An aza-cyclophane stacked in racemic columnar assemblies: Whole molecular disorder in a 2D solid solution

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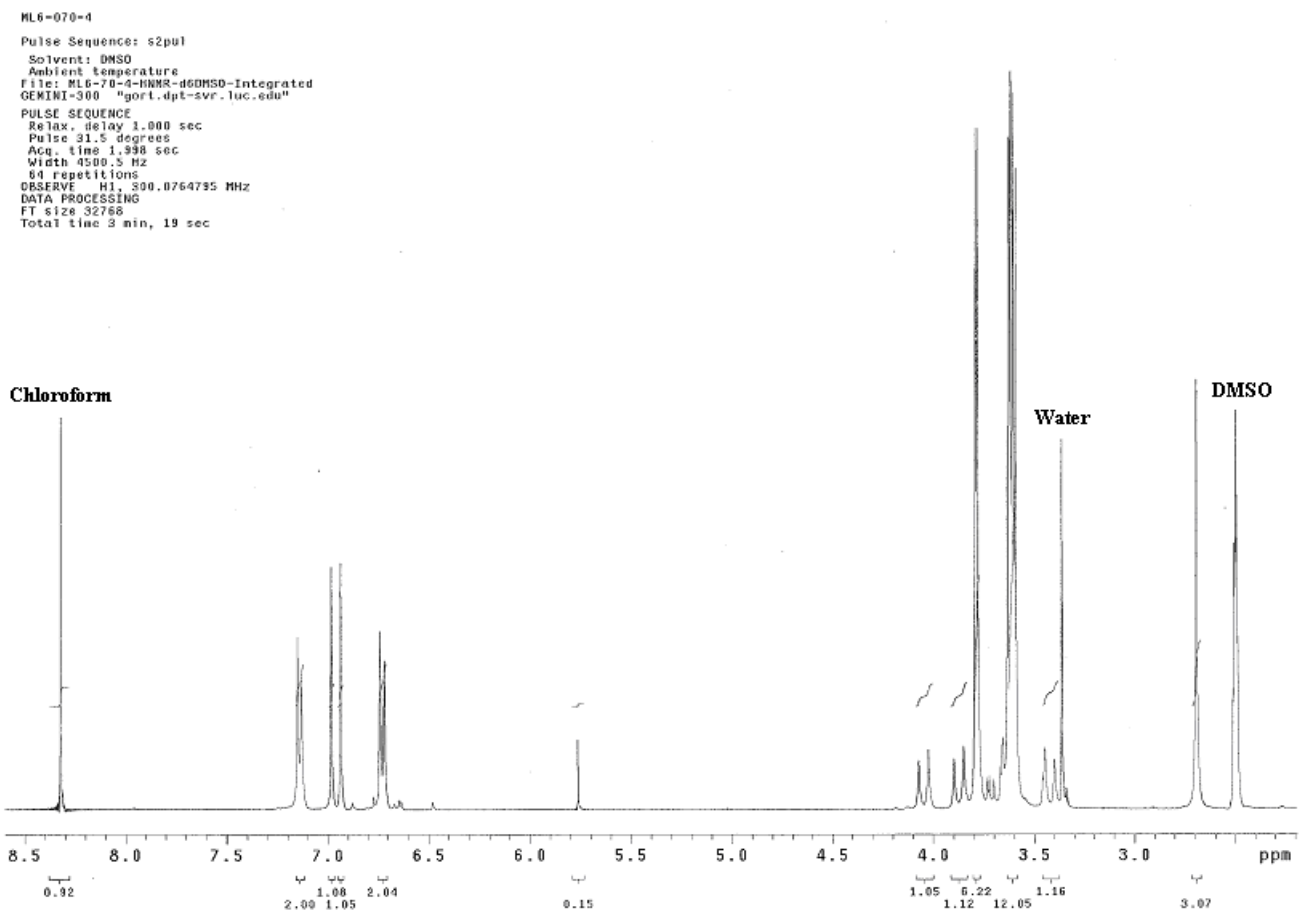
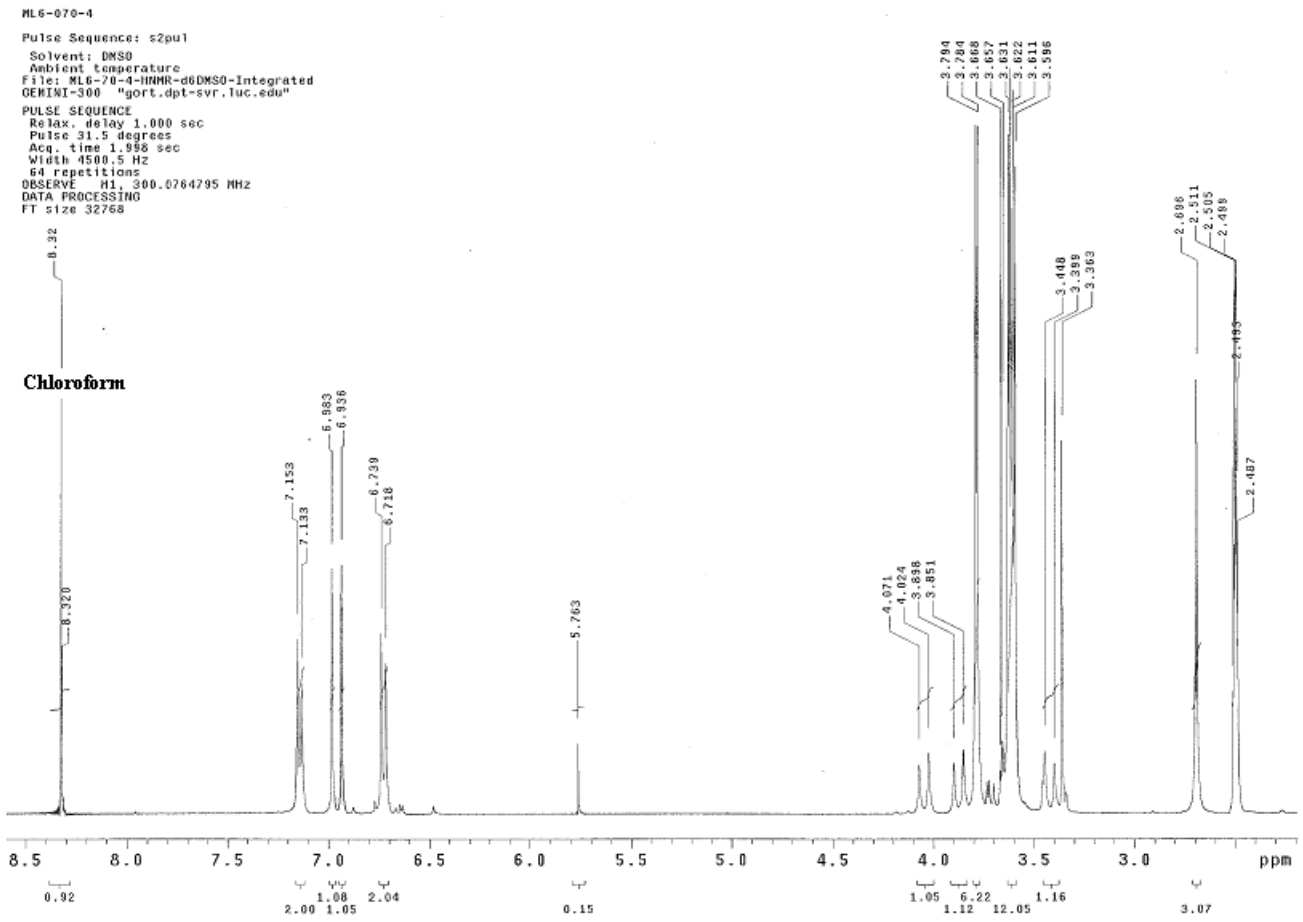
^{1}H-NMR of N-acetyl derivative 2 in d_6-DMSO with integration

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Solvent: DMSO
Ambient temperature
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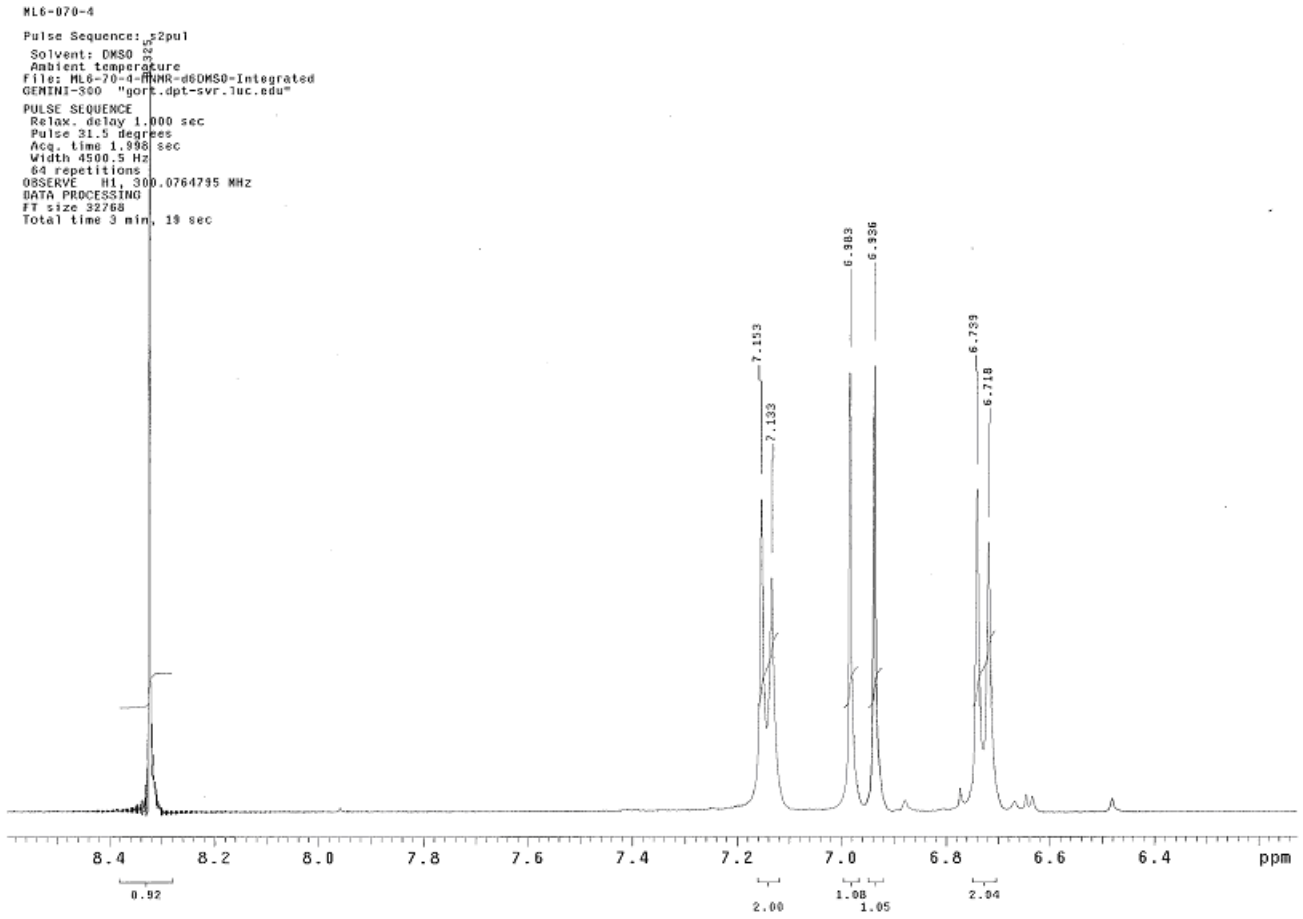
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.0764795 MHz
DATA PROCESSING
FT size 32768
Chloroform
8.32
8.320
7.153
7.133
6.983
6.936
6.739
6.718
5.763
4.071
4.024
3.898
3.851
3.794
3.784
3.668
3.657
3.631
3.622
3.611
3.596
3.448
3.399
3.363
2.696
2.511
2.505
2.498
2.493
2.487
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
0.92
2.00
1.08
1.05
2.04
0.15
1.05
1.12
6.22
12.05
1.16
3.07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Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
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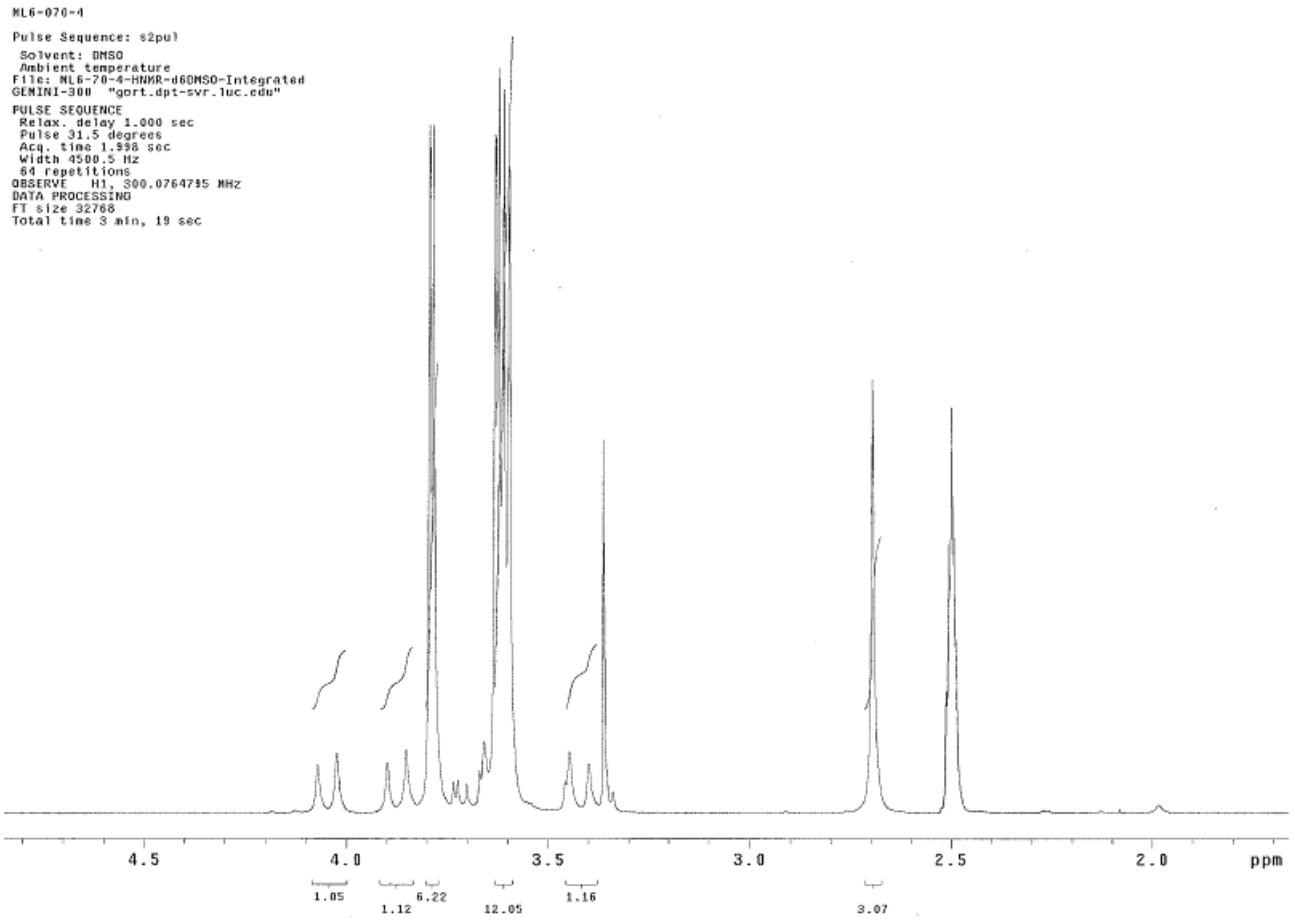
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.0764795 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 19 sec
7.153
7.133
6.983
6.936
6.739
6.718
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
0.92
2.00
1.08
1.05
2.04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Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
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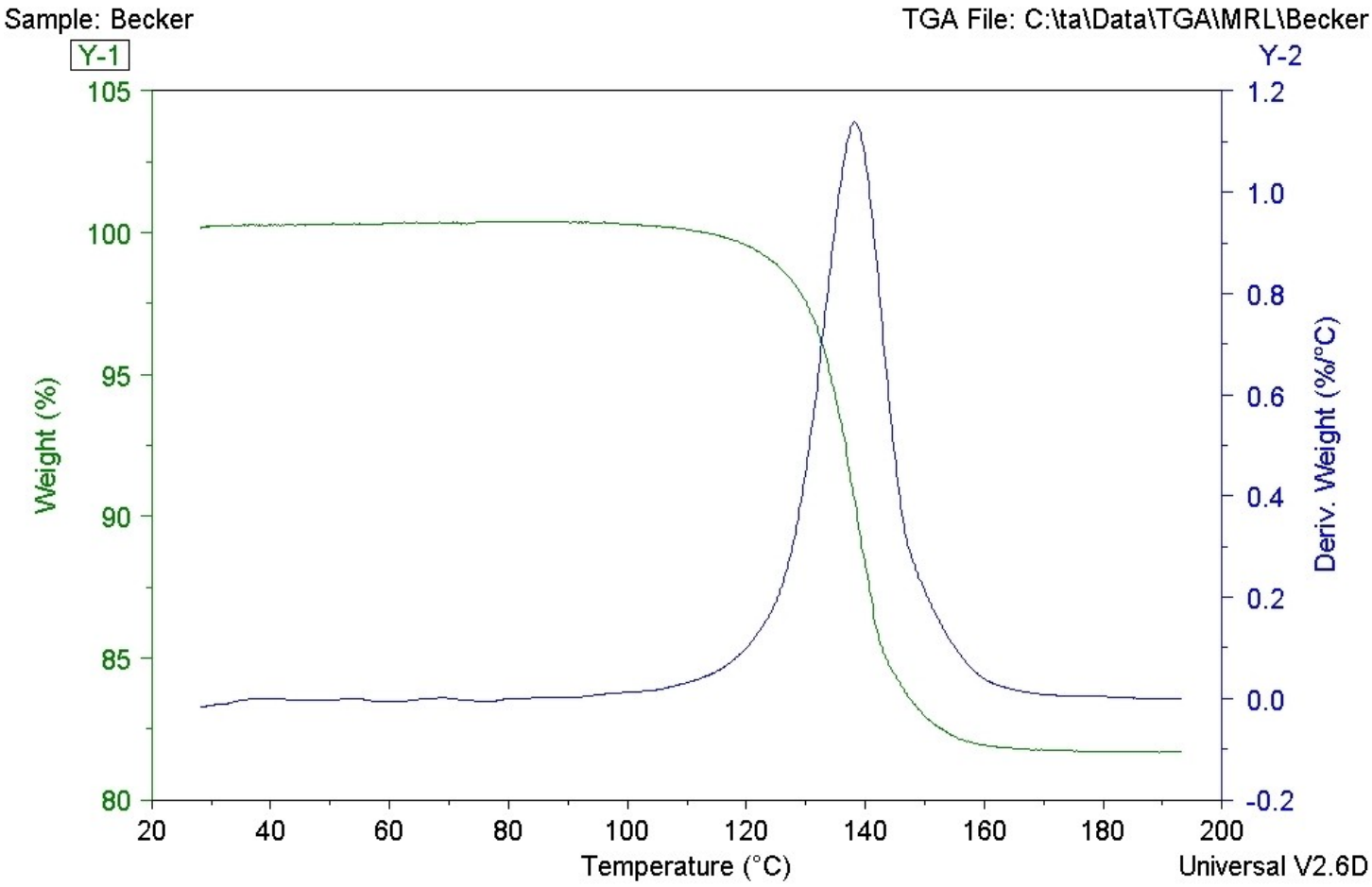
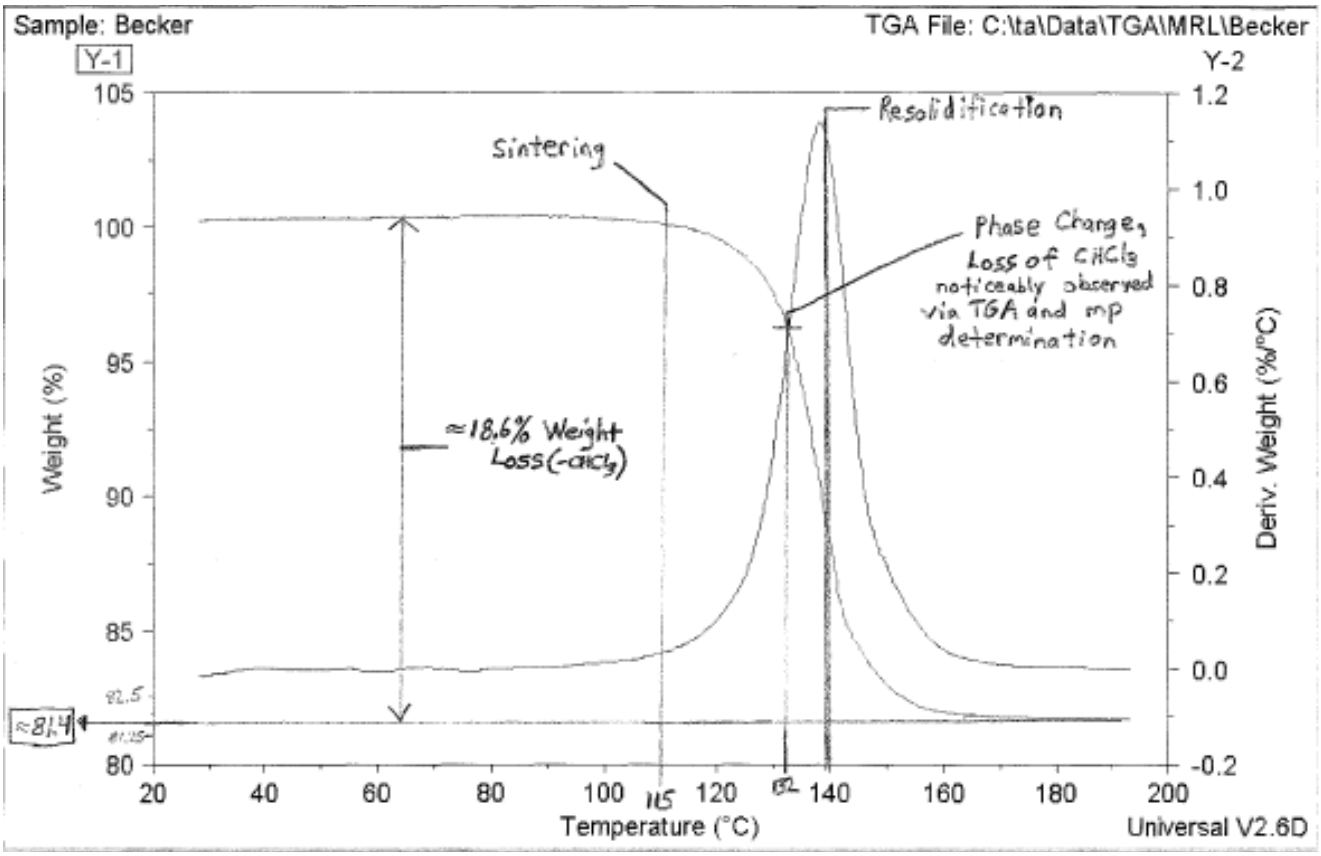
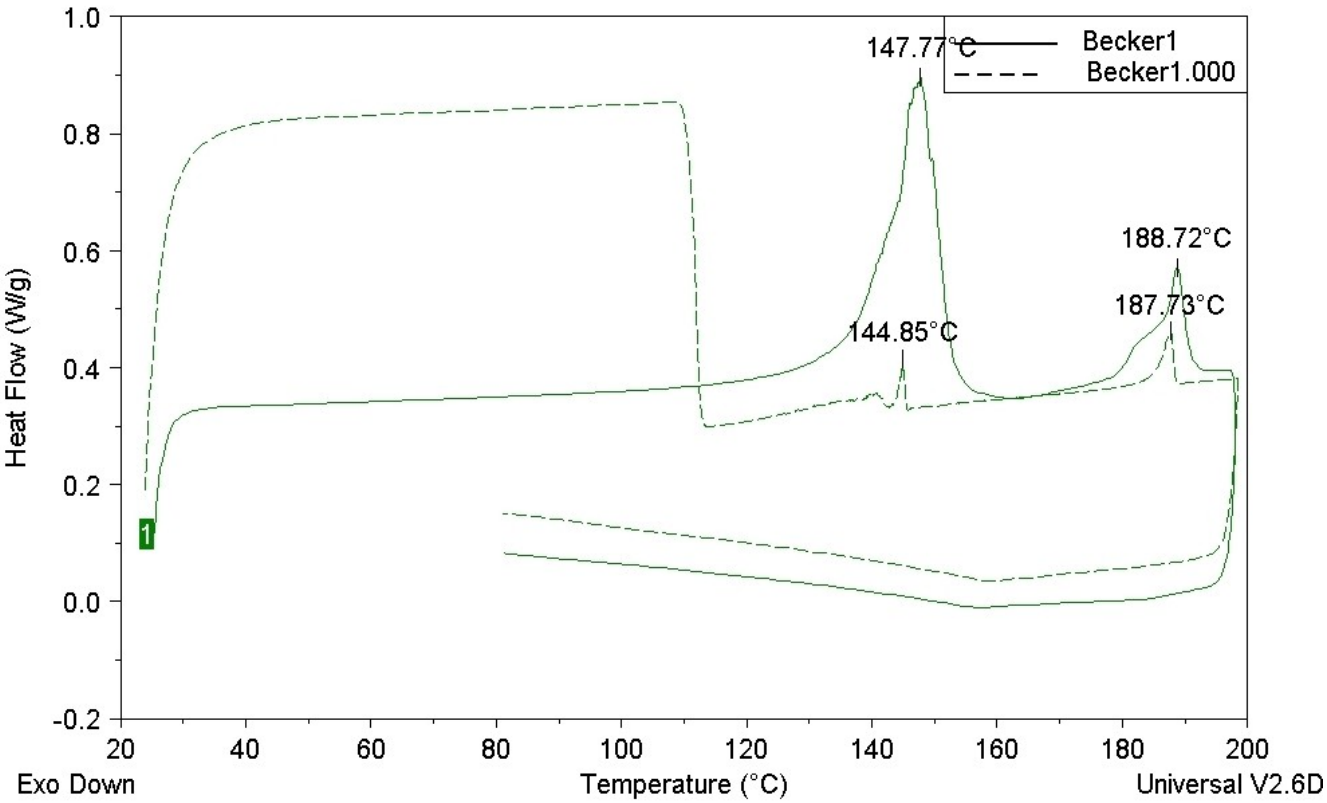
GEMINI-300 "gort.dpt-svr.luc.edu"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.0764795 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 19 sec
4.5
4.0
3.5
3.0
2.5
2.0
ppm
1.05
1.12
6.22
12.05
1.16
3.07


Sample: Becker
TGA File: C:\ta\Data\TGA\MRL\Becker
Y-1
Y-2
105
100
95
90
85
80
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
Weight (%)
Deriv. Weight (%/°C)
20
40
60
80
100
120
140
160
180
200
Temperature (°C)
Universal V2.6D


Sample: Becker
TGA File: C:\ta\Data\TGA\MRL\Becker
Y-1
Y-2
Sintering
Resolidification
Phase Change, Loss of CaCl2 noticeably observed via TGA and mp determination
≈18.6% Weight Loss (-CaCl2)
≈81.4
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V2.6D

Curve 1: Becker1

DSC File: C:\ta\Data\DSC\Becker1



TGA

TGA data were collected on a 2050 Thermographimetric Analyzer. Data were collected in open aluminum pans. Data were collected after equilibration at 28°C, followed by a 5°C/min ramp up to 200 °C.

The TGA shows loss of one chloroform molecule.

The MW of CTV-Amide N-Acetate $CHCl_3$ solvate= 640.936 g/mol
The MW of CTV-Amide N-Acetate = 521.558g/mol
The MW of $CHCl_3$ = 119.378 g/mol

Taking the difference between the $CHCl_3$ solvate and the $CHCl_3$ free CTV-Amide N-Acetate (640.936 g/mol - 521.558g/mol) gives 119.378 g/mol as expected.

Determining the weight loss: (119.378 g/mol) / (640.936 g/mol) x 100% = 18.6% weight loss. Therefore, theoretically one should observe an 18.6% weight loss if $CHCl_3$ is the solvate. Furthermore, the corresponding weight percent of 81.4% (100 - 18.6%) reflects the solvate free CTV-Amide N-acetate.

The TGA confirms the theoretical weight loss percentage (18.6%) and the remaining weight (81.4%) calculated confirming that chloroform is lost and that the ratio of chloroform to substrate is 1:1.

Also, the TGA data relates well with the classical open-capillary melting point determination. That is if you look at the bell shaped curve, this tells us when $CHCl_3$ starts and finishes evolving. At about 115 deg C, one can see that sintering occurred. At 132 deg C where the TGA curve intersects the bell shaped curve, this indicates the phase change and noticeable $CHCl_3$ evolution. At 140 deg C, over half of $CHCl_3$ has evolved, and this is the point where the material resolidifies.

MP determination observed in an open capillary using an Electrothermal Mel-Temp:

116-118 C..... sintering
132-135 C.....a phase change occurred (melting) followed by refluxing (must be $CHCl_3$ boiling off)
140 C.....resolidification
175-178 C.....a second melting point

The TGA analysis also confirms that $CHCl_3$ must be boiling off at ~ 132 C. Only one $CHCl_3$ molecule is lost.
The TGA and X-ray results complement the H-NMR results in that 1H-NMR (d6-DMSO) shows a 1:1 ratio of $CHCl_3$ to molecule **2**.

DSC

DSC data were collected on a 2910 Differential Scanning Calorimeter. Data were collected in sealed aluminum pans. The first measurement (Becker1) was conducted after equilibration at 28°C, followed by a 5° C/min ramp up to 200 °C, and recooling to 80 °C. The second measurement (Becker1.000) was conducted after equilibration at 28°C, followed by a 5°C/min ramp up to 110 °C, followed by further heating at 0.5°C/min and recooling to 80 °C, also at 0.5°C/min.

The 2nd melting point 175-178 C determined via capillary melting point is slightly different than the DSC results. The DSC data shows a melting point at about 187 C. The only two reasonable explanations of the two different results are:
1) the rate of heating
2) Closed system vs open system (Sealed pan vs open capillary). This would most likely give different results, because with the sealed pan, $CHCl_3$ is not lost, and with the capillary MP, $CHCl_3$ is lost into the atmosphere.