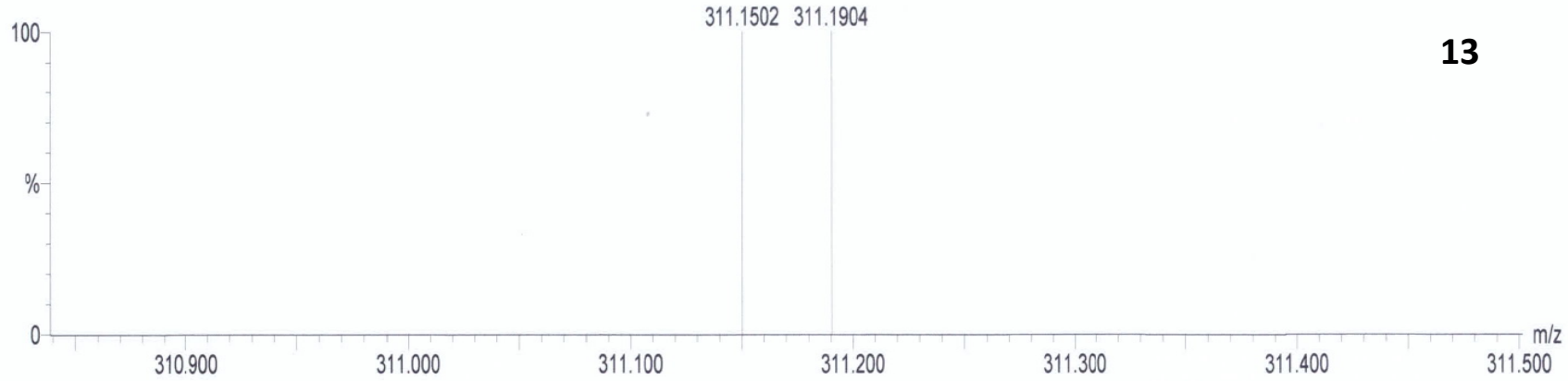


Monoisotopic Mass, Even Electron Ions
29 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26 H: 0-28 O: 0-10

C16H22O6
snv-103 215 (4.702)

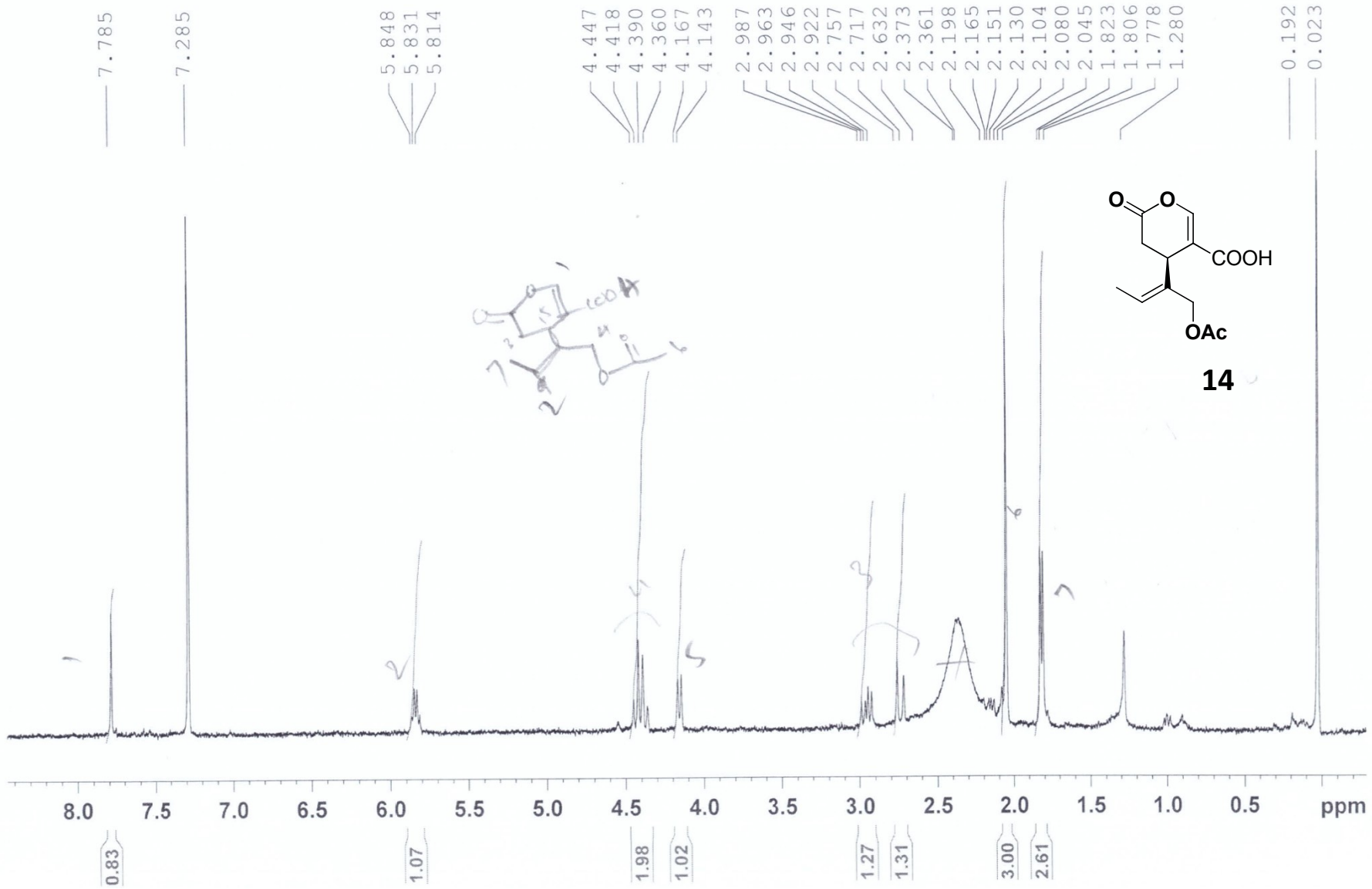
1: TOF MS ES+
1.01e+000

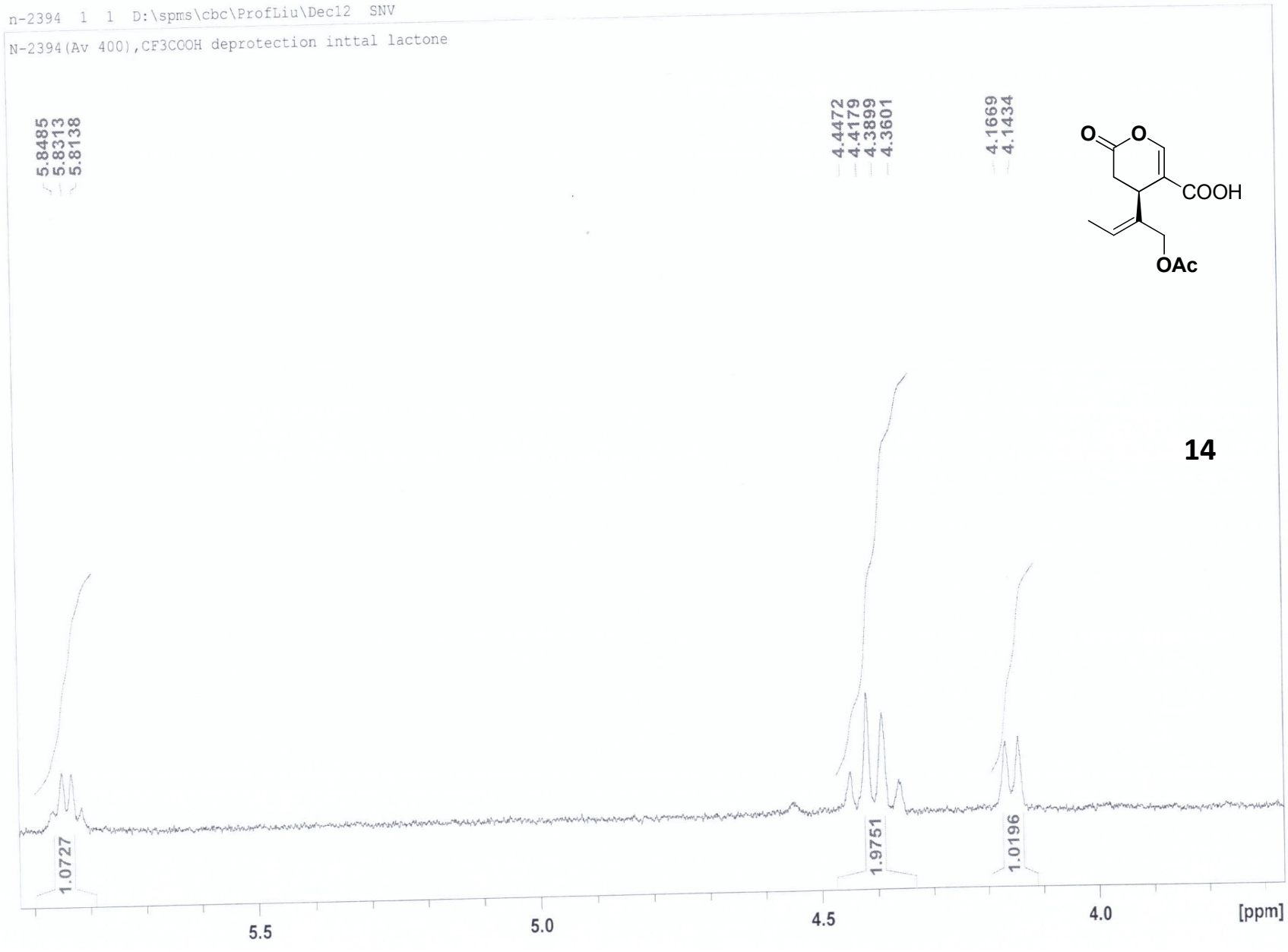
13

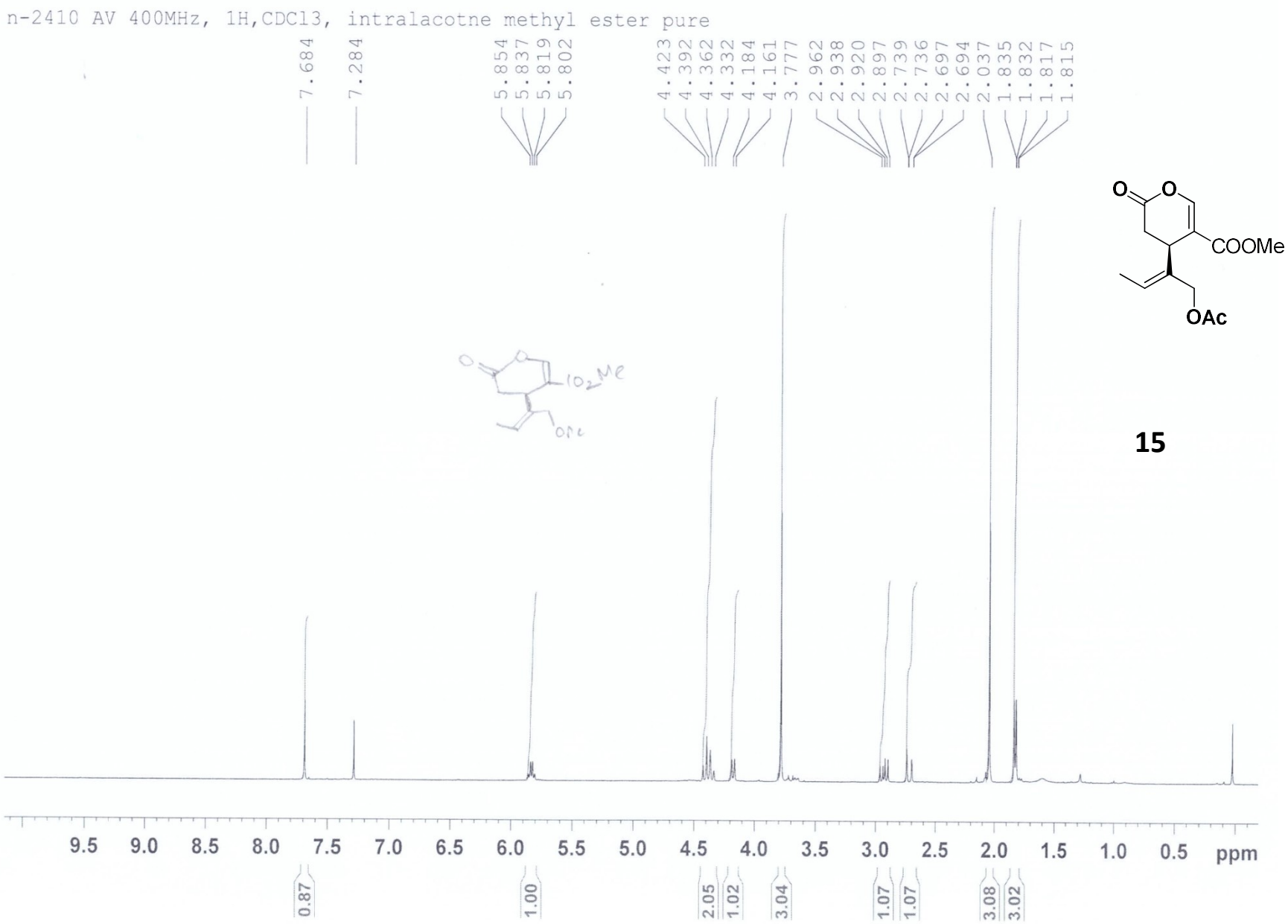


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
311.1502	311.1495	0.7	2.2	5.5	14.8	0.0	C16 H23 O6

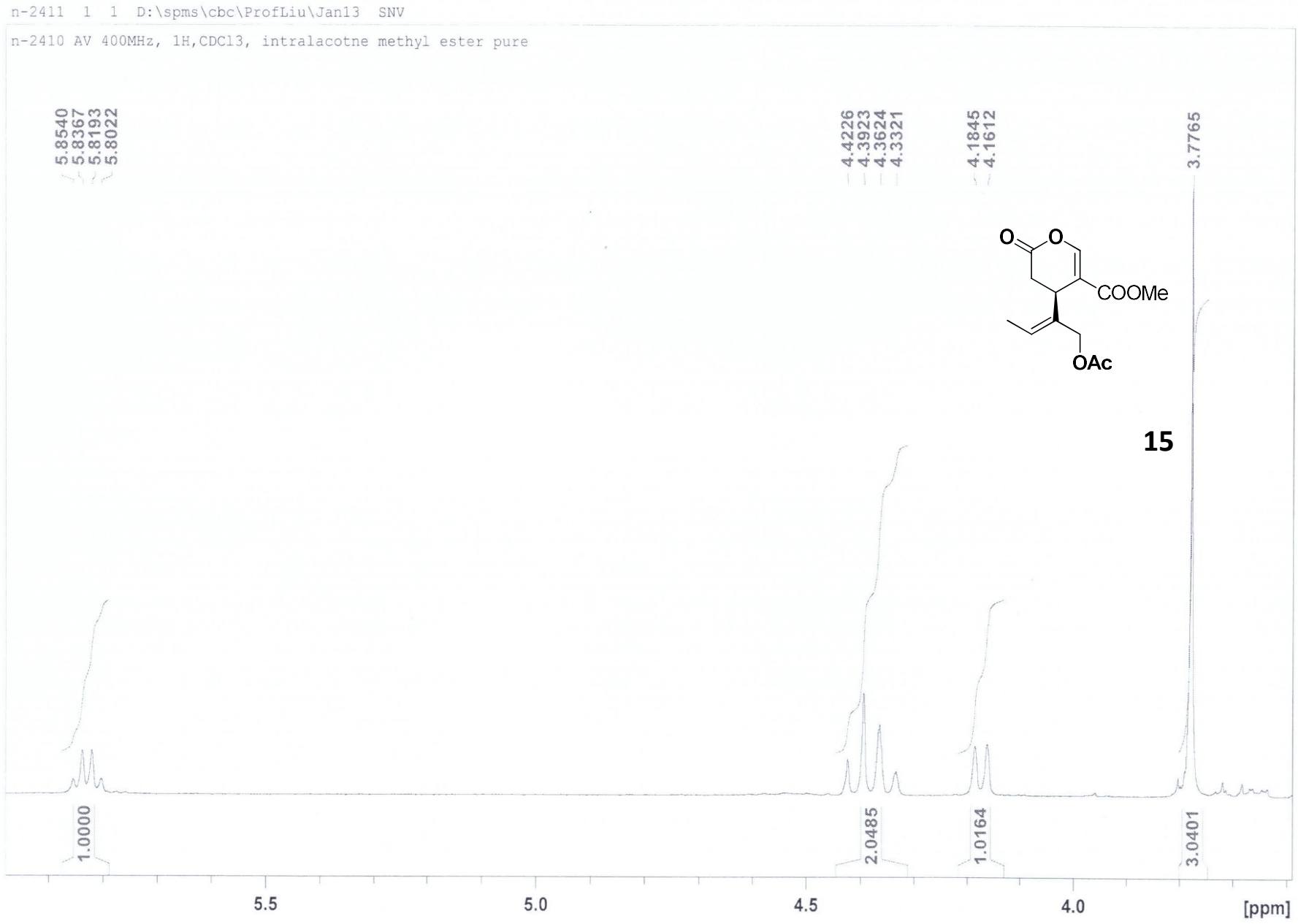
N-2394(Av 400),CF3COOH deprotection inttal lactone

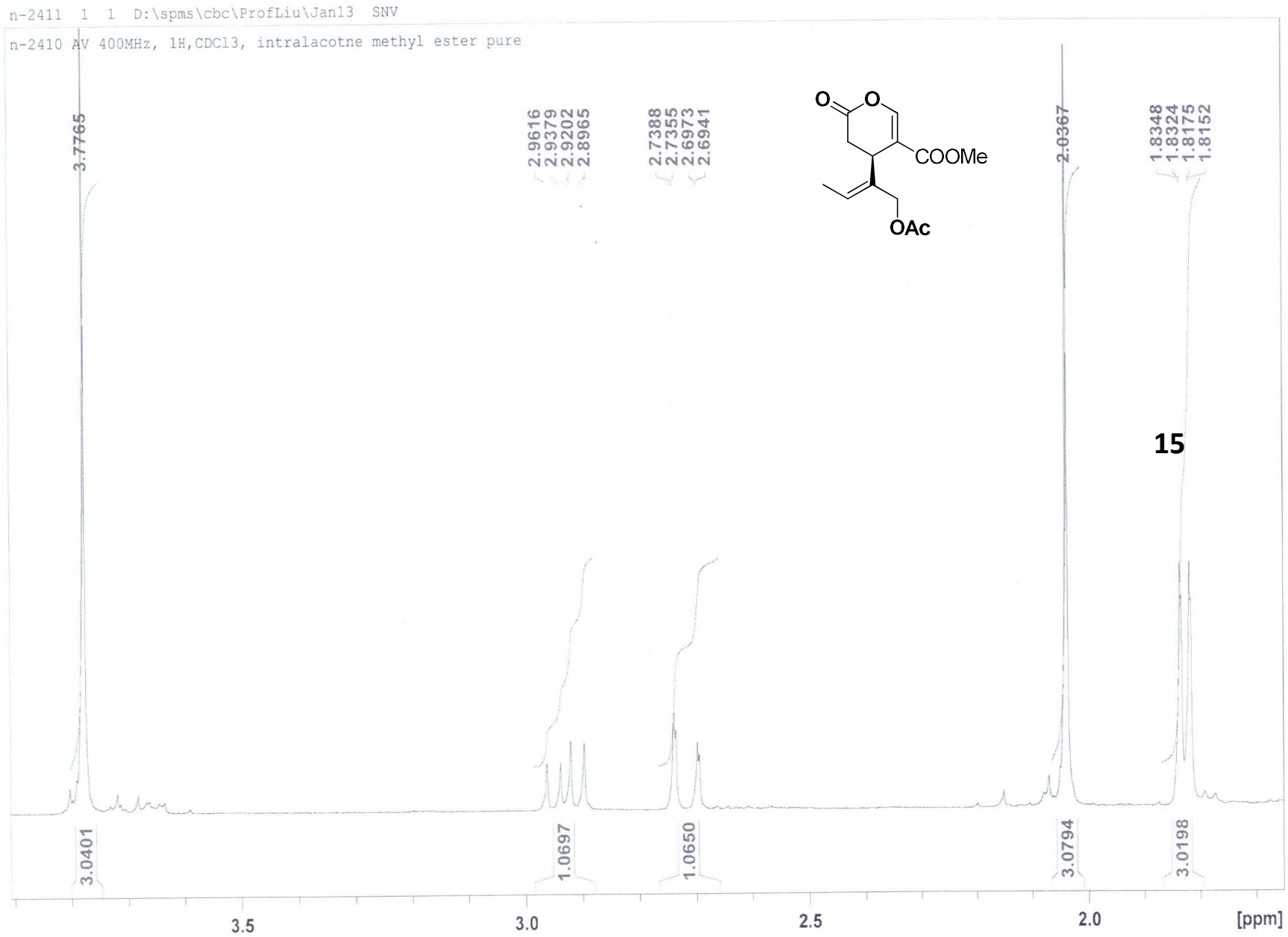


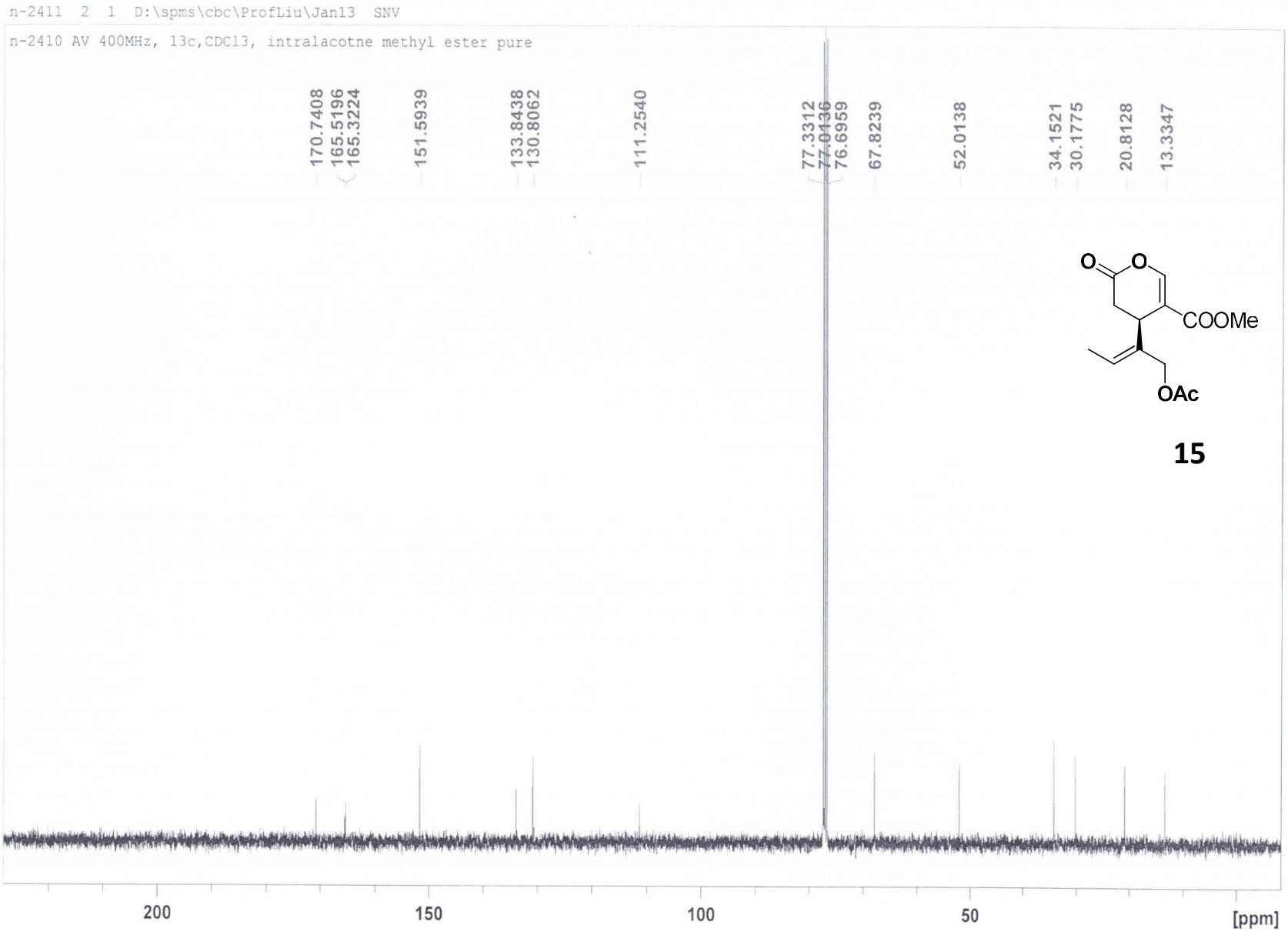

n-2394 1 1 D:\spms\cbc\ProfLiu\Dec12 SNV
N-2394(Av 400),CF3COOH deprotection inttal lactone
5.8485
5.8313
5.8138
4.4472
4.4179
4.3899
4.3601
4.1669
4.1434
O
O
COOH
OAc
14
1.0727
1.9751
1.0196
5.5
5.0
4.5
4.0
[ppm]


n-2410 AV 400MHz, 1H,CDCl3, intralacotne methyl ester pure
7.684
7.284
5.854
5.837
5.819
5.802
4.423
4.392
4.362
4.332
4.184
4.161
3.777
2.962
2.938
2.920
2.897
2.739
2.736
2.697
2.694
2.037
1.835
1.832
1.817
1.815
COOMe
OAc
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.87
1.00
2.05
1.02
3.04
1.07
1.07
3.08
3.02

15


n-2411 1 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2410 AV 400MHz, 1H,CDCl3, intralacotne methyl ester pure
5.8540
5.8367
5.8193
5.8022
4.4226
4.3923
4.3624
4.3321
4.1845
4.1612
3.7765
O
O
COOMe
OAc
15
1.0000
2.0485
1.0164
3.0401
5.5
5.0
4.5
4.0
[ppm]


n-2411 1 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2410 AV 400MHz, 1H,CDCl3, intralacotne methyl ester pure
3.7765
2.9616
2.9379
2.9202
2.8965
2.7388
2.7355
2.6973
2.6941
2.0367
1.8348
1.8324
1.8175
1.8152
O
O
COOMe
OAc
15
3.0401
1.0697
1.0650
3.0794
3.0198
3.5
3.0
2.5
2.0
[ppm]

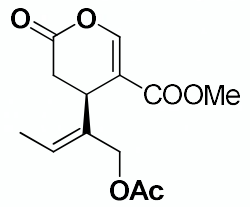

n-2411 2 1 D:\spms\cbc\ProfLiu\Jan13 SNV
n-2410 AV 400MHz, 13c,CDCl3, intralacotne methyl ester pure
170.7408
165.5196
165.3224
151.5939
133.8438
130.8062
111.2540
77.3312
77.0136
76.6959
67.8239
52.0138
34.1521
30.1775
20.8128
13.3347
O
O
COOMe
OAc
200
150
100
50
[ppm]

15

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

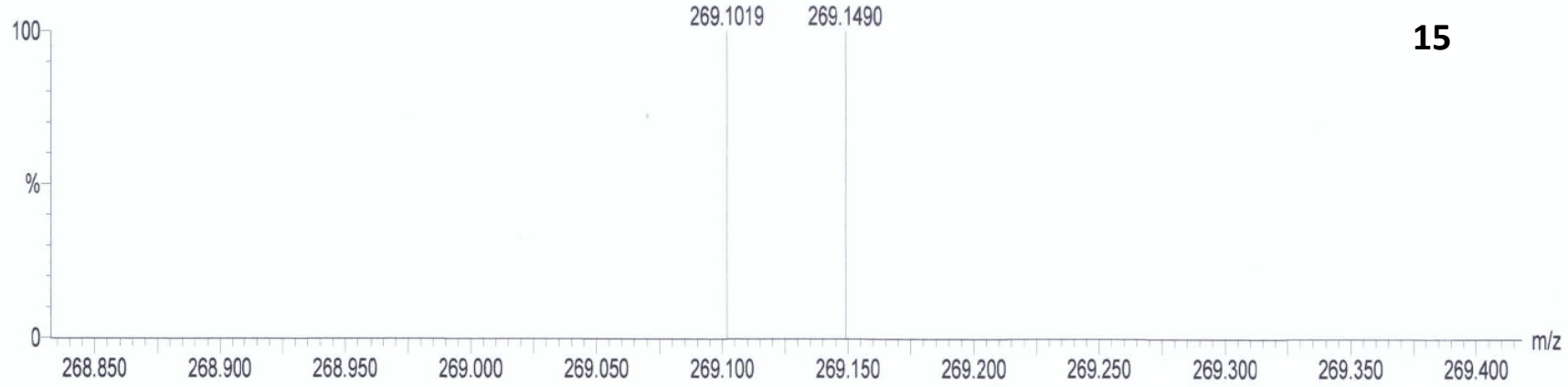


Monoisotopic Mass, Even Electron Ions
26 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26 H: 0-28 O: 0-10

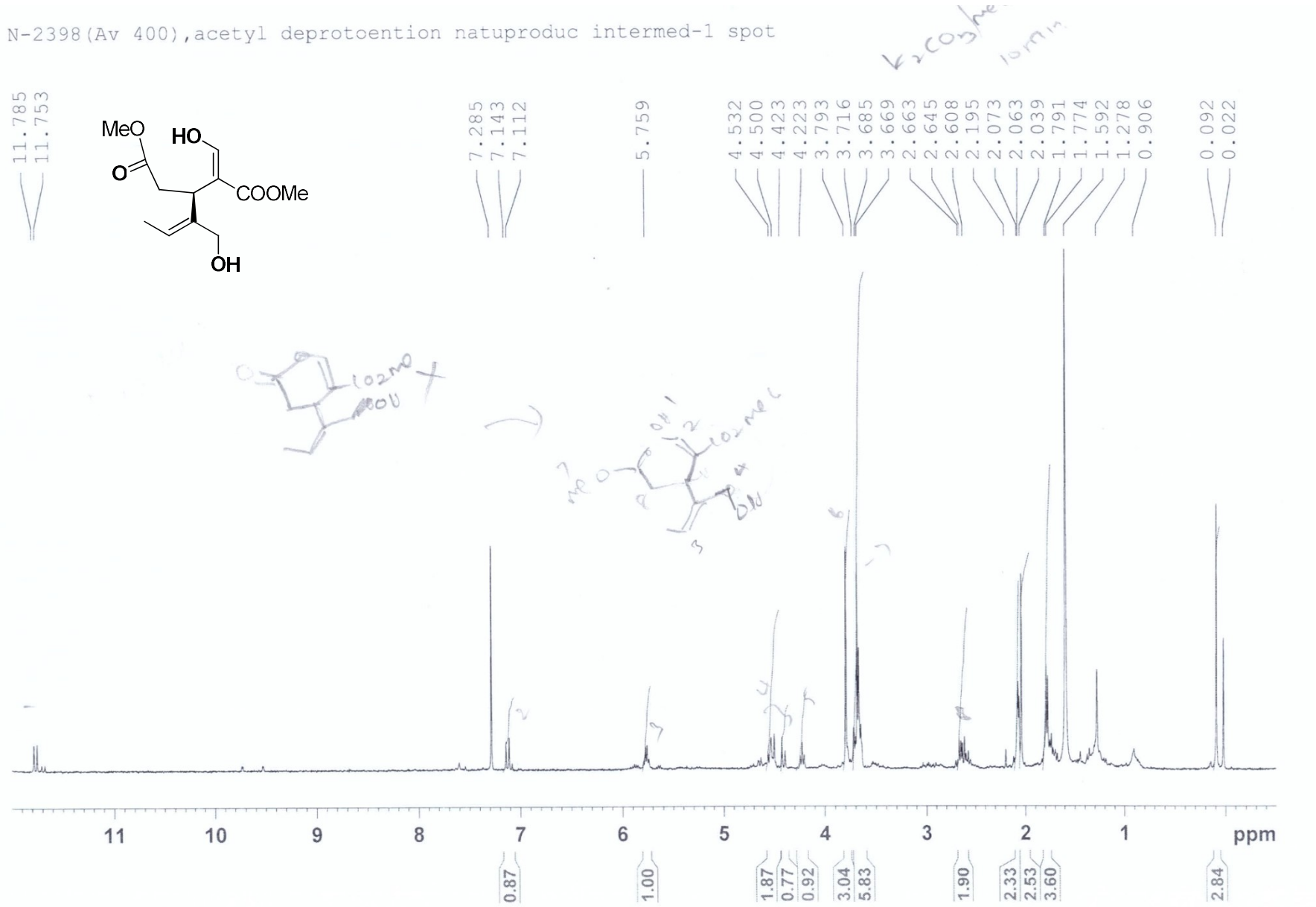
C13H16O6
snv-104 13 (0.294)

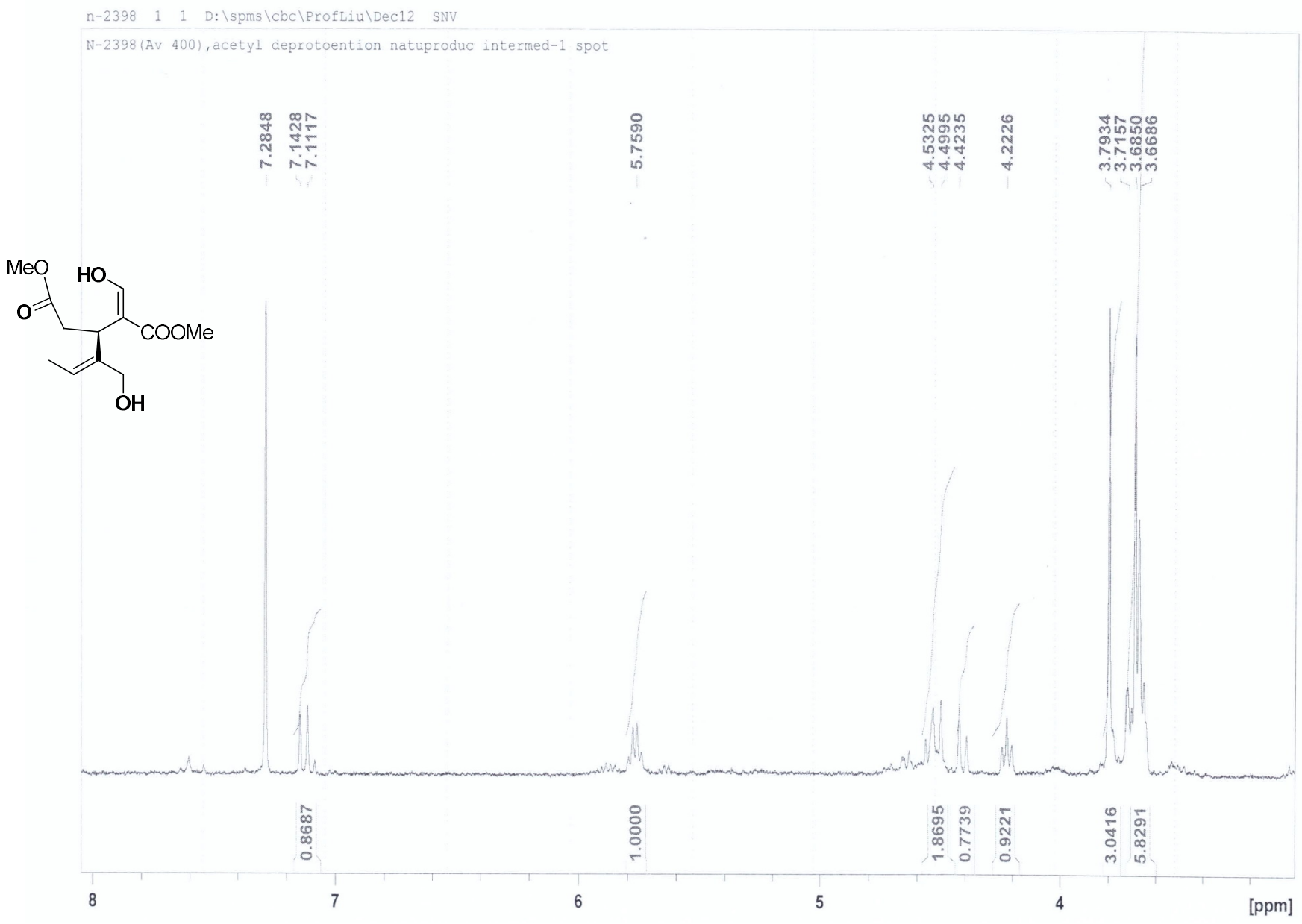
1: TOF MS ES+
1.01e+000

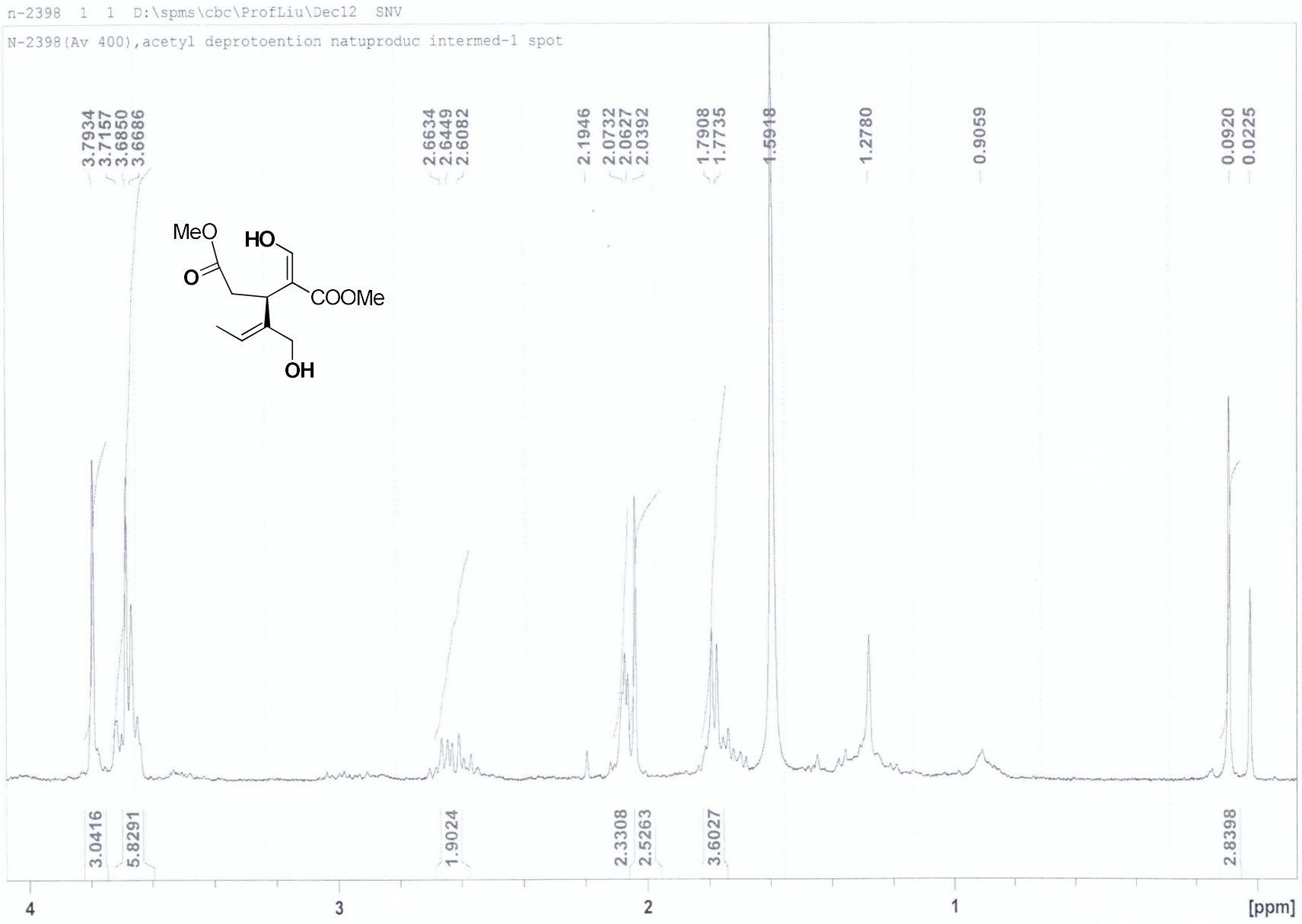
15



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
269.1019	269.1025	-0.6	-2.2	5.5	14.7	0.0	C13 H17 O6


N-2398(Av 400),acetyl deprotoention natuproduc intermed-1 spot
11.785
11.753
7.285
7.143
7.112
5.759
4.532
4.500
4.423
4.223
3.793
3.716
3.685
3.669
2.663
2.645
2.608
2.195
2.073
2.063
2.039
1.791
1.774
1.592
1.278
0.906
0.092
0.022
MeO
HO
O
COOMe
OH
11
10
9
8
7
6
5
4
3
2
1
ppm
0.87
1.00
1.87
0.77
0.92
3.04
5.83
1.90
2.33
2.53
3.60
2.84


n-2398 1 1 D:\spms\cbc\ProfLiu\Dec12 SNV
N-2398(Av 400),acetyl deprotoention natuproduc intermed-1 spot
7.2848
7.1428
7.1117
5.7590
4.5325
4.4995
4.4235
4.2226
3.7934
3.7157
3.6850
3.6686
MeO
O
HO
COOMe
OH
0.8687
1.0000
1.8695
0.7739
0.9221
3.0416
5.8291
8
7
6
5
4
[ppm]


n-2398 1 1 D:\spms\cbc\ProfLiu\Dec12 SNV
N-2398(Av 400),acetyl deprotoention natuproduc intermed-1 spot
3.7934
3.7157
3.6850
3.6686
2.6634
2.6449
2.6082
2.1946
2.0732
2.0627
2.0392
1.7908
1.7735
1.5918
1.2780
0.9059
0.0920
0.0225
MeO
HO
O
COOMe
OH
3.0416
5.8291
1.9024
2.3308
2.5263
3.6027
2.8398
4
3
2
1
[ppm]