

Supplementary Material

Isolation of the Saddle and Crown Conformers of Cyclotrivenatrylene (CTV) Oxime

Marlon R. Lutz Jr., David C. French, Peter Rehage and Daniel P. Becker*

Loyola University Chicago, Department of Chemistry, 6525 North Sheridan Road, Chicago, IL 60626

Experimental Section

All solvents and reagents were used without further purification unless otherwise noted. Reactions were performed under an atmosphere of nitrogen. Merck silica gel 60 (230-400 mesh) was used for flash chromatography. Merck Kieselgel 60 F254 DC-Fertigplatten (0.25 mm, Art. 5719) were used for TLC. ^1H NMR spectra were obtained from either a Varian INOVA 300 or Varian Gemini 2000 300 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. Noise-decoupled and ^{13}C NMR spectra were recorded at 75 MHz on either the Varian INOVA 300 or Varian Gemini 2000 spectrometer. IR spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR using an Alfa Aesar NaCl crystal polished optic disc, (25mm x 4mm). Mass spectra were run on a Thermo Finnigan LCQ Advantage instrument. UV-Vis spectra were obtained from an Agilent 8452 Value Analysis UV-Vis Spectrometer and using Agilent UV-Vis Chemstation version 8.2 software. Melting points were obtained using an Electrothermal Mel-Temp®. CTV was prepared from veratryl alcohol in formic acid according to the procedure of Collet [Garcia, C.; Andraud, C.; Collet, A. *Supramolecular Chemistry*. **1992**, 1, 31-45] and was recrystallized from dry toluene affording guest-free crystals according to Atwood [Zhang, H.; Atwood, J. L. *J Cryst Spec Res*. **1990**, 20, 465-470].

10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTV Ketone – (2). An improvement of the method of Stevens [Cookson, R. C.; Halton, B.; Stevens, I. D. R. *J Chem Soc B: Phys Org*. **1968**, 767-774] was employed. To a solution of cyclotrivenatrylene (13.52 g, 30.0 mmol, 1.0 eq) in glacial acetic acid (91 mL) was added water (107 mL) and sodium dichromate (16.2 g, 54.0 mmol, 1.6 eq) and the dark orange solution was heated under reflux for 25 h. ^1H NMR indicated only 2-3% CTV remaining. The dark green solution was cooled to room temperature, diluted with methylene chloride (120 mL) and washed with sodium bicarbonate until the pH was basic by pH paper. The aqueous portion was extracted with methylene chloride (2 X 20 mL) and the combined organic layers were successively washed with water and brine. The organic layer was then dried over Na_2SO_4 and concentrated to give a yellow-brown foam which was chromatographed on silica gel (1080 g) eluting with EA/ CH_2Cl_2 (15/85) to afford the desired ketone (6.67 g, 48%) as a pale yellow crystalline solid: mp 207-208°C (lit 213-214 °C: Cookson, R. C.; Halton, B.; Stevens, I. D. R. *J Chem Soc B: Phys Org*. **1968**, 767-774]. UV-vis and IR identical to reported values; 60 MHz ^1H NMR reported previously. ^1H NMR (300 MHz, CDCl_3) δ 7.43 (2H, s), 6.76 (2H, s), 6.49 (2H, s), 3.96 (6H, s),

3.92 (6H, s), 3.81 (6H, s), 3.77 (4H, br s). ^{13}C NMR (75 MHz, CDCl_3) δ 194.3, 152.8, 148.0, 147.7, 133.2, 133.0, 132.2, 114.5, 112.9, 111.7, 56.4, 56.2, 56.0, 37.1.

10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV Oxime Crown (3) and CTV Oxime Saddle (4). To a solution of CTV ketone **2** (194 mg, 0.430 mmol, 1.0 eq) in pyridine (2.0 mL) was added hydroxylamine hydrochloride (4.30 mmol, 10.0 eq) and the resulting solution was heated under reflux for 16 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in methylene chloride (12 mL) and washed successively with 1N hydrochloric acid (2 X 25 mL), water (1 X 20 mL), and brine. The organic layer was then dried over Na_2SO_4 and concentrated to give an off white foam which was chromatographed on silica gel (18 g) eluting with EA/ CH_2Cl_2 (20/80) to afford the oxime crown conformer **3** (0.144 g, 70%) as a colorless solid that was crystallized from MeOH to afford colorless needles: mp 139-141°C; UV-Vis (EtOH): λ_{max} 235 (log ϵ = 4.54), 290 (log ϵ = 4.07); IR (thin film from CH_2Cl_2) 3441, 3288, 3203, 3057, 3001, 2934, 2846, 1606 (str, C=N), 1514, 1464, 1345, 1263, 1223, 1127, 1081, 734 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 9.41 (1H, br s), 6.96 (1H, s), 6.90 (1H, s), 6.86 (1H, s), 6.81 (2H, s), 6.71 (1H, s), 4.77 (1H, d, J = 13.8 Hz), 4.38 (1H, d, J = 13.5 Hz), 3.89 (3H, s), 3.87 (3H, s), 3.83 (12 H, s), 3.58 (1H, d, J = 13.8 Hz), 3.50 (1H, d, J = 13.5 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 158.4, 149.2, 149.1, 147.7, 147.5, 147.4, 147.2, 133.0, 131.2, 131.1, 131.0, 128.0, 127.0, 112.6, 112.5, 112.4, 110.9, 108.6, 56.0, 55.9, 55.8, 55.7, 36.7, 36.0. MS MH^+ calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_7$ 480.20, found 480.20. The sample was stored at -80°C immediately after chromatographic isolation and concentration.

Further elution afforded saddle oxime **4** (0.055 g, 27%) as a colorless glass: mp 222-224°C (softens at 201-203°C); UV-Vis (EtOH): λ_{max} 237 (log ϵ = 4.54), 286 (log ϵ = 4.10) nm. IR (thin film from CH_2Cl_2) 3442, 3296, 3057, 3001, 2933, 2851, 1607 (str, C=N), 1514, 1464, 1347, 1263, 1214, 1215, 1081, 735 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 8.88 (1H, br), 7.32 (1H, s), 6.70 (2H, s), 6.67 (1H, s), 6.64 (1H, s), 6.53 (1H, s), 4.02 (2H, s), 3.89 (3H, s), 3.86 (3H, s), 3.85 (3H, s), 3.84 (6H, s), 3.80 (3H, s), 3.54 (2H, s). ^{13}C NMR (75 MHz, CDCl_3) δ 157.3, 149.6, 149.4, 147.4, 147.2, 147.0, 146.9, 132.8, 132.1, 130.4, 130.3, 127.2, 125.1, 113.9, 113.7, 113.6, 112.2, 110.8, 110.5, 60.3, 55.8, 38.7, 36.9 ppm. MS MH^+ calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_7$ 480.20, found 480.20. The sample was stored at -80°C immediately after chromatographic isolation and concentration.

^1H NMR Study of the Cyclotrimeratrylene Oxime Saddle-Crown Equilibrium and Its Interconversion Kinetics

^1H NMR was utilized to study the conversion of the saddle conformer to the crown conformer. The equilibrium constants K_{eq} and conversion time constants for the oxime of CTV dissolved in CDCl_3 and $\text{dmsO}-d_6$ were determined at 25°C.

Samples of the crown and saddle conformers of the oxime of CTV were isolated by column chromatography. Samples of the saddle conformer dissolved in CDCl_3 and $\text{dmsO}-d_6$ were maintained at 25°C for one week until the ratio of the two conformers ceased to change and equilibrium had been reached. The equilibrium ratio of saddle and crown conformers was then determined by ^1H NMR spectroscopy at 25°C by measuring the ratio of saddle to crown peak intensities in the aromatic region of the spectra. This ratio was found to be 48:52 (saddle to

crown) for the oxime dissolved in CDCl_3 , and 8:92 (saddle to crown) for the oxime dissolved in $\text{dmsO}-d_6$. These data furnished an equilibrium constant $K_{\text{eq}} = 0.92$ for the oxime dissolved in CDCl_3 , and a $K_{\text{eq}} = 0.087$ in $\text{dmsO}-d_6$ at 25°C .

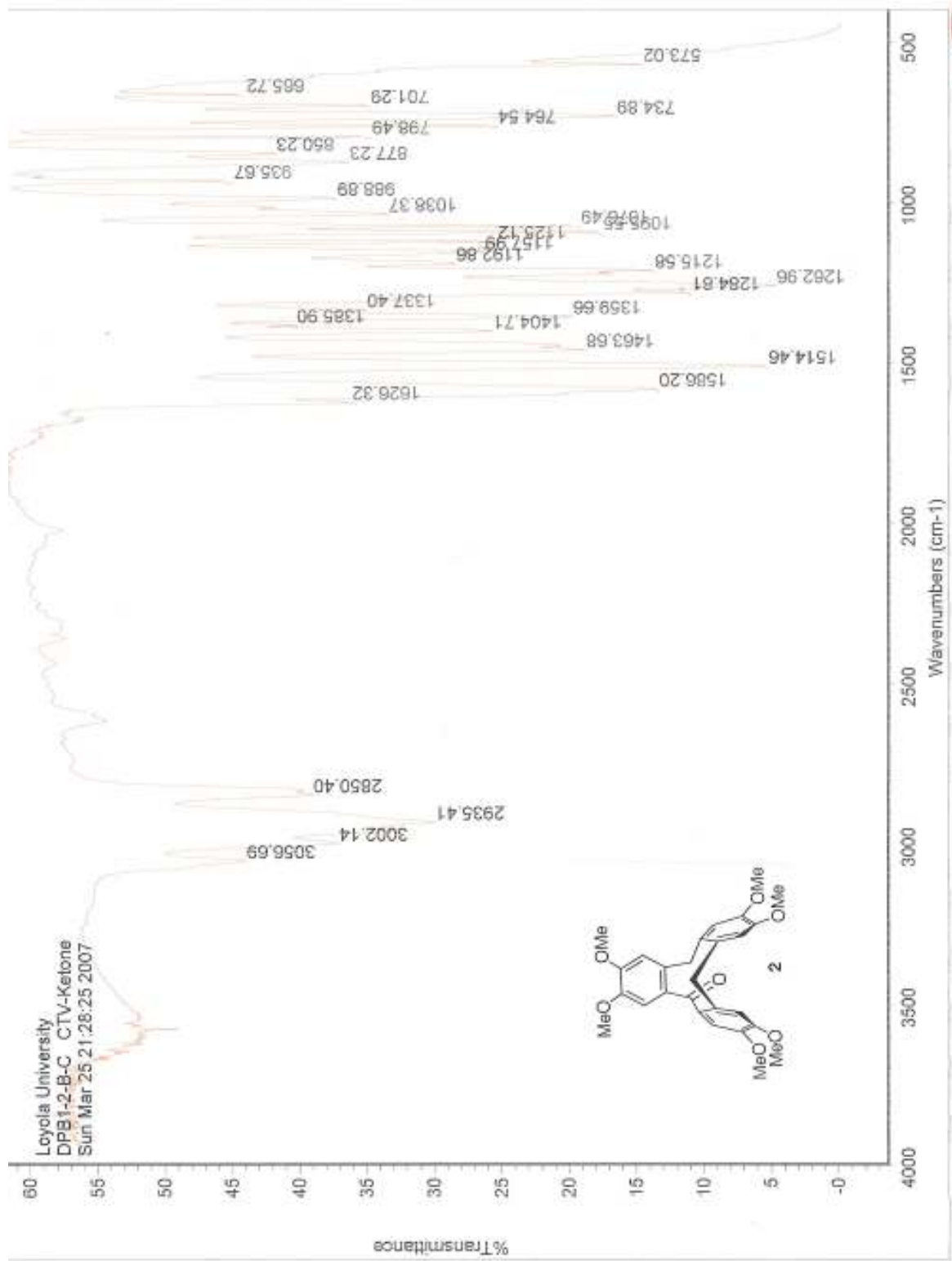
Freshly prepared samples of the saddle conformer dissolved in CDCl_3 and $\text{dmsO}-d_6$ were maintained at 25°C in the NMR for 18 and 20 hrs, respectively. The decrease in the ^1H NMR saddle peak intensities in the aromatic region was recorded as a function of time. Non-linear curve fitting of the exponential decrease of the saddle peak intensity, utilizing the Varian kinetics software, furnished the time constant $\tau = 1.275 \times 10^4$ s (3.54 hr) for the conversion of saddle to crown dissolved in CDCl_3 and $\tau = 1.926 \times 10^4$ s (5.35 hr) in $\text{dmsO}-d_6$ at 25°C .

The time constant τ is the inverse of the rate constant k . Thus, $k = 7.843 \times 10^{-5} \text{ s}^{-1}$ for the conversion of saddle to crown dissolved in CDCl_3 and $k = 5.192 \times 10^{-5} \text{ s}^{-1}$ in $\text{dmsO}-d_6$. From the first order rate law, the half-life for the conversion is $t_{1/2} = \ln(2) / k$. Therefore,

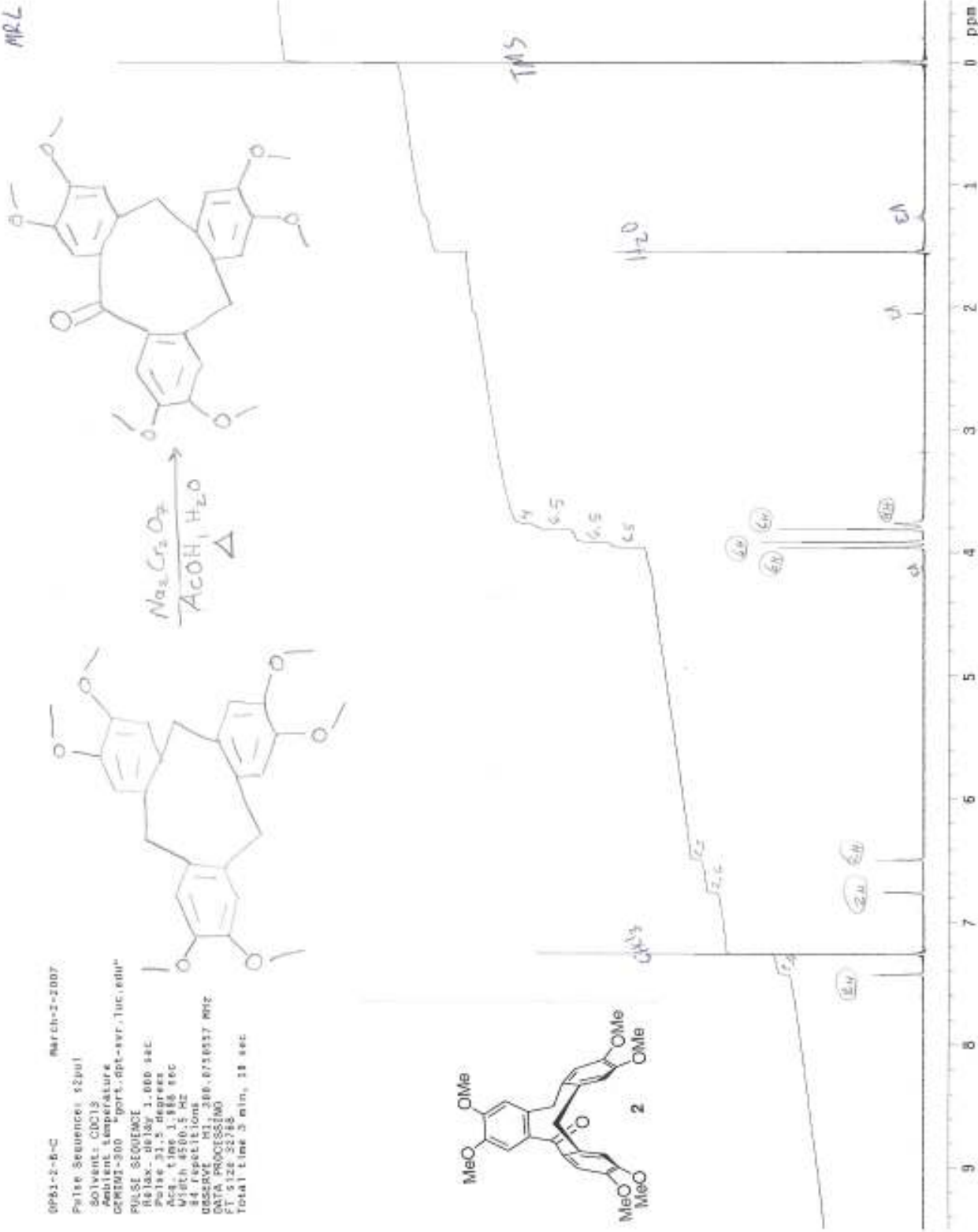
$t_{1/2} = \ln(2) / 7.843 \times 10^{-5} \text{ s}^{-1} = 8,837.6 \text{ s}^{-1}$ (2.45 hr) in CDCl_3 and $t_{1/2} = \ln(2) / 5.192 \times 10^{-5} \text{ s}^{-1} = 13,350.0 \text{ s}^{-1}$ (3.71 hr) in $\text{dmsO}-d_6$ at 25°C .

This investigation shows that there is a definite solvent dependence for both the rate of conversion from saddle to crown and the final equilibrium saddle : crown ratio. Conversion of the saddle to the crown is faster for the CTV oxime dissolved in CDCl_3 than in $\text{dmsO}-d_6$ at 25°C , and the final equilibrium ratio of crown to saddle is an order of magnitude greater in $\text{dmsO}-d_6$ than in CDCl_3 .

10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTV
Ketone – (2). Infrared spectrum

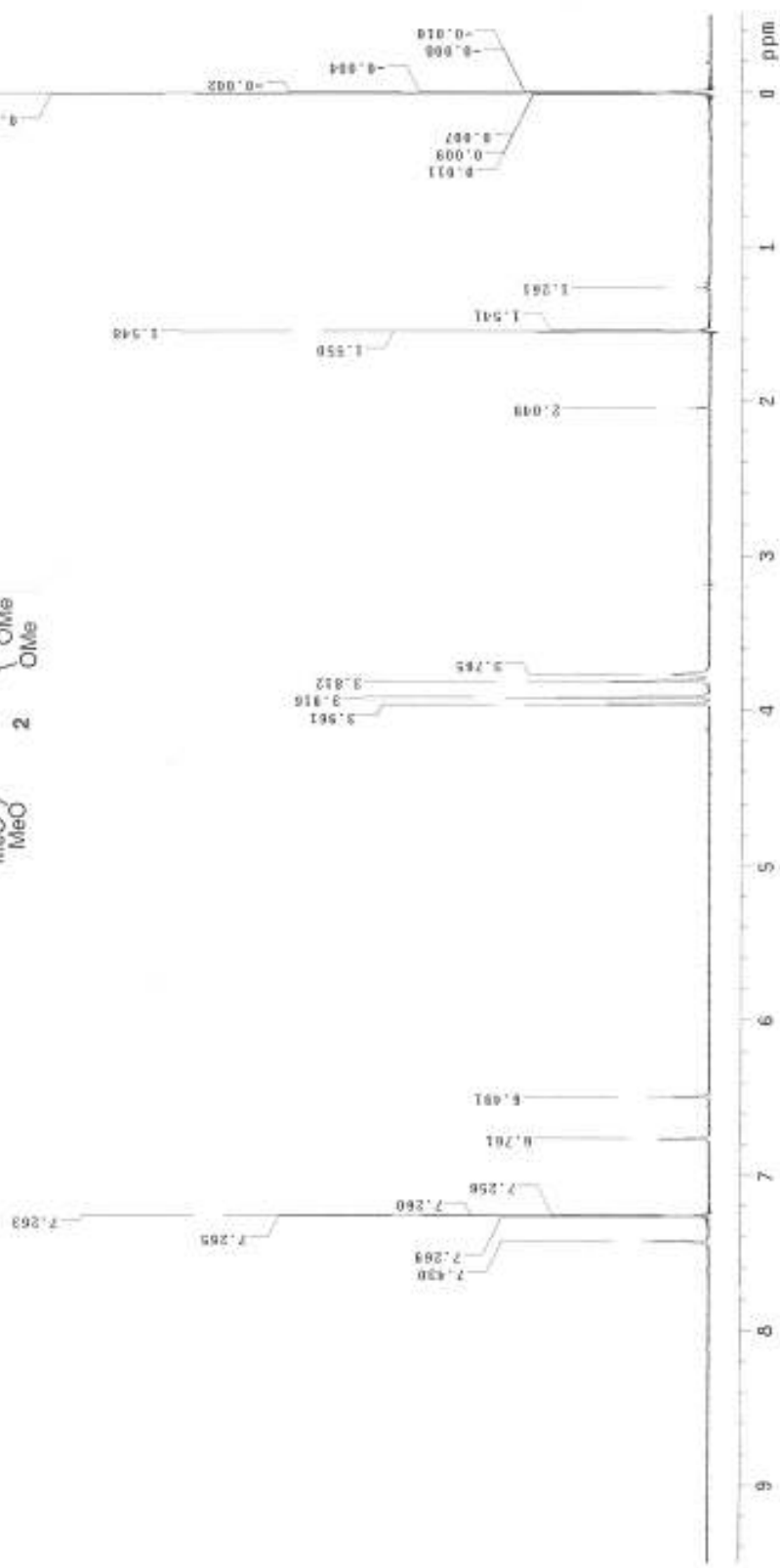
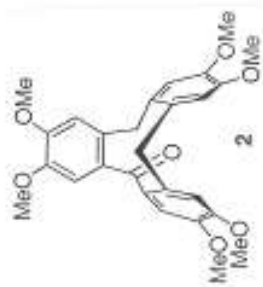


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTV
Ketone - (2). ¹H NMR Spectrum



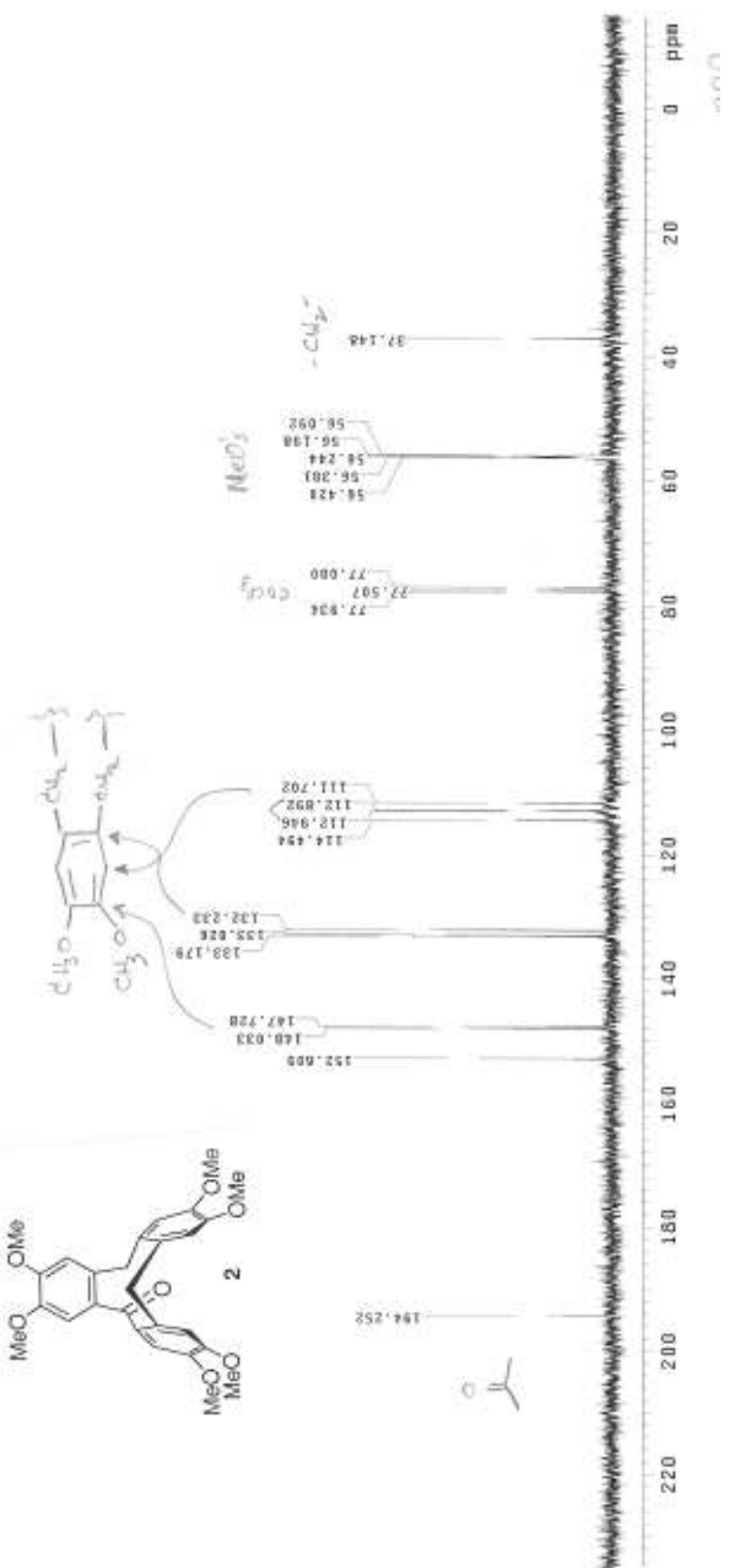
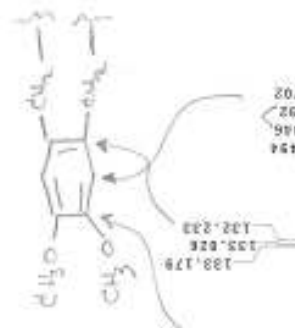
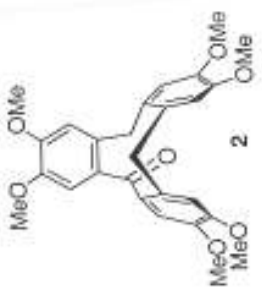
**10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTV
Ketone – (2). ¹H NMR Spectrum**

DPBI-2-B-C March-2-2007
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 CPMAS-300 90pt-90t-svt-1uc.edu*
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 Relax delay: 1.000 sec
 pulse: 31.5 degree
 Acq. time: 1.995 sec
 Vprch: 6500.5 Hz
 64 repetitions
 QASERVE M1 300.6750517 MHz
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 F1 size 32748
 Total time 3 min, 18 sec

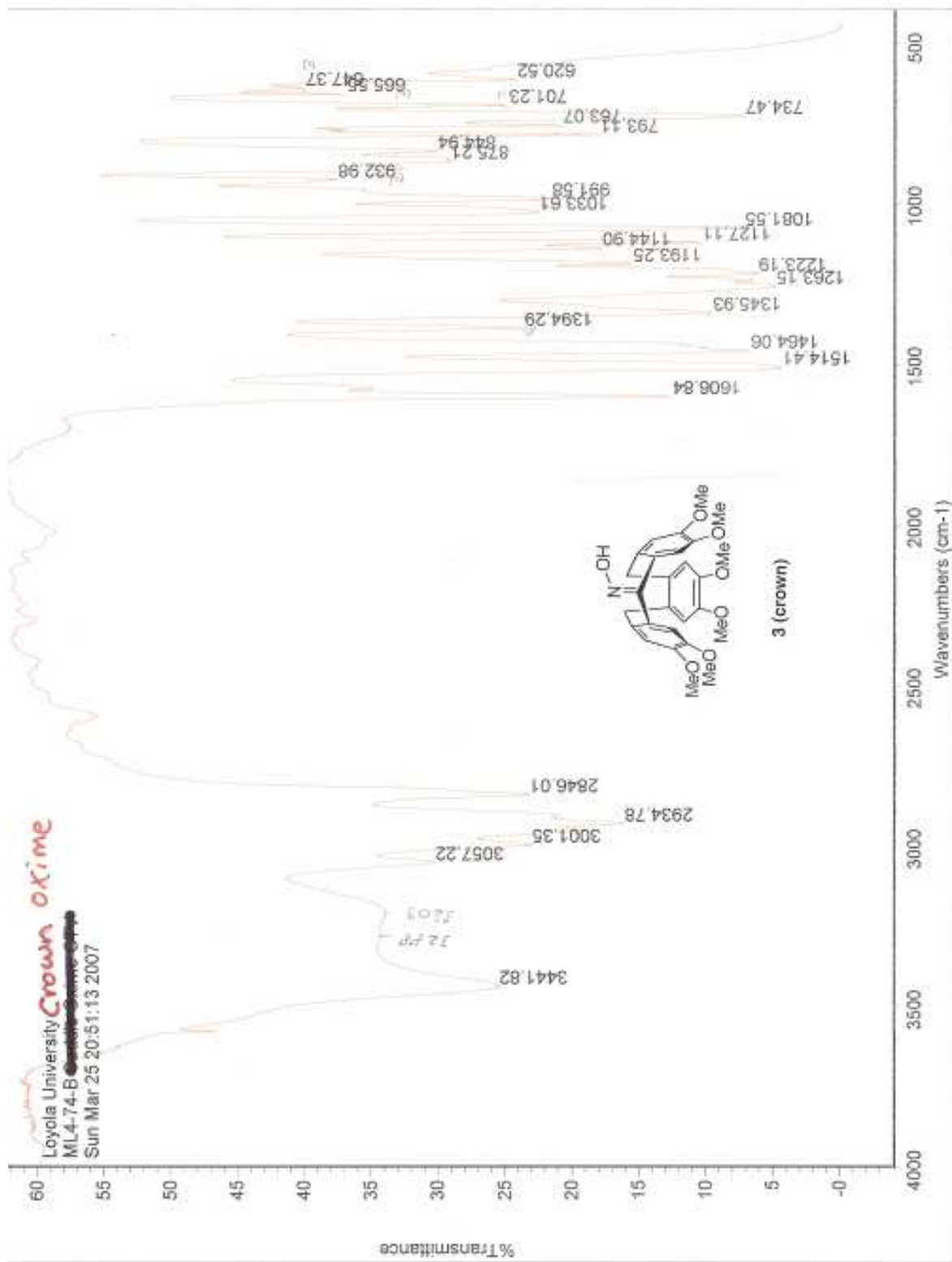


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTU
 Ketone – (2). ¹³C NMR Spectrum

DP51-2-5-C March-2-2007
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 Sample directory:
 File: CARBON
 Pulse sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 2NOVA-308 "rodan.dpt-svr.luc.edu"
 Relax delay: 1.000 sec
 Pulse 45.8 degrees
 Acq. time: 1.888 sec
 Visc: 38645.7 Hz
 256 repetitions
 OBSERVE C13, 75.3829134 MHz
 DECOUPLE H1, 251.731873 MHz
 Power 34 dB
 Continuously on
 VALTZ-18 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65538
 Total time 8 min, 34 sec



10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclonon-5-oxime, CTV Oxime Crown (3) Infrared Spectrum

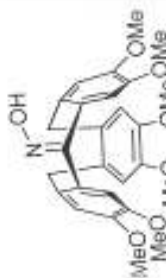


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV
Oxime Crown (3) ¹H NMR Spectrum

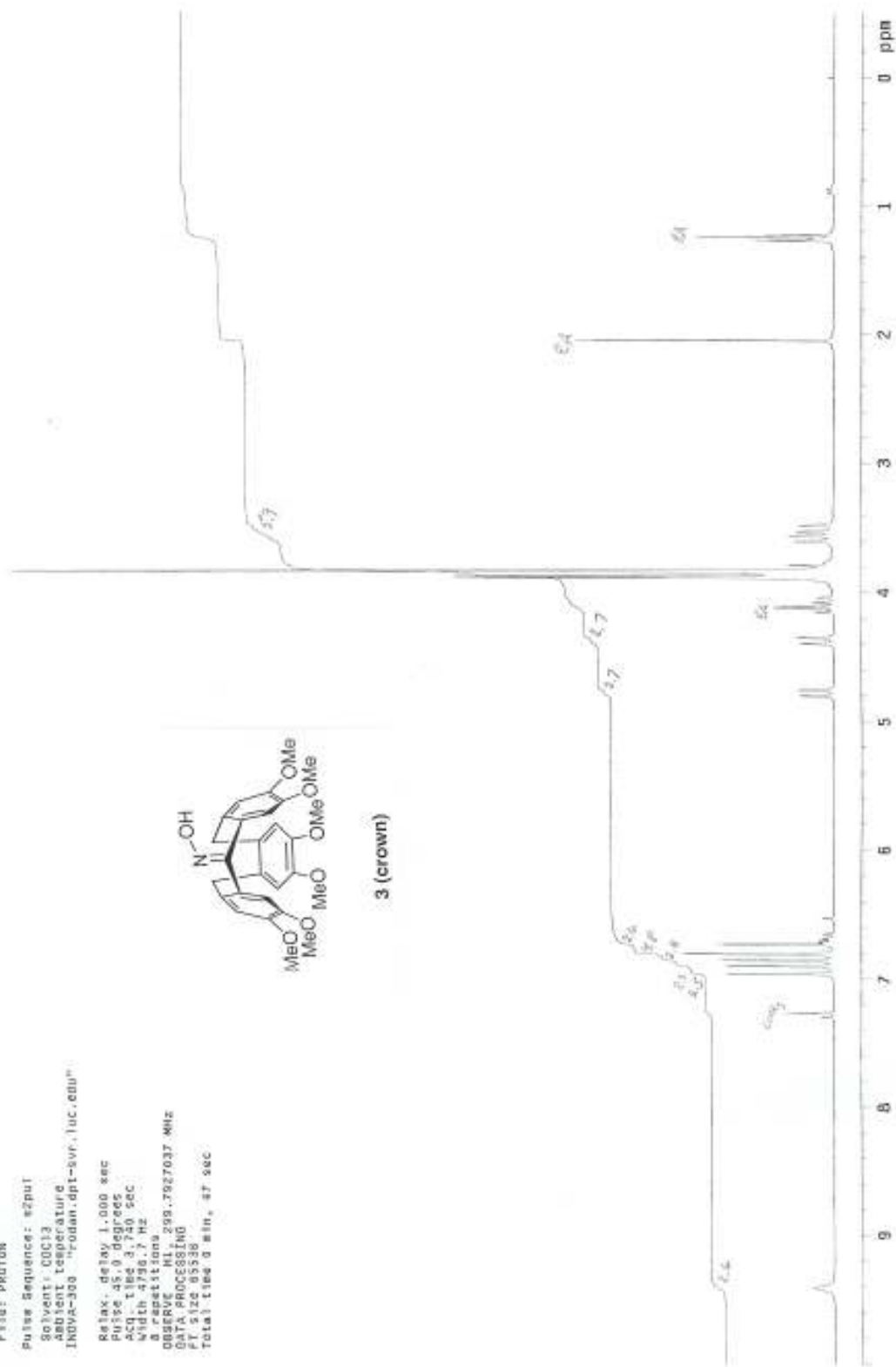
MLA-73-D
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Sample directory:
File: PROTON

Pulse sequence: zgpg30
Solvent: CDCl3
Ambient temperature
INOVA-300 ¹Hadam.dpt-svr.luc.edu

Relax. delay: 1.000 sec
Pulse: 45.0 degrees
Acq. time: 3.740 sec
Width: 4796.7 Hz
repetitions
OBSERVE: ML 298.7927037 MHz
DATA PROCESSING
File size: 85536
Total time: 9 min, 47 sec



3 (crown)



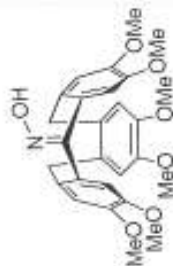
10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclonon-5-oxime, CTV Oxime Crown (3) ¹H NMR Spectrum

ML4-74-0

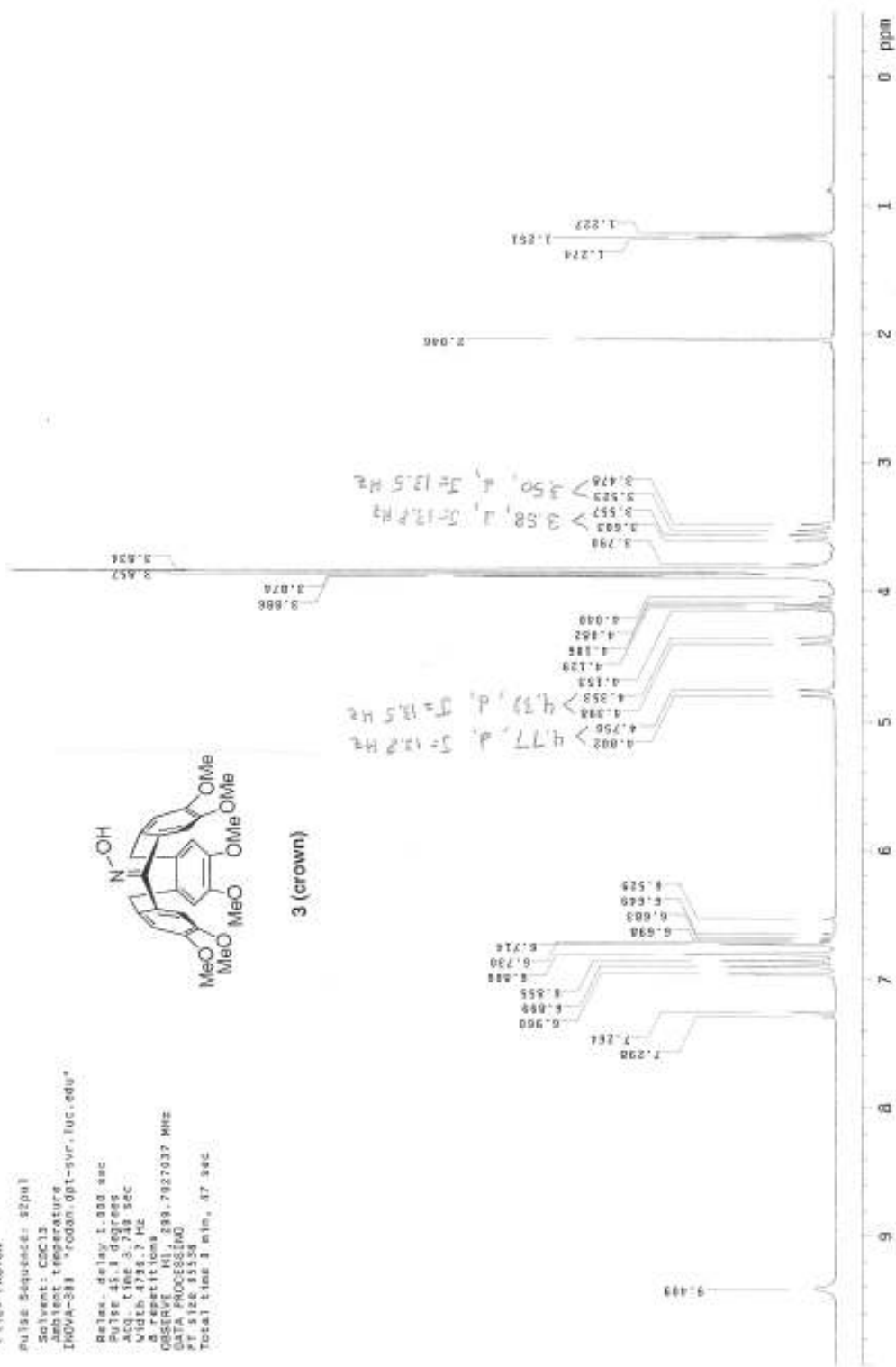
Archive directory: /export/home/vmerli/vmerlys/data/dbecker
 Sample directory:
 File: PROTON

Pulse Sequence: s2ou1
 Solvent: CDCl3
 Ambient temperature
 INOVA-300 - rcdon.opt-svr.tuc.edu*

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.743 sec
 A 100.618 MHz
 OBSERVE 1H 299.7927037 MHz
 DATA PROCESSING
 FT size 31358
 Total time 3 min. 47 sec



3 (crown)



10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclonon-5-oxime, CTV Oxime Crown (3) ¹³C NMR Spectrum

ML4-74-B

Archive directory: /export/home/vnarr1/vnarr1s/data/dbecker

Sample directory:

Pulse sequence: zgpg30

Solvent: CDCl3

Ambient temperature

File: ML4-74-B-CNMR

INOVA-300 -prodan.dpt-svr.luc.edu

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.000 sec

Width 18895.7 Hz

Observed frequency 382851.7 MHz

DECOUPLE CH1: 239.7641873 MHz

power 33 dB

continuously on

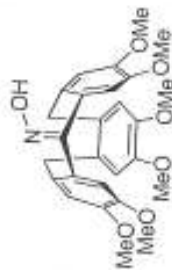
WALTZ-16 modulated

DATA PROCESSING

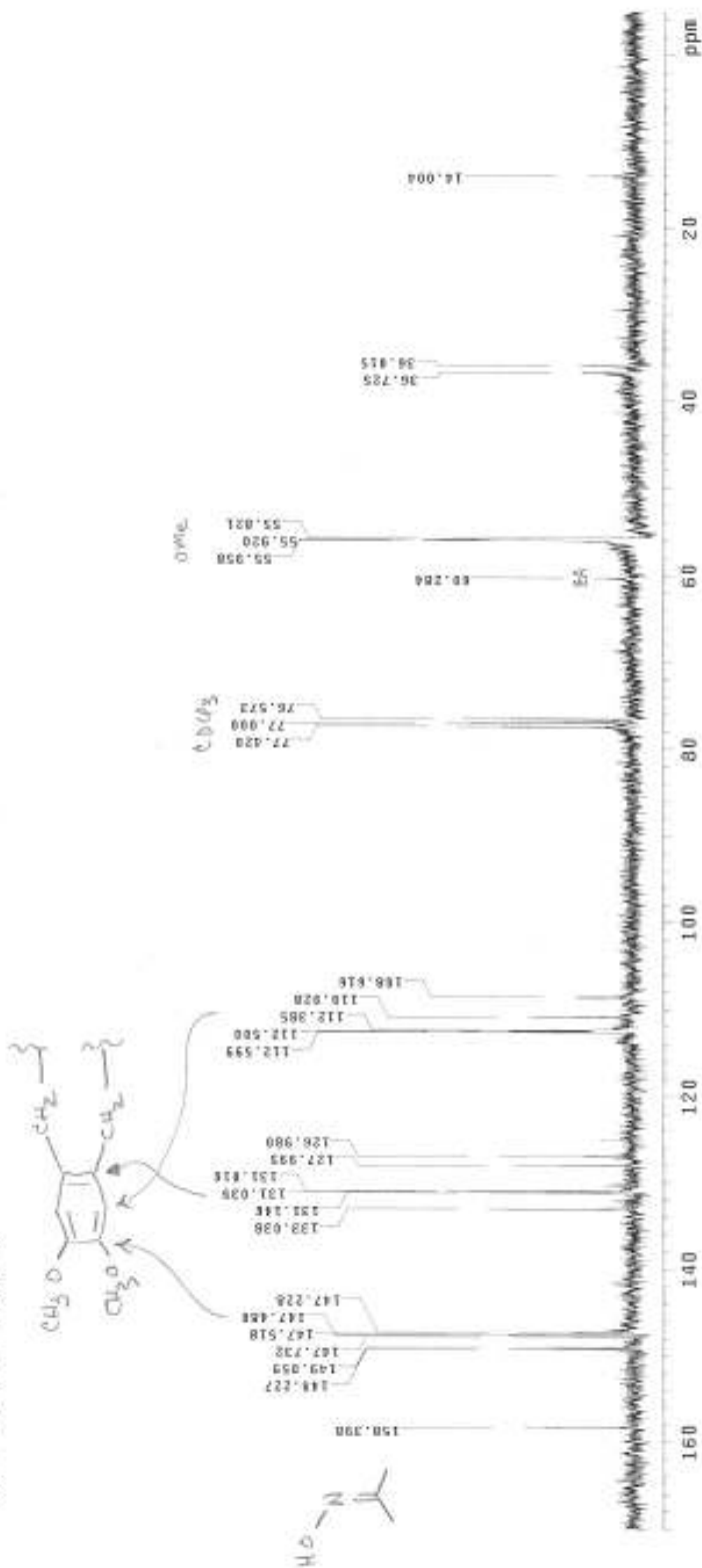
Line broadening 1.0 Hz

FT size 65236

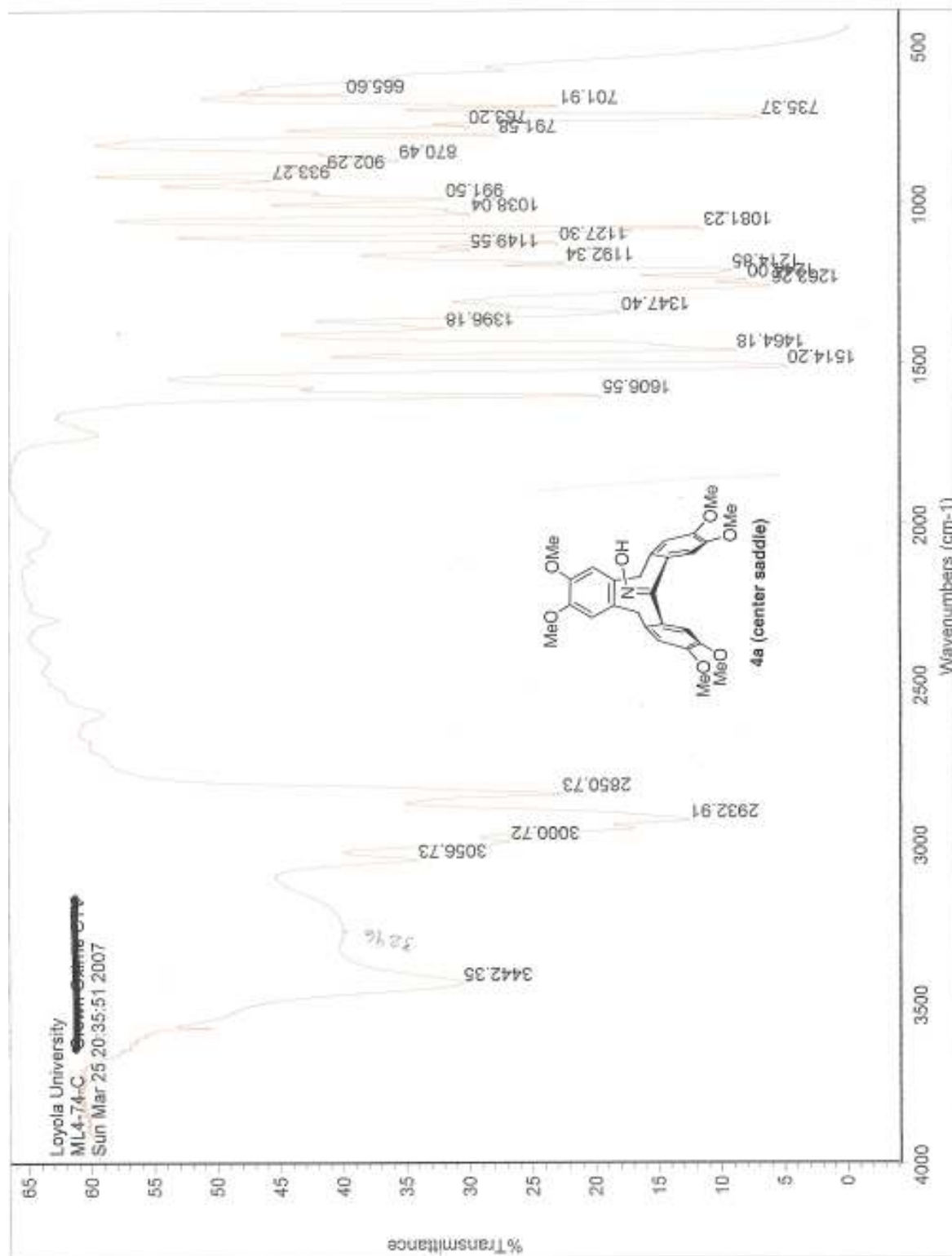
Total time 2 hr, 17 min, 8 sec



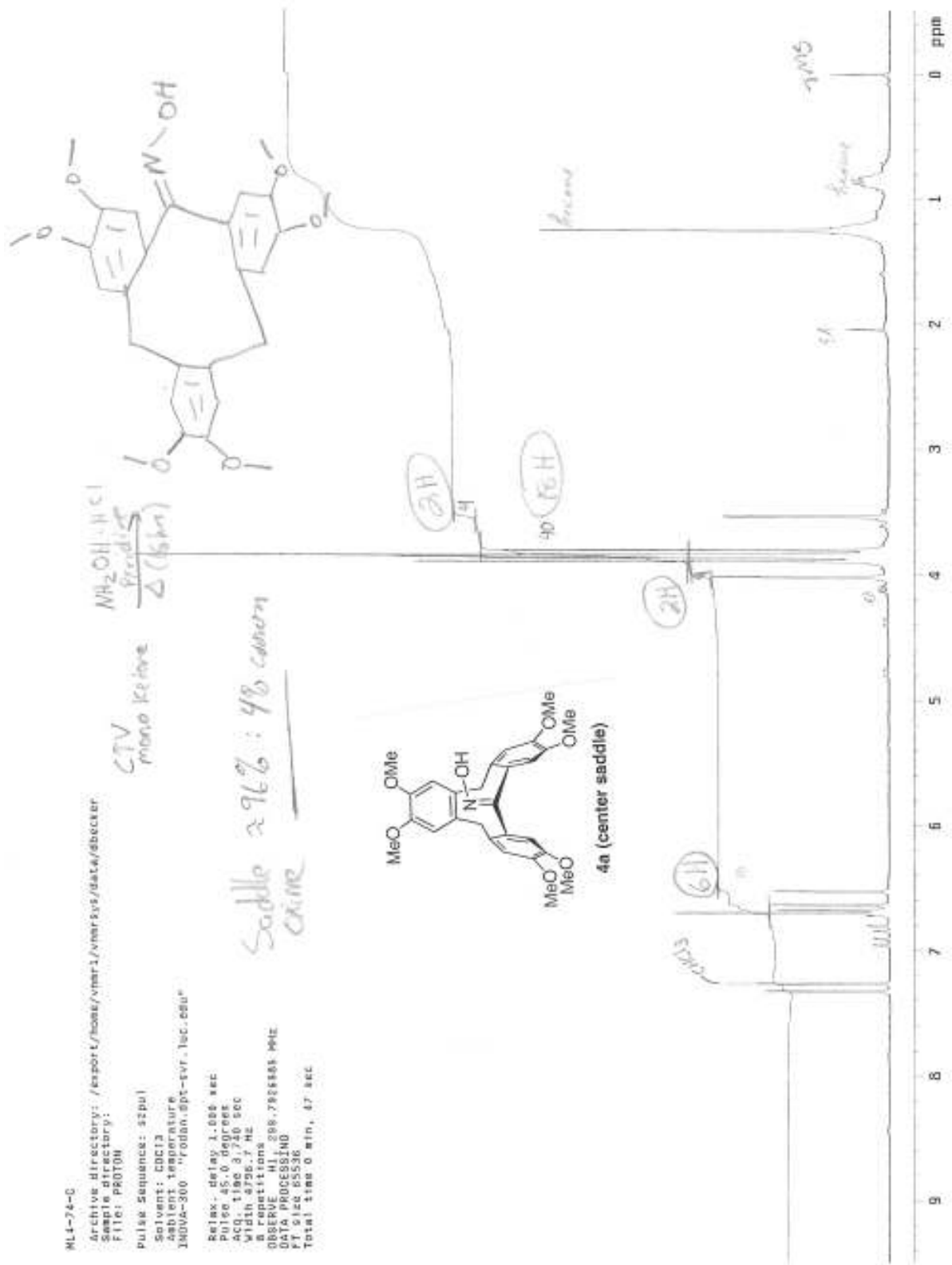
3 (crown)



10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV Oxime Saddle (4) Infrared Spectrum



10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV Oxime Saddle (4) ¹H NMR Spectrum

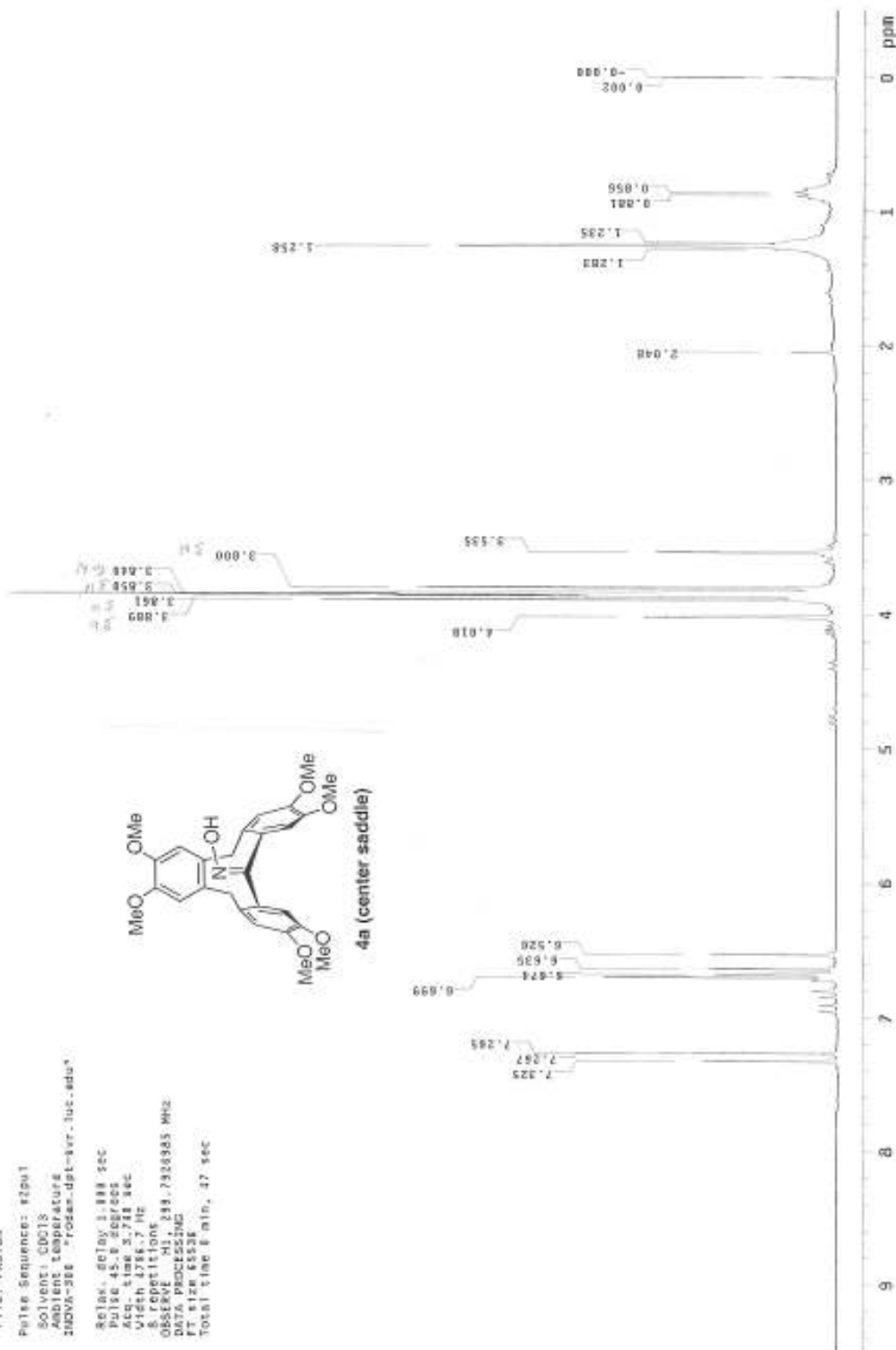
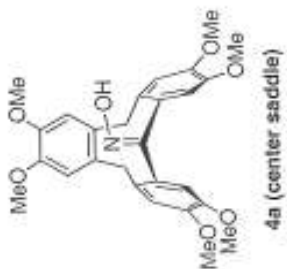


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV Oxime Saddle (4) ¹H NMR Spectrum

MLF-74-C
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 Sample directory:
 File: PK0101

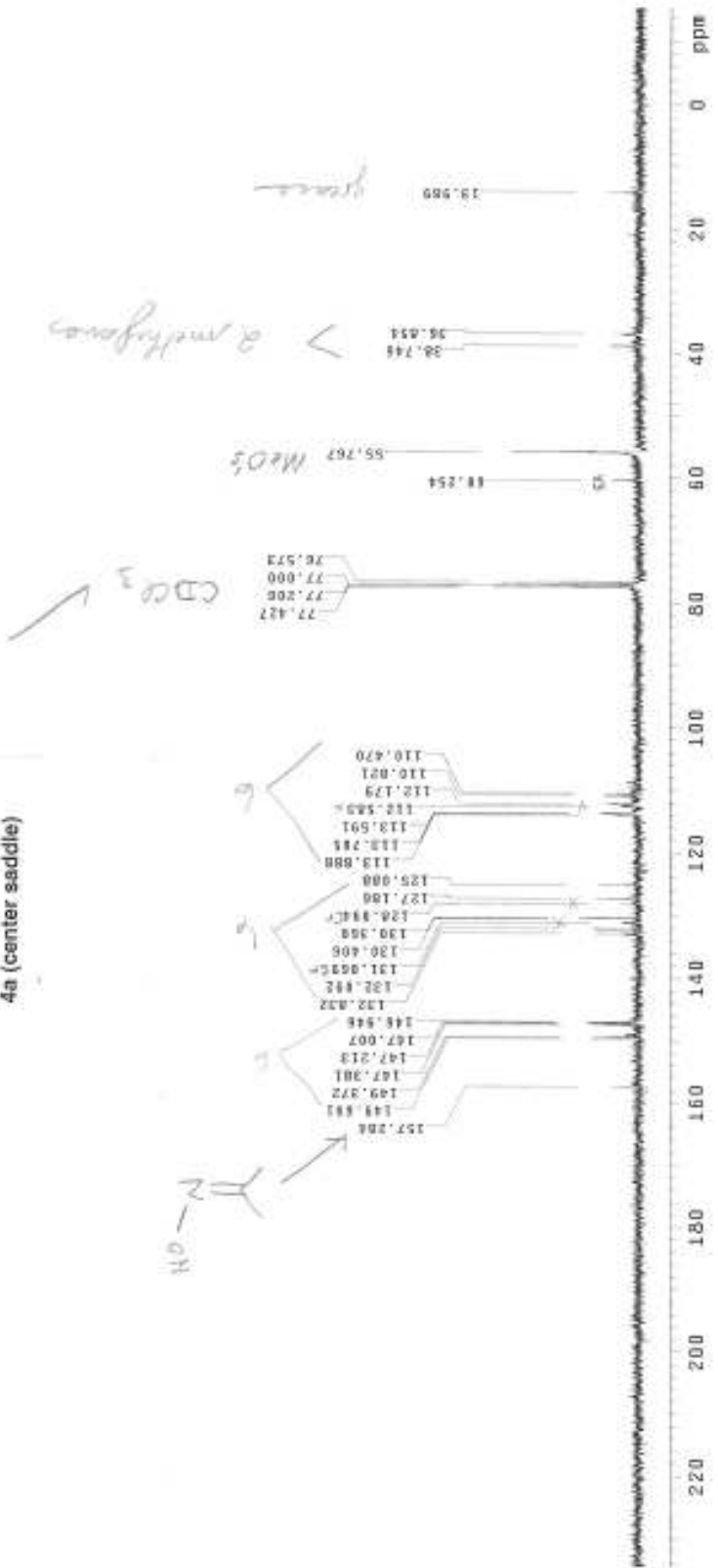
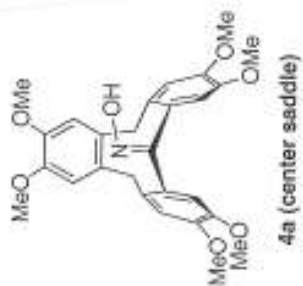
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 Ambient temperature
 INOVA-300 P00001-dpt-avr-luc.edu*

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 Pulse: 45.0 degrees
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 DATA PROCESSING
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 Total time: 8 min, 47 sec

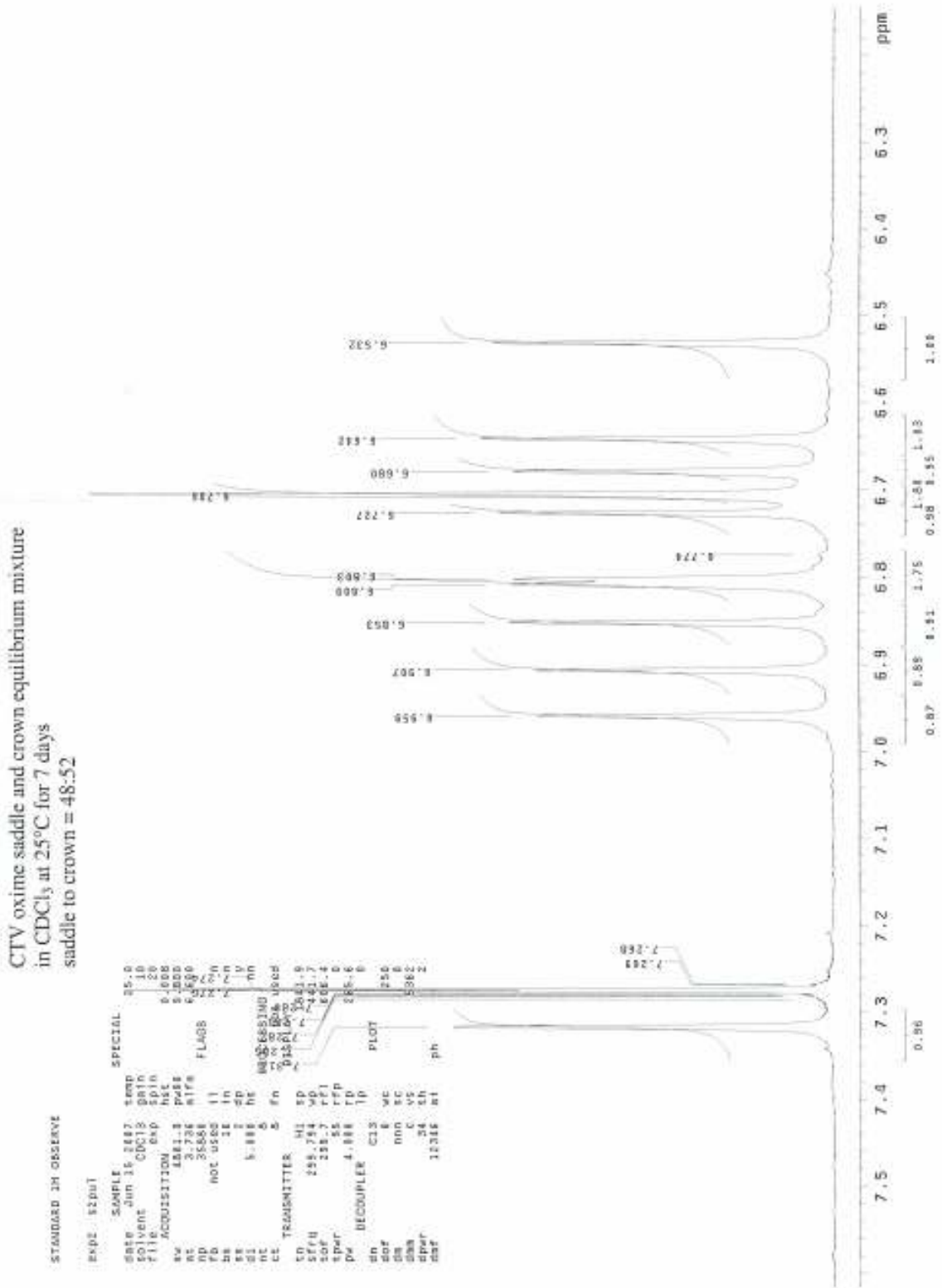


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV Oxime Saddle (4) ¹³C NMR Spectrum

ML3-31-C
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 Sample directory:
 FILE: C00000
 Pulse sequence: eFpu1
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 Ambient temperature
 INOVA-300 "rosen-dpt-svr_lut-eds"
 Relax delay 1.888 sec
 Pulse 45.8 degrees
 Acq. time 1.888 sec
 Width 18441.7 Hz
 1344 repetitions
 OBSERVE C13, 75.5825165 MHz
 DECOUPLE H1, 259.7318573 MHz
 Power 31 dB
 continuously on
 waltz-16 modulated
 DATA PROCESSING
 Line broadening 1.1 Hz
 F1 size 81538
 Total time 2 hr, 17 min, 8 sec



CTV oxime saddle and crown equilibrium mixture in CDCl₃ at 25°C for 7 days:
saddle to crown = 48:52



CTV oxime saddle and crown equilibrium mixture in dms0-d6 at 25°C for 6 days:
saddle to crown = 8:92

CTV oxime saddle and crown equilibrium mixture
in dms0-d6 at 25°C for 6 days
saddle to crown = 8:92

ctv oxime at 25c for 6 days

exp7 stpu1

```

SAMPLE          SPECIAL  25.0
DATE   DEC 27 2006  TEMP
SOLVENT  DMSO  DMSO    21
FILE  /export/home/~sp1n  28
VMNR3/VMNR30/DATA/~  311
VMNR3/CTV_OXIME.ctv  3.885
106_25C.F15  3.888
106_25C.F15  3.888
ACQUISITION  FLAGS
AV  4861.2  11  n
AL  3.228  10  n
TD  3.088  10  y
TS  NOT USED  00  PROCESSING  00
BS  2  2  fn  not used
DI  1.888  2  fn  DISPLAY
OC  1.888  5D  -152.2
CL  125  125  5D  5633.5
TR  TRANSMITTER  M1  RFP  3257.3
TO  289.716  1D  744.3
TOD  295.44  1D  -113.8
TOW  4.816  1D  PLOT  258
PW  DECOUPLER  C13  VS  3824
DN  nnn  at  ph
DA  nnn  e  th
SOL  c
SOL  84
SOL  1234E
  
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CTV oxime saddle to crown interconversion in CDCl_3 kinetics data at 25°C

Exponential data analysis:

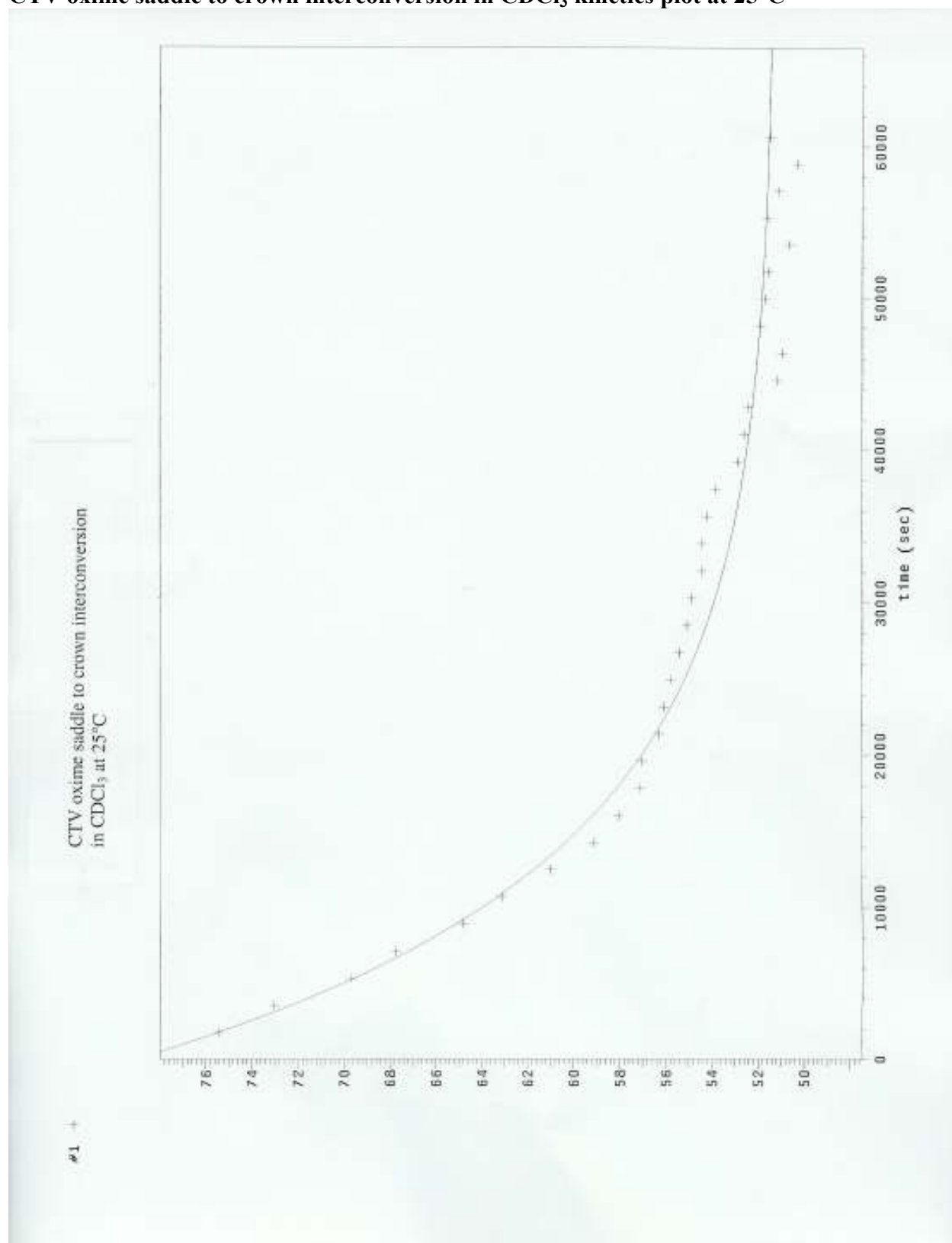
CTV oxime saddle to crown interconversion
in CDCl_3 at 25°C

peak	tau	error
1	1.275e+04	640.7

peak number 1

tau =	1.28e+04	error =	641
time	observed	calculated	difference
1783	75.4	75.5	-0.0295
3566	73	72.3	0.721
5349	69.7	69.6	0.129
7132	67.7	67.2	0.559
8914	64.8	65.1	-0.313
1.07e+04	63.1	63.3	-0.187
1.248e+04	61	61.7	-0.726
1.426e+04	59.1	60.3	-1.26
1.605e+04	58	59.2	-1.13
1.783e+04	57.1	58.1	-1.01
1.961e+04	57	57.2	-0.201
2.139e+04	56.3	56.5	-0.19
2.318e+04	56.1	55.8	0.289
2.496e+04	55.8	55.2	0.589
2.674e+04	55.4	54.7	0.733
2.853e+04	55	54.2	0.819
3.031e+04	54.8	53.8	1.02
3.209e+04	54.4	53.5	0.935
3.387e+04	54.4	53.2	1.22
3.566e+04	54.2	52.9	1.24
3.744e+04	53.8	52.7	1.07
3.922e+04	52.8	52.5	0.318
4.101e+04	52.6	52.4	0.206
4.279e+04	52.4	52.2	0.162
4.457e+04	51.1	52.1	-0.951
4.636e+04	50.9	52	-1.06
4.814e+04	51.8	51.9	-0.035
4.992e+04	51.7	51.8	-0.132
5.17e+04	51.5	51.7	-0.209
5.349e+04	50.6	51.7	-1.07
5.527e+04	51.5	51.6	-0.0612
5.705e+04	51.1	51.6	-0.494
5.884e+04	50.2	51.5	-1.28
6.062e+04	51.4	51.5	-0.046

CTV oxime saddle to crown interconversion in CDCl_3 kinetics plot at 25°C



CTV oxime saddle to crown interconversion in dms0-d6 kinetics data at 25°C

Exponential data analysis:

CTV oxime saddle to crown interconversion
in dms0-d6 at 25°C

peak	tau	error
1	1.926e+04	375.2

peak number 1

tau =	1.93e+04	error =	375
time	observed	calculated	difference
303.1	151	151	0.167
3893	130	130	-0.247
7483	111	113	-1.84
1.107e+04	99.3	98.4	0.906
1.466e+04	87.2	86.4	0.801
1.825e+04	77.6	76.5	1.13
2.184e+04	69.2	68.2	0.907
2.543e+04	61.3	61.4	-0.0897
2.902e+04	55.6	55.7	-0.179
3.261e+04	51.4	51	0.358
3.62e+04	47.1	47.1	-0.0565
3.979e+04	42.4	43.9	-1.53
4.338e+04	39.8	41.2	-1.43
4.697e+04	37.3	39	-1.69
5.056e+04	35.9	37.1	-1.18
5.415e+04	35.7	35.6	0.108
5.774e+04	34.2	34.3	-0.146
6.133e+04	34.3	33.2	1.03
6.492e+04	33.5	32.4	1.16
6.852e+04	33	31.6	1.32

CTV oxime saddle to crown interconversion in dms0-d₆ kinetics plot at 25°C

#1 +

