Electronic Supplementary Material (ESI) for New Journal of Chemistry.

1.Electronic Supporting Information

Bile acid hydrazides: gelation, structural, physical and spectroscopic properties

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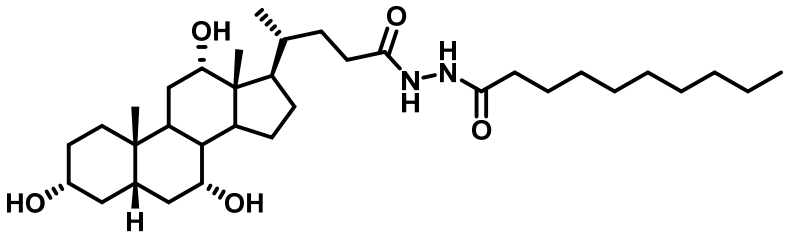


Contents

Experimental

Melting point: Melting points were determined on a Buchi Melting Point B-540 and are uncorrected.

FTIR: for FTIR study, comparison of gelator **1** in powder form and its xerogel was carried on Shimadzu FTIR-8400 spectrophotometer. Xerogel was prepared by allowing gel to dry completely in cool condition (~10^{o}C).

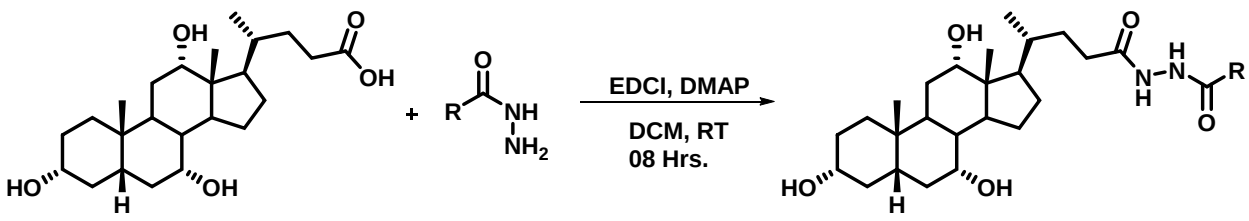
NMR spectroscopy:

All the liquid state 1D-NMR spectra (^{1}H, ^{13}C NMR) were recorded in $CDCl_3$ (comp 1), $CDCl_3$ + CD_3OD (comp 5 and 6) and CD_3OD (comp 2,3 and 4) on AC 200 MHz and AV-500 MHz Bruker NMR spectrometers. The temperature dependent ^{1}H NMR experiments for comp **1** (2 % W/V) were carried out in $CDCl_3$ by increasing temperature in 5 steps (25^{o}c, 30^{o}c, 35^{o}c, 40^{o}c and 45^{o}c successively) and for concentration dependent ^{1}H NMR experiments for comp **1** were carried out in $CDCl_3$ by using different NMR tubes of concentrations 0.2%, 0.4%, 0.8%, 1.2%, 1.7%, 2.0% and 2.5%. The ^{1}H chemical shifts were referenced to the trace of $CHCl_3$ (7.27 ppm) and MeOH (3.3 ppm).

Gelation studies:

In the gelation experiments, 5mg of the gelator was placed in a glass sample vial and 0.25 ml of solvent was added. The mixture containing 2% (w/v) of the gelator **1** in solvents DCM, $CHCl_3$ and CCl_4 dissolves at RT, while for solvents Benzene and Toluene it was warmed to the boiling point until the solid was dissolved. The vial was sealed with a cap and allowed to cool down to room temperature. After a few minutes (2 to 5 min.) the tube was inverted. The sample was defined as a gel, if no flow was observed.

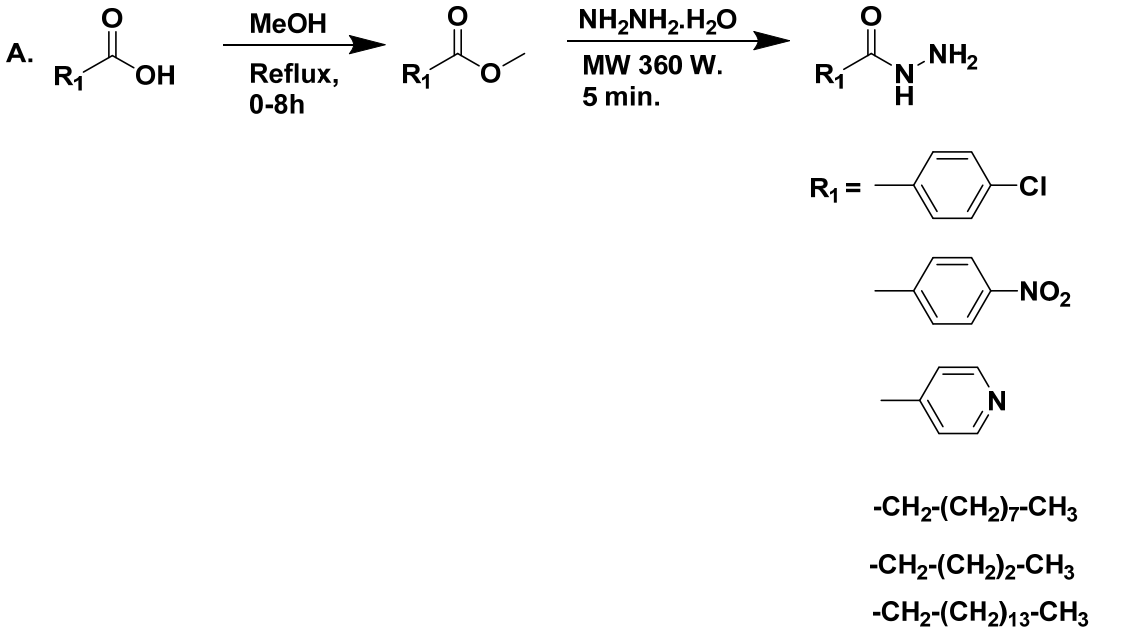
General Procedure for the synthesis of bile acid hydrazides:

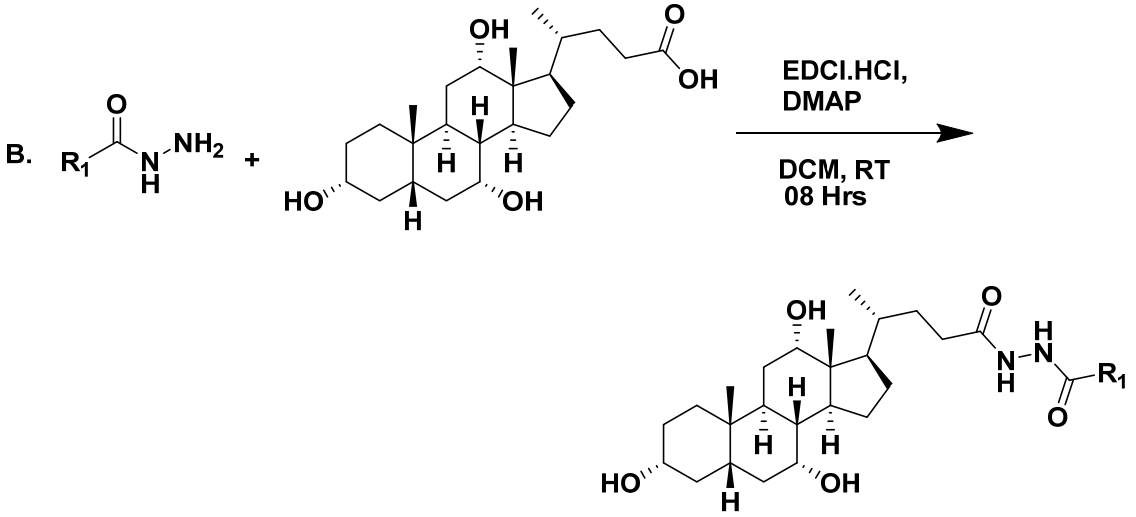


A **B** **C**

To a solution of cholic acid **(A)** (1 mmol), acid hydrazide **(B)** (1 mmol), and EDCI (1.2 mmol) dissolved in DCM (10 mL), DMAP (1.2 mmol) was added in one portion at room temperature. The reaction mixture was stirred at room temperature. After completion of the reaction, reaction mixture was extracted with 10% methanol in DCM. The organic layer was washed with saturated aqueous $NaHCO_3$, brine and was dried over Na_2SO_4. The crude product **(C)** on purification by column chromatography on silica gel yielded pure product.

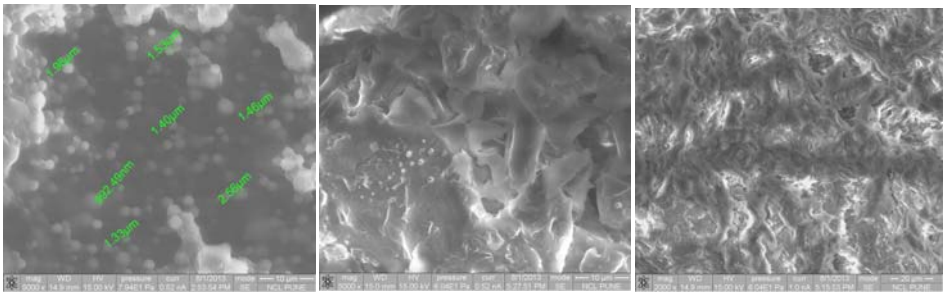
SCHEME


A.
MeOH
Reflux,
0-8h
NH2NH2.H2O
MW 360 W.
5 min.
R1 =
Cl
NO2
N
-CH2-(CH2)7-CH3
-CH2-(CH2)2-CH3
-CH2-(CH2)13-CH3

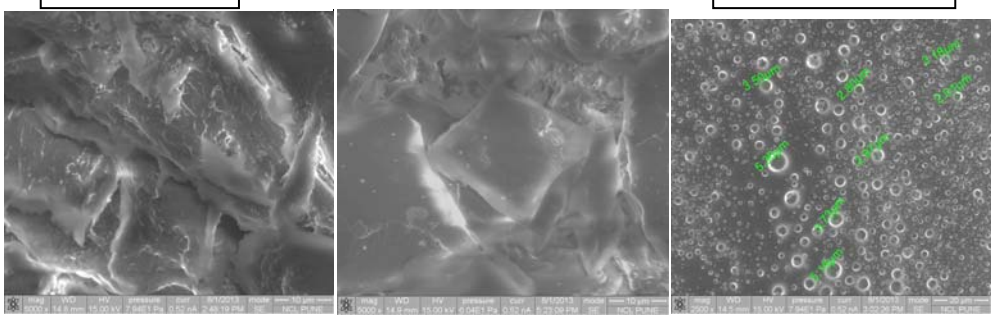

B.
+
EDCI.HCl,
DMAP
DCM, RT
08 Hrs

1 to 6

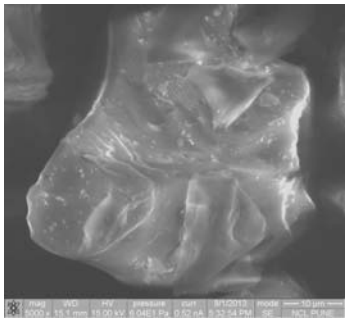
E-SEM images



Benzene Gel | Benzene Gel after Sonication | Benzene Xerogel

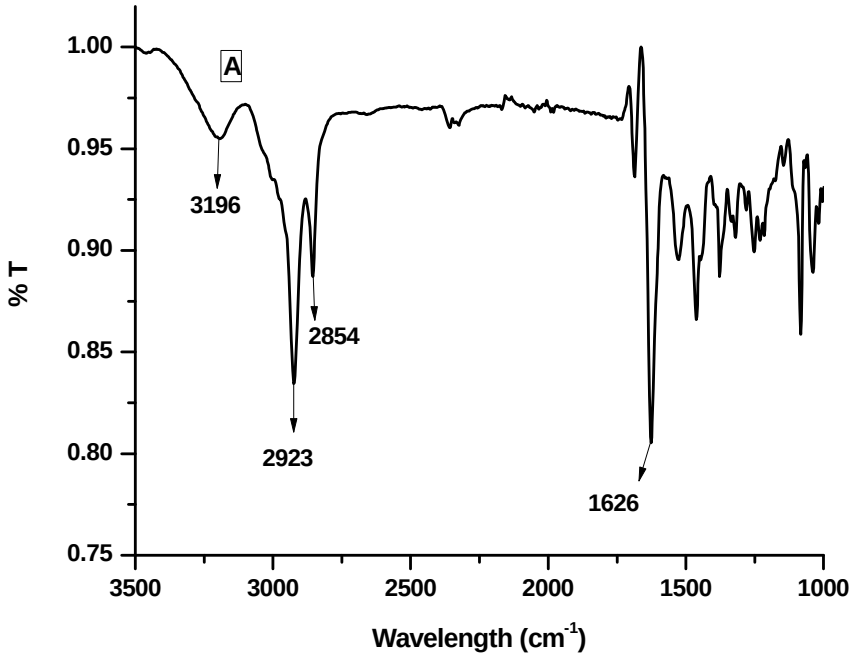


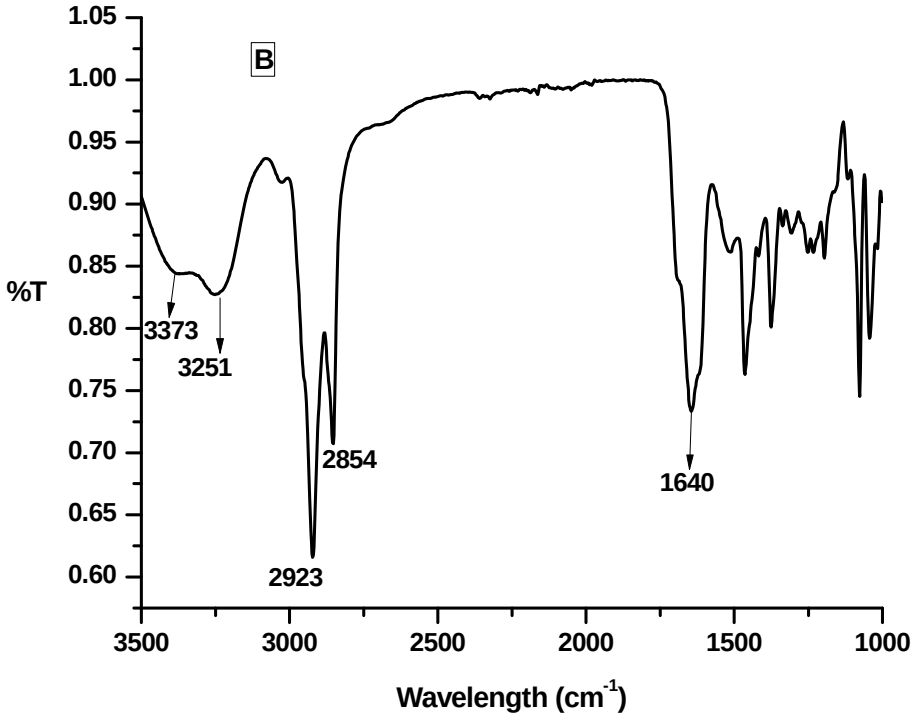
Chloroform Gel | Chloroform Gel after Sonication | Chloroform Xerogel



Sample after drying

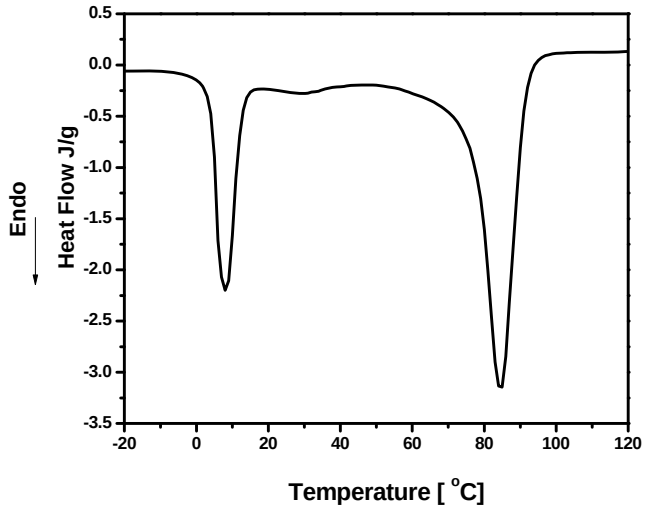
E-SEM images of gels of 2% (w/v) compound **1** (Scale bars 10 μm)



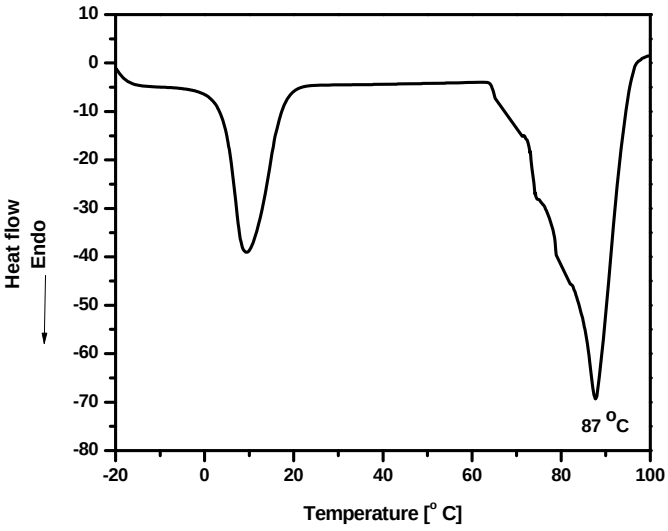


IR Spectra of (A) Chloroform Solution of 1 and (B) Chloroform gel of 1

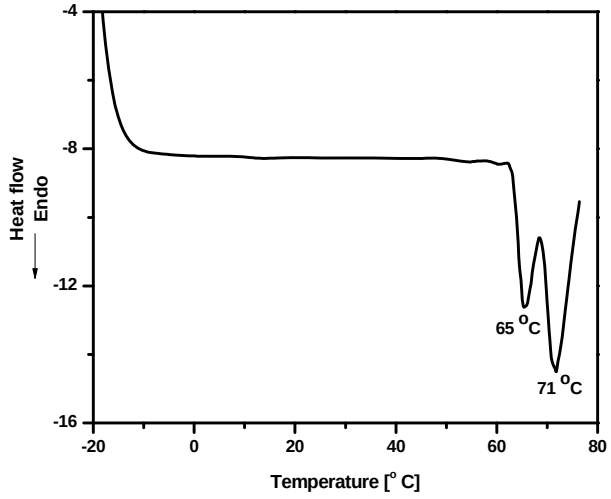
Differential Scanning Calorimetry (DSC)



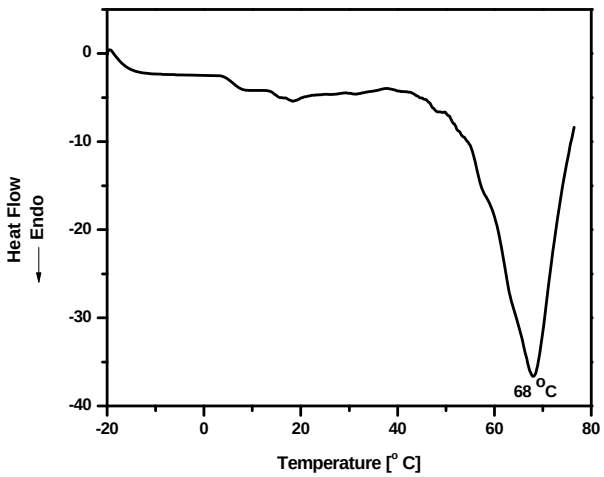
Benzene gel of compound 1



Benzene gel of compound 3



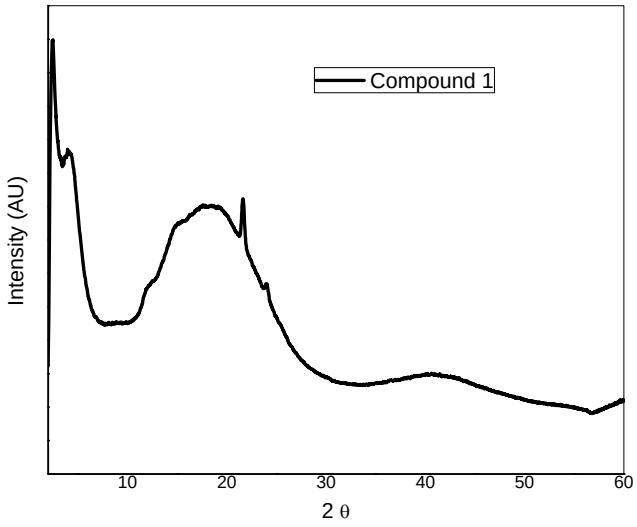
Choloroform gel of compound 1



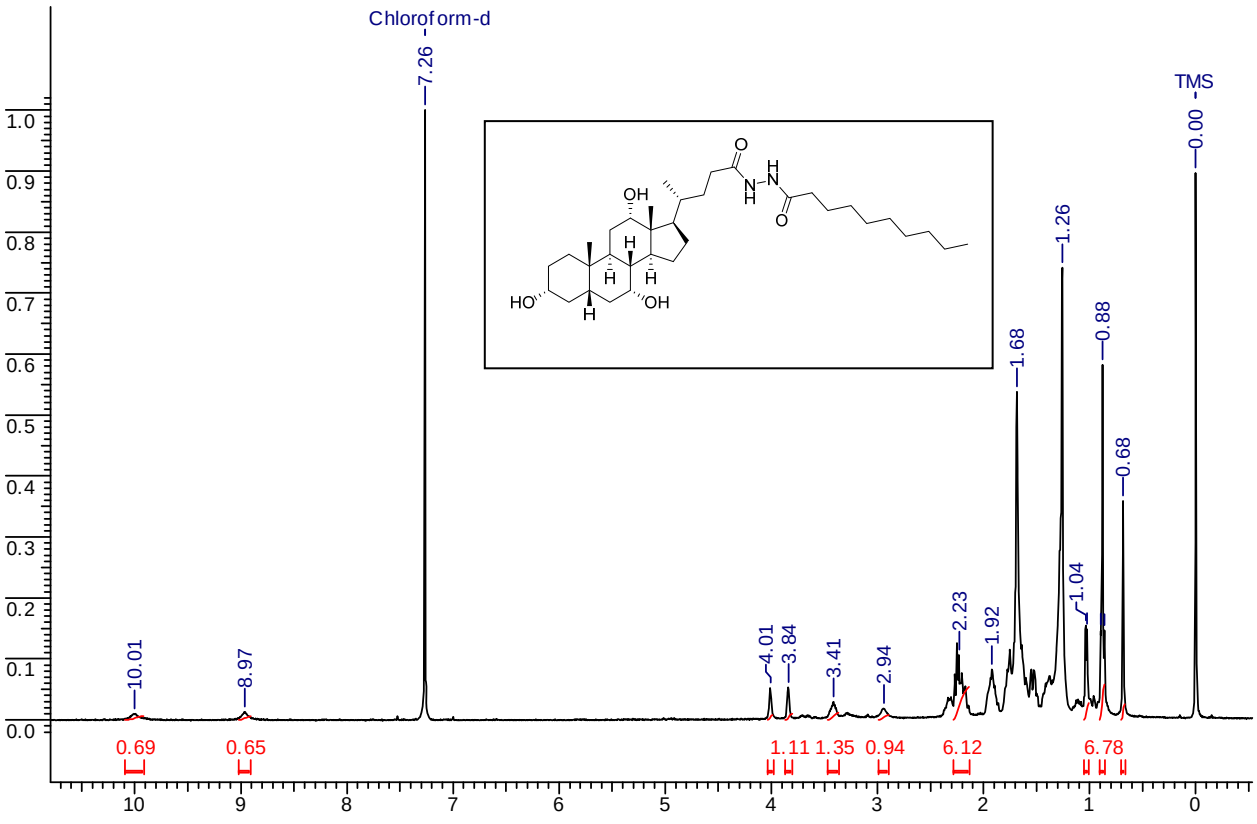
Chloroform gel of compound 3

X-ray Diffraction:

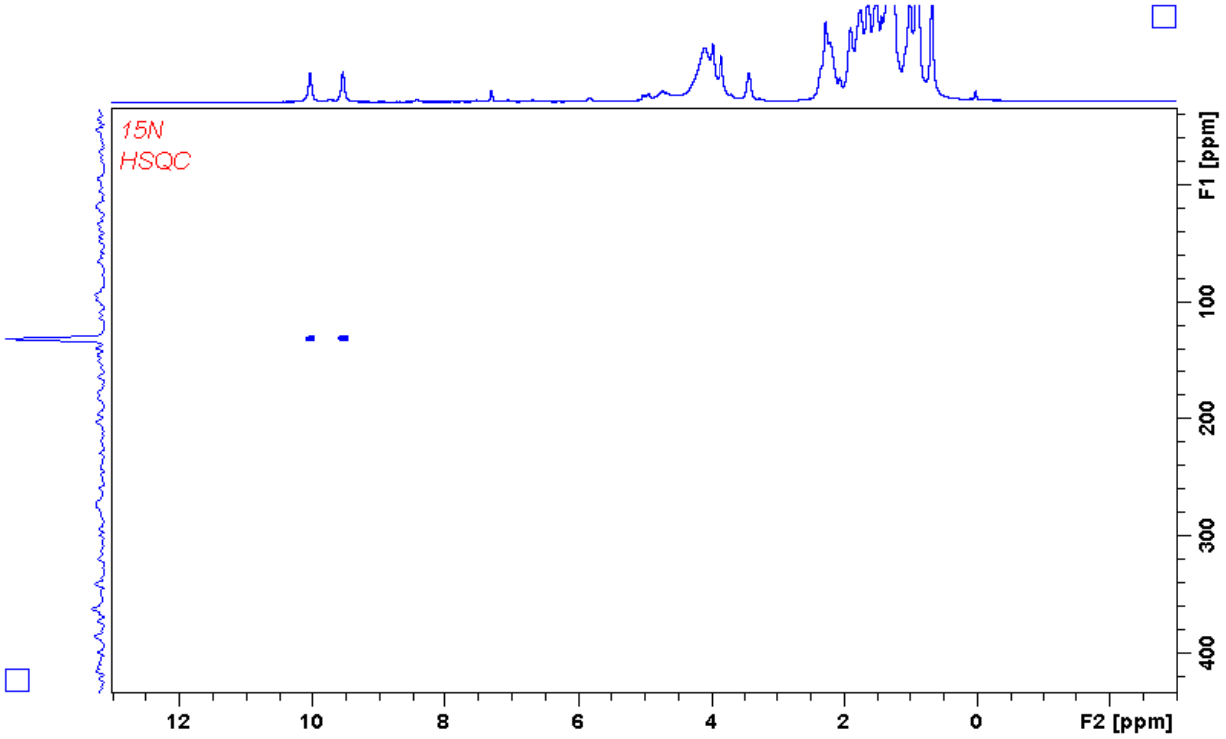
Compound **1**, 2% w/v gels are prepared in chloroform. All the solvent from gel was evaporated under vacuum. The xerogel of the compound was obtained by scratching the compound from round bottom flask and analyzed for structure using X-ray diffraction. The X-ray diffraction study of xerogel was performed on Rigaku X-ray diffraction machine with MicroMax 007 HF generator and R-AXIS IV++ detector. X-ray with Cu k_α radiation source used for the experiment. X-ray diffraction machine was operated at 40kV and 30mA. The wavelength of X-ray is 0.154nm. Xerogel sample of compound **1** was scanned from 2 ^{o} to 60^{o}. X-ray diffraction spectrum shows two broad diffraction peaks from 10 ^{o} to 30 ^{o} and 35 ^{o} to 50 ^{o} suggest high amorphous content of xerogel.

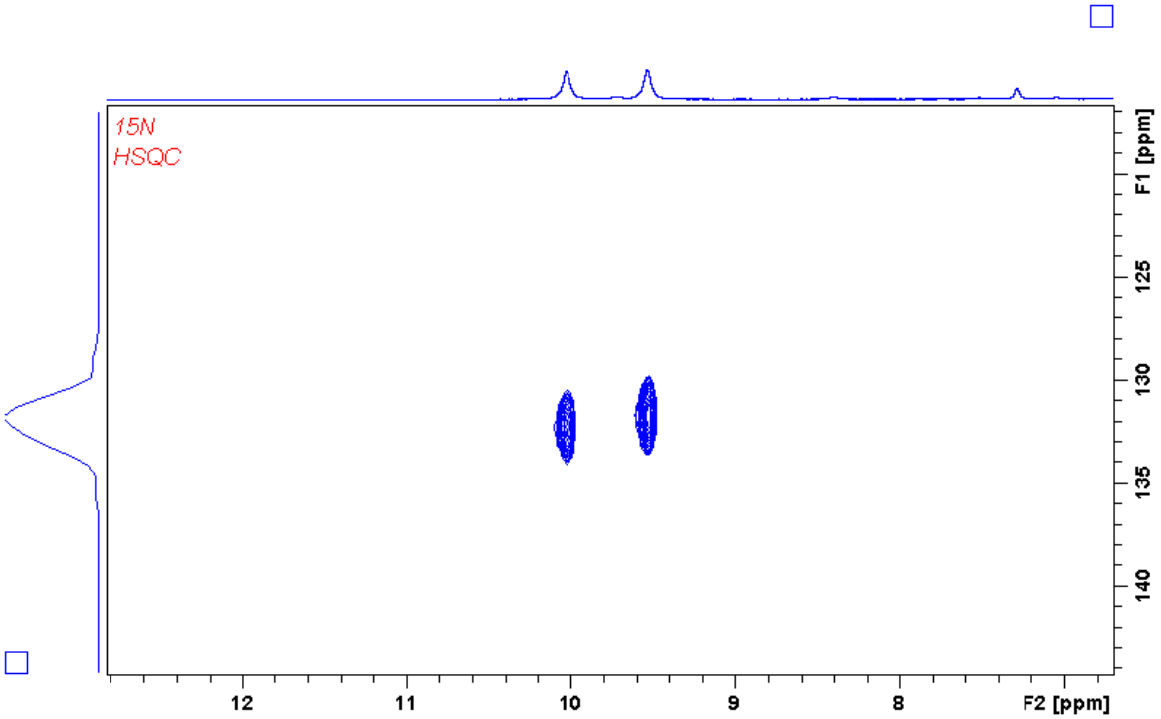


^{1}H NMR: Compound 1

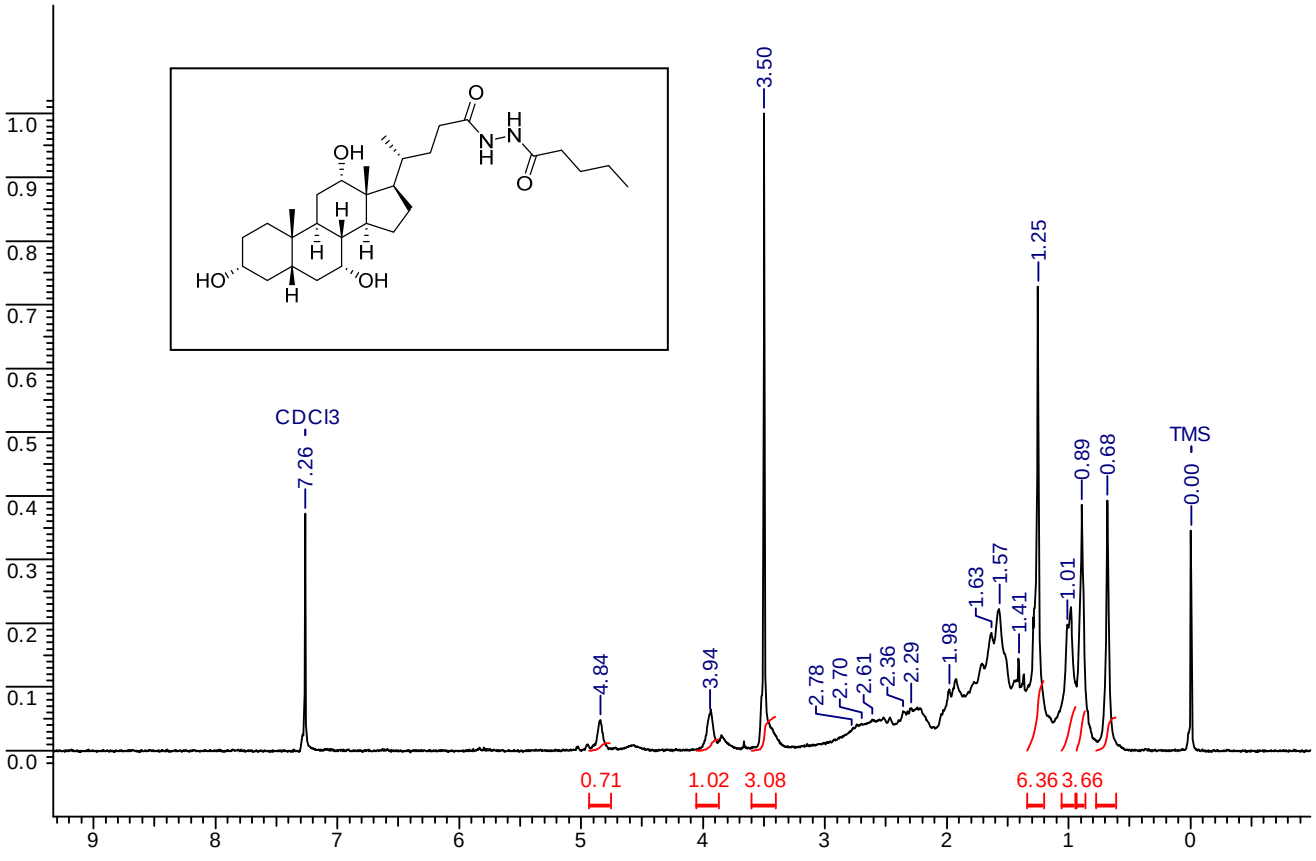


Proton-nitrogen (^{1}H-^{15}N) correlation spectrum of compound 1

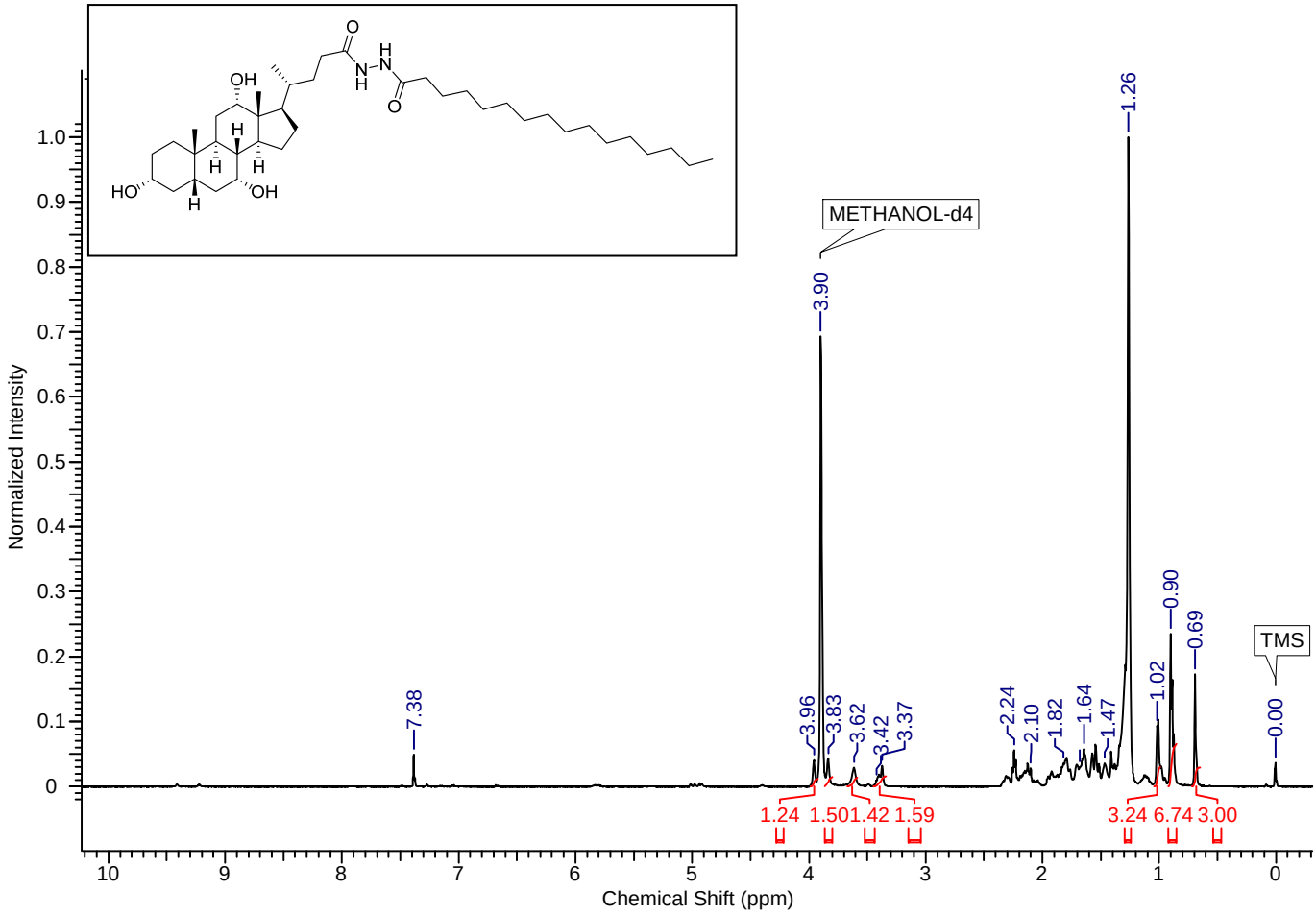




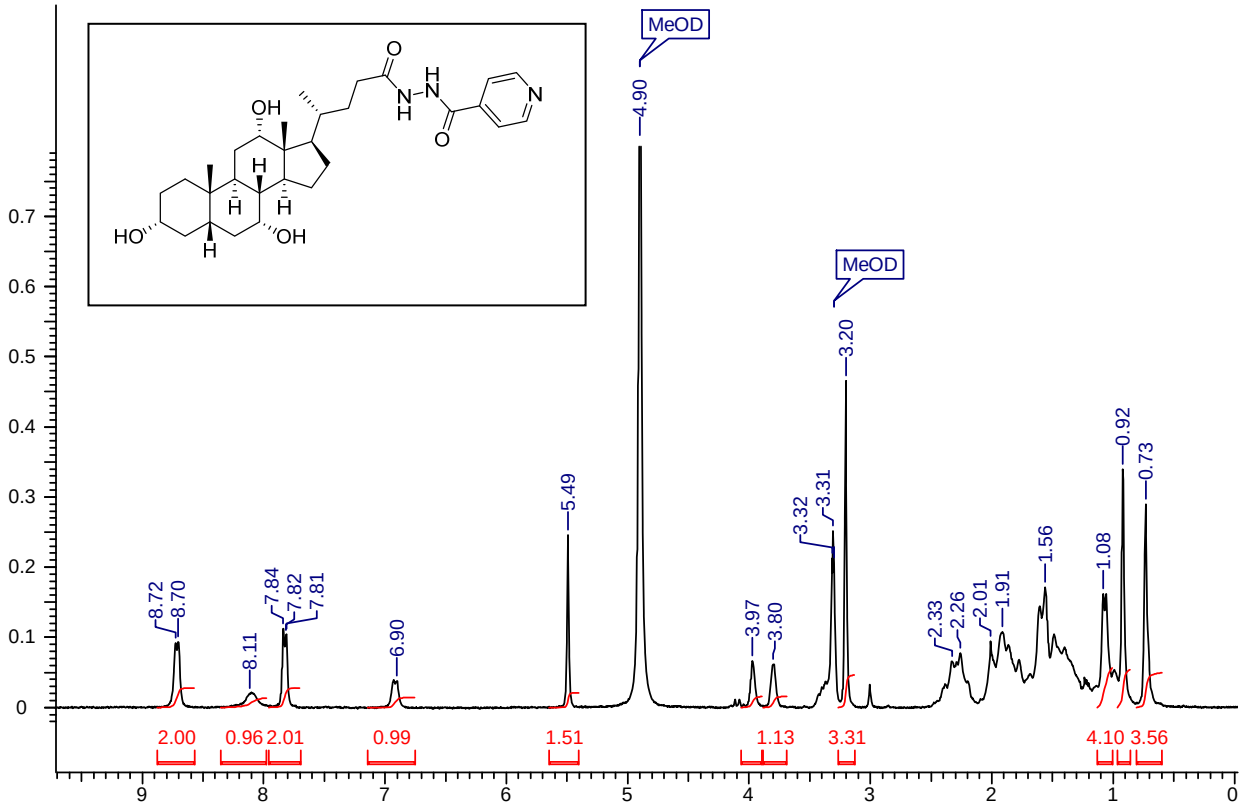
Compound 2


CDCl3
7.26
4.84
3.94
3.50
2.78
2.70
2.61
2.36
2.29
1.98
1.63
1.57
1.41
1.25
1.01
0.89
0.68
TMS
0.00
0.71
1.02
3.08
6.36
3.66
OH
HO
OH
H
N
N
O

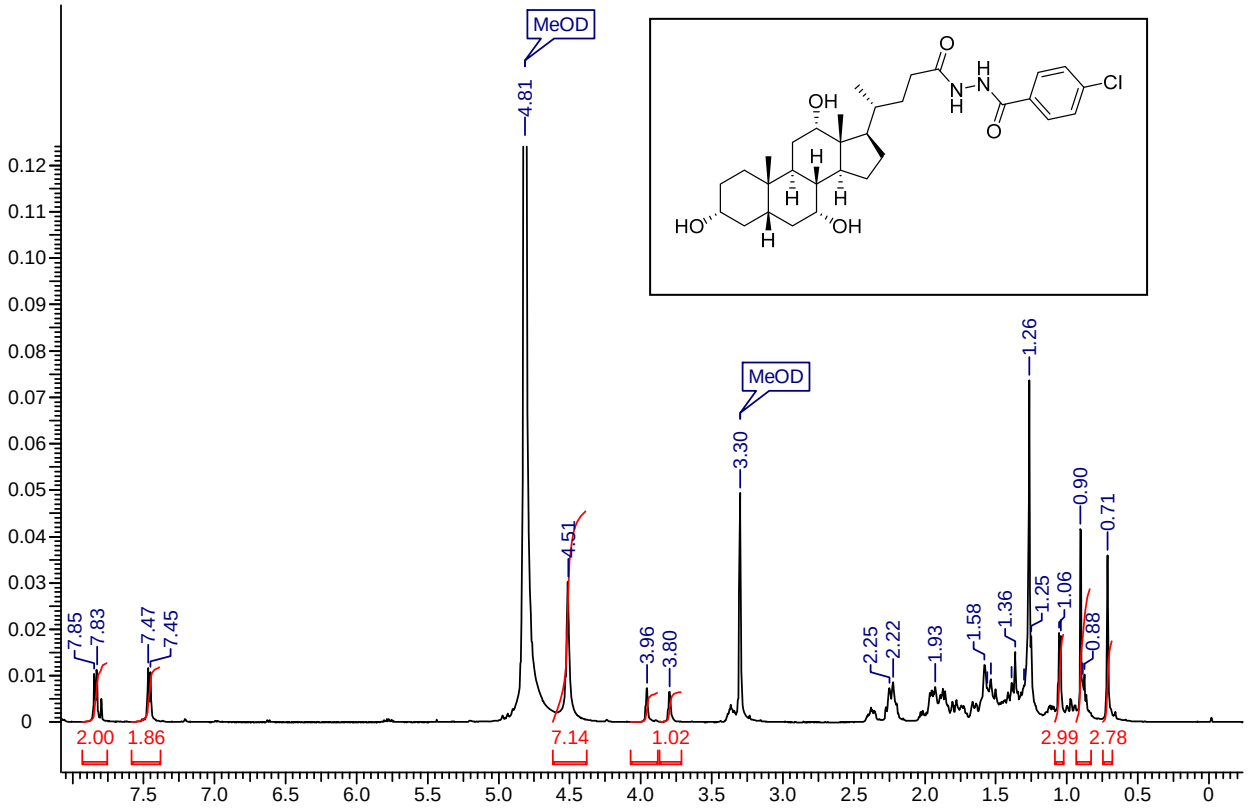
Compound 3


Normalized Intensity
Chemical Shift (ppm)
METHANOL-d4
TMS
7.38
3.96
3.90
3.83
3.62
3.42
3.37
2.24
2.10
1.82
1.64
1.47
1.26
1.02
0.90
0.69
0.00
1.24
1.50
1.42
1.59
3.24
6.74
3.00

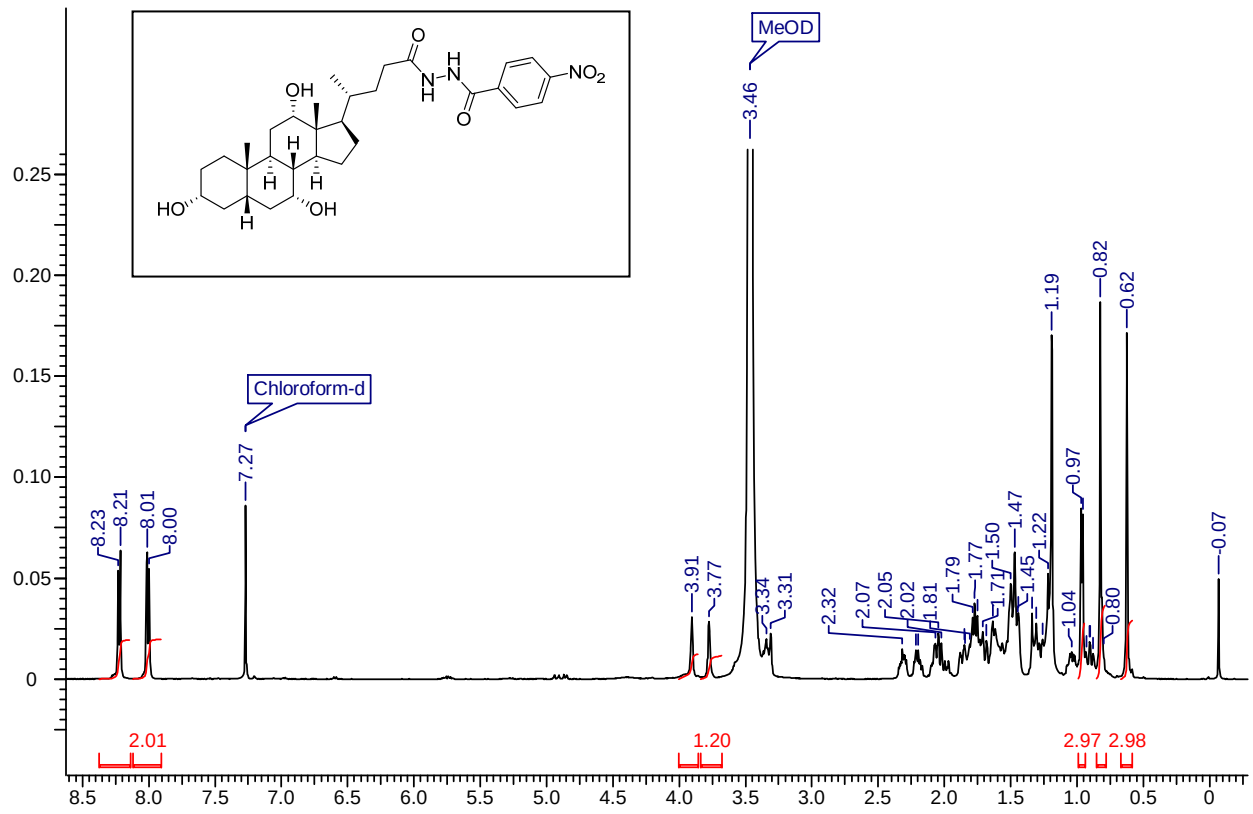
Compound 4


MeOD
4.90
MeOD
3.20
5.49
3.32
3.31
0.92
0.73
1.56
1.08
8.72
8.70
8.11
7.84
7.82
7.81
6.90
3.97
3.80
2.33
2.26
2.01
1.91
2.00
0.96
2.01
0.99
1.51
1.13
3.31
4.10
3.56

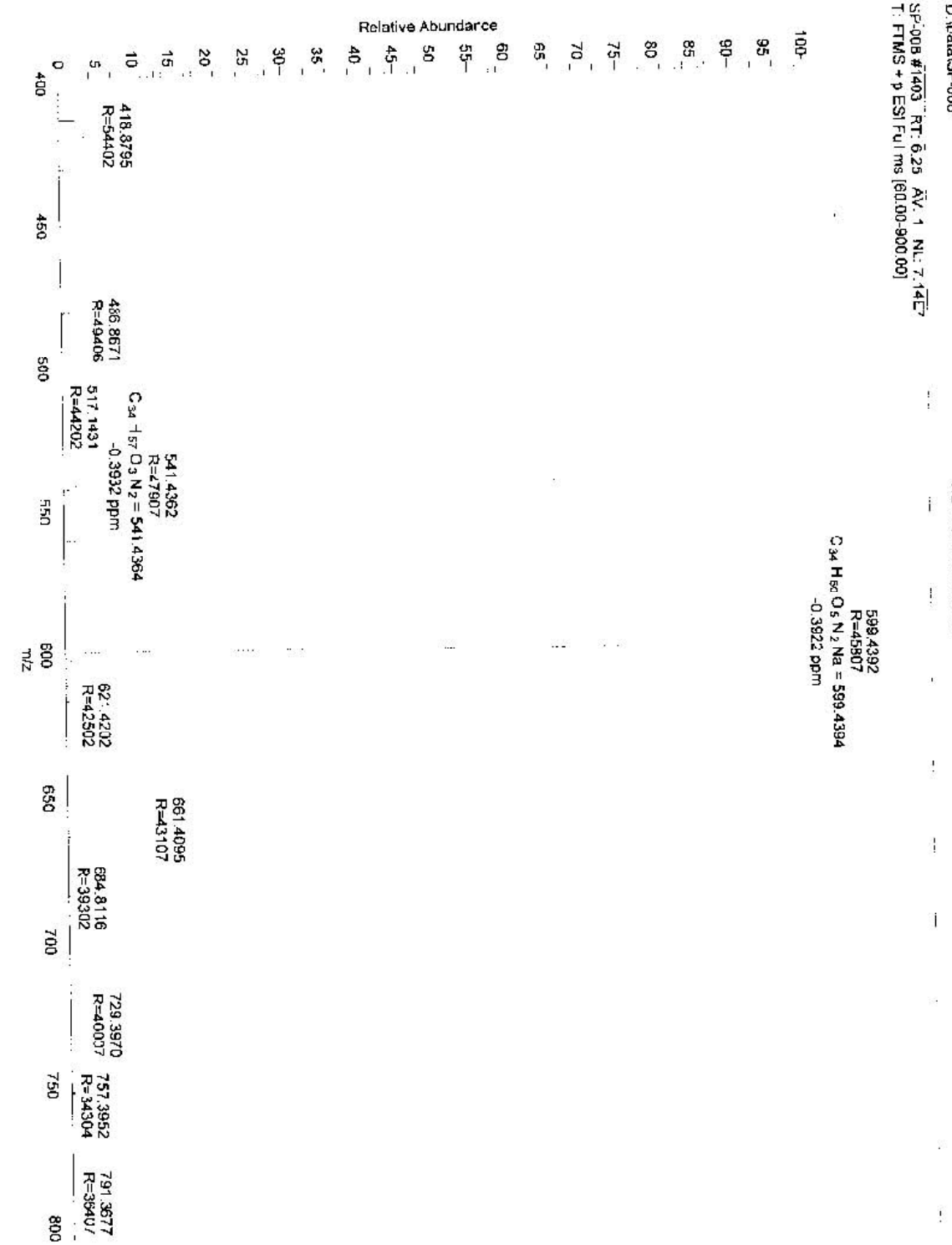
Compound 5


MeOD
4.81
4.51
MeOD
3.30
1.26
0.90
0.71
7.85
7.83
7.47
7.45
3.96
3.80
2.25
2.22
1.93
1.58
1.36
1.25
1.06
0.88
2.00
1.86
7.14
1.02
2.99
2.78
OH
HO
OH
H
H
H
H
O
N
H
N
H
O
Cl

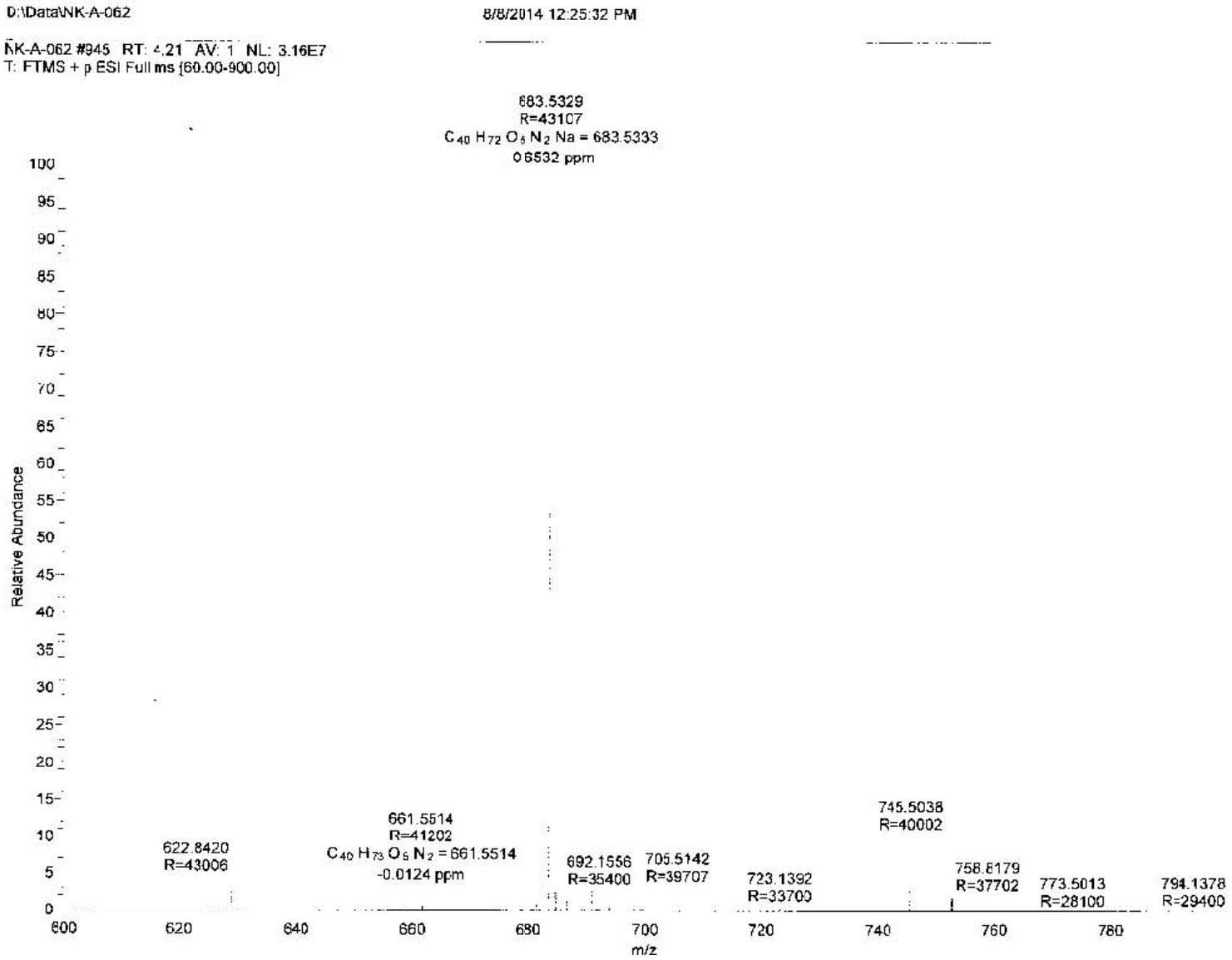
Compound 6


MeOD
Chloroform-d
8.23
8.21
8.01
8.00
7.27
3.91
3.77
3.46
3.34
3.31
2.32
2.07
2.05
2.02
1.81
1.79
1.77
1.71
1.50
1.47
1.45
1.22
1.19
1.04
0.97
0.82
0.80
0.62
0.07
2.01
1.20
2.97
2.98

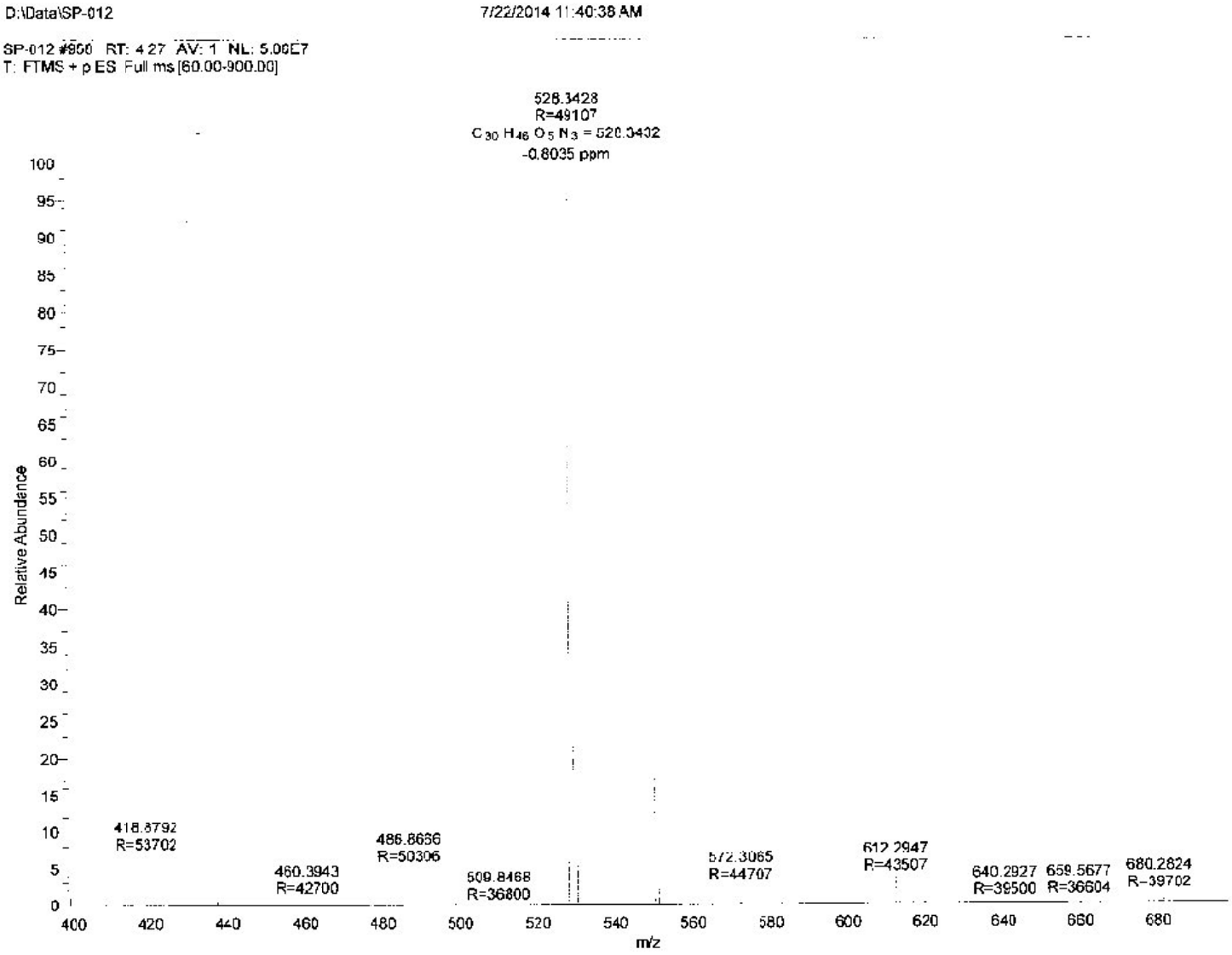
HRMS: Compound 1



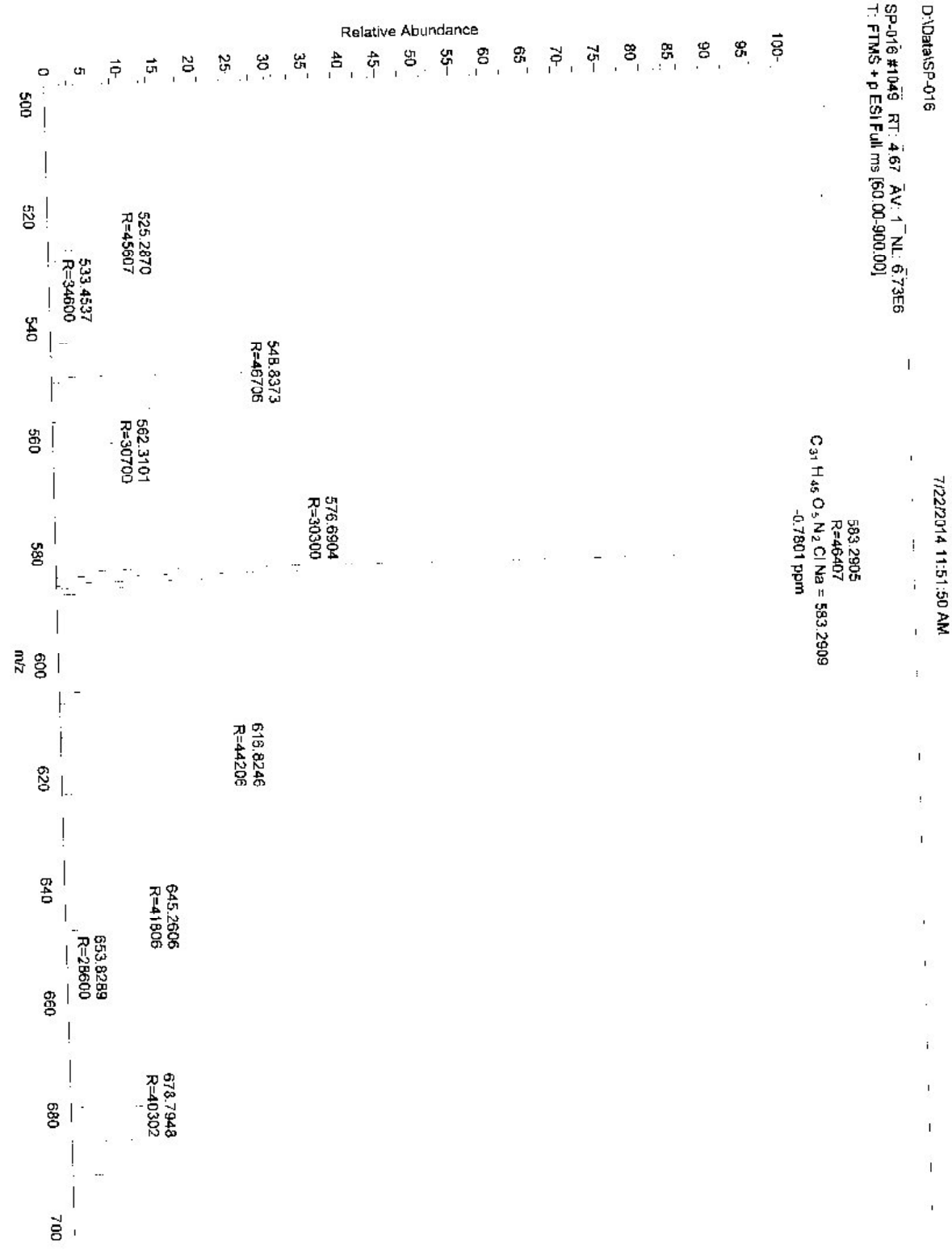
Compound 3


D:\Data\NK-A-062
8/8/2014 12:25:32 PM
NK-A-062 #945 RT: 4.21 AV: 1 NL: 3.16E7
T: FTMS + p ESI Full ms [60.00-900.00]
683.5329
R=43107
C40 H72 O5 N2 Na = 683.5333
0.6532 ppm
Relative Abundance
m/z
622.8420
R=43006
661.5514
R=41202
C40 H73 O5 N2 = 661.5514
-0.0124 ppm
692.1556
R=35400
705.5142
R=39707
723.1392
R=33700
745.5038
R=40002
758.8179
R=37702
773.5013
R=28100
794.1378
R=29400

Compound 4


D:\Data\SP-012
7/22/2014 11:40:38 AM
SP-012 #860 RT: 4.27 AV: 1 NL: 5.06E7
T: FTMS + p ESI Full ms [60.00-900.00]
528.3428
R=49107
C30 H46 O5 N3 = 528.3432
-0.8035 ppm
Relative Abundance
m/z
418.8792
R=53702
460.3943
R=42700
486.8656
R=50306
509.8468
R=36800
572.3065
R=44707
612.2947
R=43507
640.2927
R=39500
659.5677
R=36604
680.2824
R=39702

Compound 5


D:\Data\SP-016
7/22/2014 11:51:50 AM
SP-016 #1049 RT: 4.67 AV: 1 NL: 6.73E6
T: FTMS + p ESI Full ms [60.00-900.00]
583.2905
R=46407
C31 H45 O5 N2 Cl Na = 583.2909
-0.7801 ppm
Relative Abundance
m/z
525.2870
R=45607
533.4537
R=34600
548.8373
R=46706
562.3101
R=30700
576.6904
R=30300
618.8246
R=44206
645.2606
R=41806
653.8289
R=28600
678.7948
R=40302

Compound 6

D:\Data\SP-022
SP-022 #994 RT: 4.43 AV: 1 NL: 2.17E7
T: FTMS + p ESI Full ms [60.00-900.00]
594.3146
R=46507
C31 H45 O7 N3 Na = 594.3150
-0.6674 ppm
548.8372
R=46206
560.8718
R=43802
589.3597
R=43407
604.7914
R=39500
616.2963
R=43602
628.8589
R=38200
641.3095
R=39804
650.8192
R=35600
656.2850
R=43607
663.3051
R=27100
678.2672
R=34302
Relative Abundance
m/z