

## 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. <sup>1</sup>H 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 <sup>13</sup>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. <sup>1</sup>H 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<sub>2</sub>SO<sub>4</sub> and concentrated to give a yellow-brown foam which was chromatographed on silica gel (1080 g) eluting with EA/CH<sub>2</sub>Cl<sub>2</sub> (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 <sup>1</sup>H NMR reported previously. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  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]cyclononon-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  $\text{Na}_2\text{SO}_4$  and concentrated to give an off white foam which was chromatographed on silica gel (18 g) eluting with EA/ $\text{CH}_2\text{Cl}_2$  (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):  $\lambda_{\text{max}}$  235 (log  $\epsilon$  = 4.54), 290 (log  $\epsilon$  = 4.07); IR (thin film from  $\text{CH}_2\text{Cl}_2$ ) 3441, 3288, 3203, 3057, 3001, 2934, 2846, 1606 (str, C=N), 1514, 1464, 1345, 1263, 1223, 1127, 1081, 734  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{MH}^+$  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):  $\lambda_{\text{max}}$  237 (log  $\epsilon$  = 4.54), 286 (log  $\epsilon$  = 4.10) nm. IR (thin film from  $\text{CH}_2\text{Cl}_2$ ) 3442, 3296, 3057, 3001, 2933, 2851, 1607 (str, C=N), 1514, 1464, 1347, 1263, 1214, 1215, 1081, 735  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  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).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{MH}^+$  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.

### **$^1\text{H}$ NMR Study of the Cyclotrimeratrylene Oxime Saddle-Crown Equilibrium and Its Interconversion Kinetics**

$^1\text{H}$  NMR was utilized to study the conversion of the saddle conformer to the crown conformer. The equilibrium constants  $K_{\text{eq}}$  and conversion time constants for the oxime of CTV dissolved in  $\text{CDCl}_3$  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  $\text{CDCl}_3$  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  $^1\text{H}$  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  $\text{CDCl}_3$ , 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  $\text{CDCl}_3$ , and a  $K_{\text{eq}} = 0.087$  in  $\text{dmsO}-d_6$  at  $25^\circ\text{C}$ .

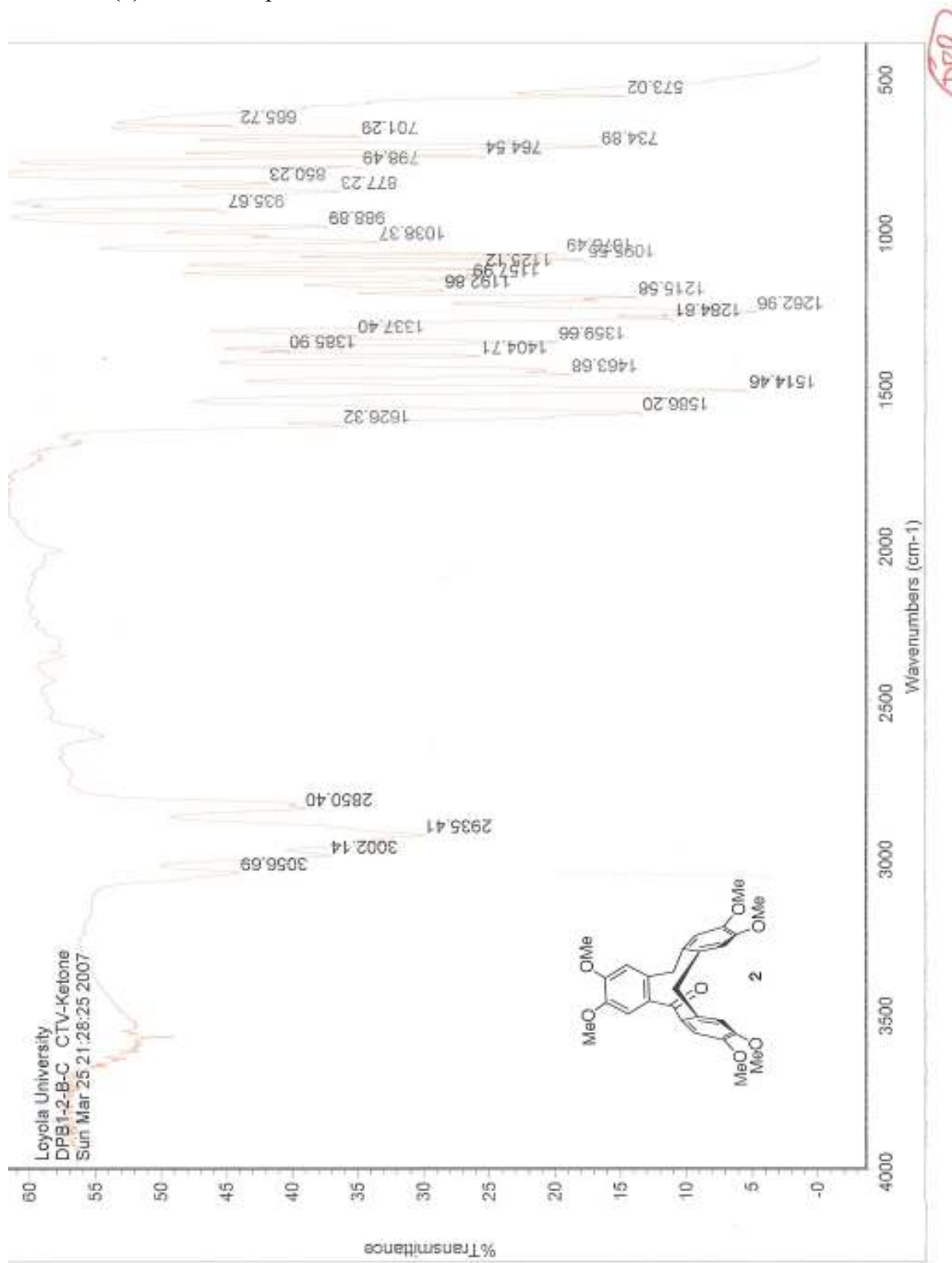
Freshly prepared samples of the saddle conformer dissolved in  $\text{CDCl}_3$  and  $\text{dmsO}-d_6$  were maintained at  $25^\circ\text{C}$  in the NMR for 18 and 20 hrs, respectively. The decrease in the  $^1\text{H}$  NMR saddle peak intensities in the aromatic region was recorded as a function 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  $\text{CDCl}_3$  and  $\tau = 1.926 \times 10^4$  s (5.35 hr) in  $\text{dmsO}-d_6$  at  $25^\circ\text{C}$ .

The time constant  $\tau$  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  $\text{CDCl}_3$  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  $\text{CDCl}_3$  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  $25^\circ\text{C}$ .

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  $\text{CDCl}_3$  than in  $\text{dmsO}-d_6$  at  $25^\circ\text{C}$ , and the final equilibrium ratio of crown to saddle is an order of magnitude greater in  $\text{dmsO}-d_6$  than in  $\text{CDCl}_3$ .

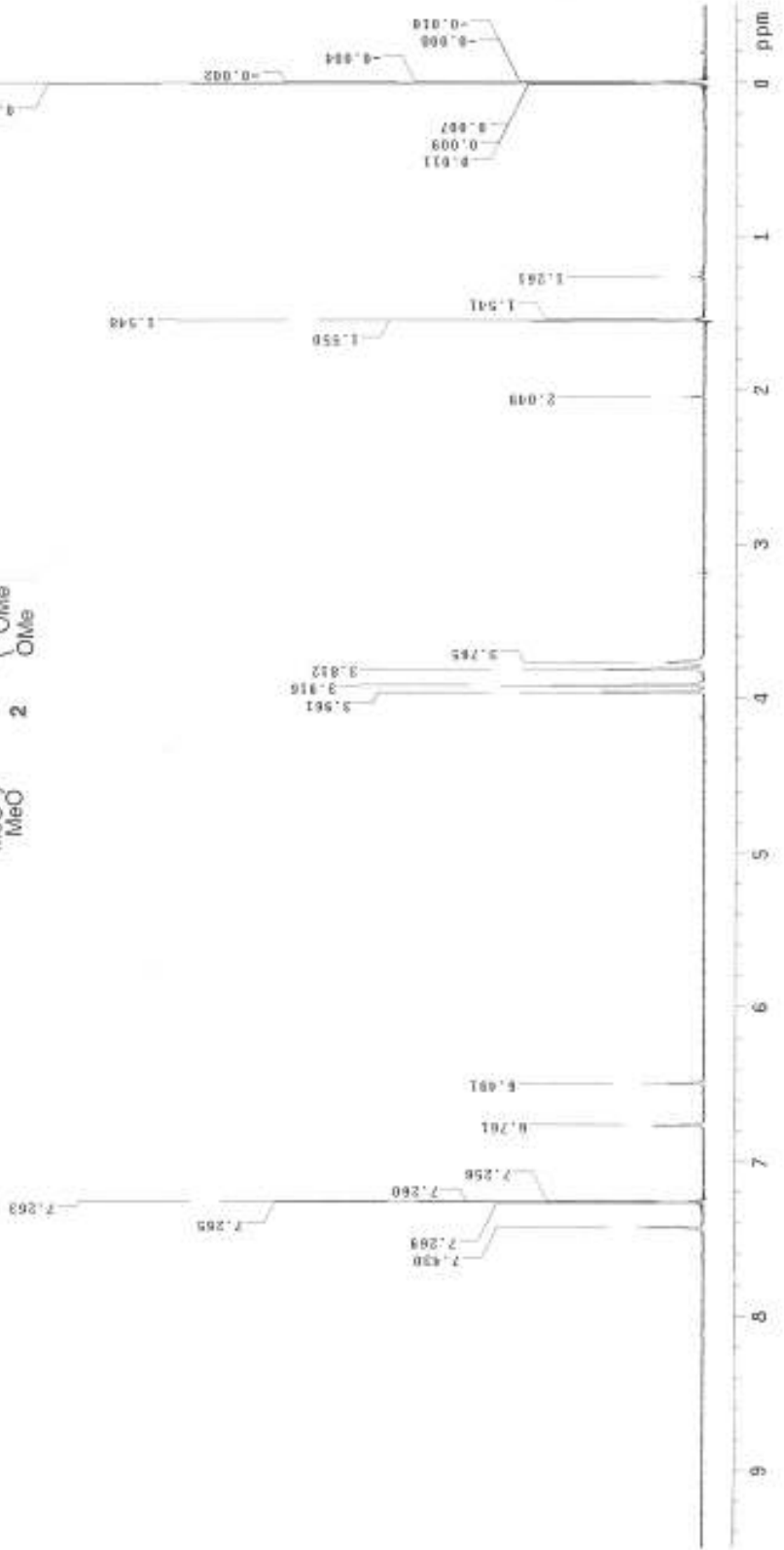
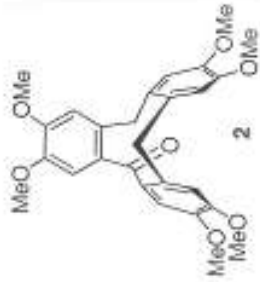
10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTV  
Ketone – (2). Infrared spectrum





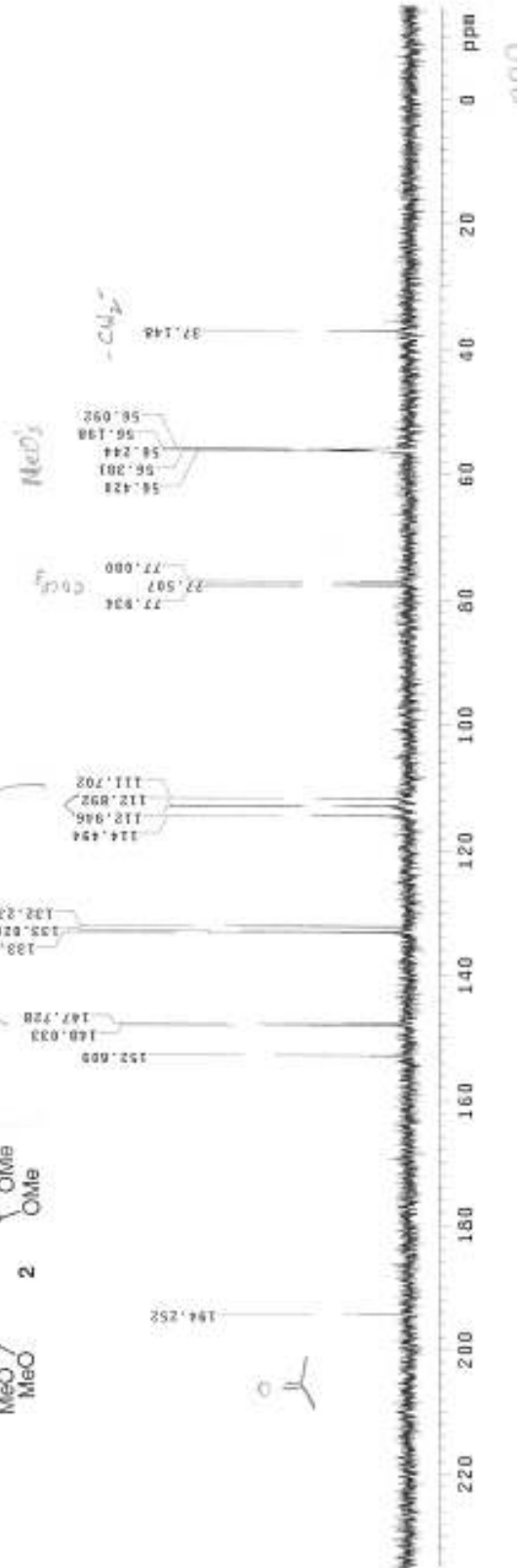
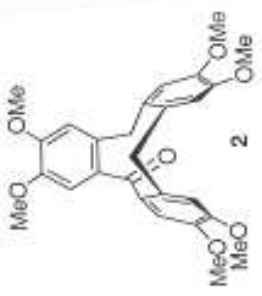
**10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTV  
Ketone – (2). <sup>1</sup>H NMR Spectrum**

DPB1-2-B-C March-2-2007  
Pulse Sequence: s2pu1  
Solvent: CDCl3  
Ambient Temperature  
CTM1M1-300 %port .dpt-svt.luc.edu#  
PULSE SEQUENCE  
relax delay 1.000 sec  
pulse 31.5 degree  
Acq. time 1.995 sec  
Vinh 5500.5 Hz  
#4 repetitions  
QASERVE M1 300.0750517 MHz  
DATA PROCESSING  
F1 size 32748  
Total time 3 min, 18 sec

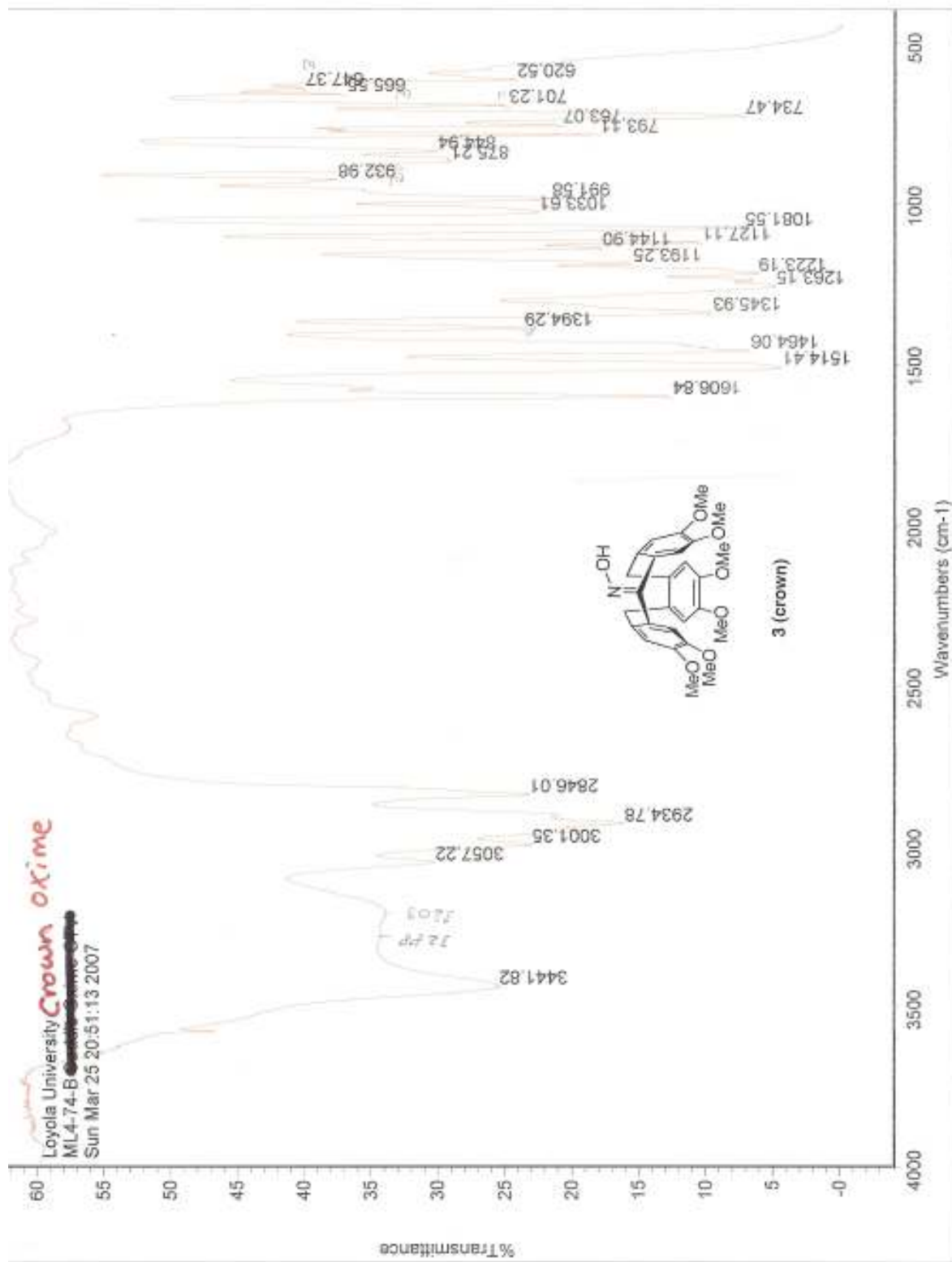


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-one, CTU  
Ketone – (2). <sup>13</sup>C NMR Spectrum

DP51-2-5-C      March-2-2007  
 Archive directory: /export/home/vmr1/vmr1/sys/data/dbcker  
 Sample directory:  
 File: CARBON  
 Pulse sequence: zgpg1  
 Solvent: CDCl3  
 Ambient temperature  
 2DQV2-308 "rodan.dqt-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**



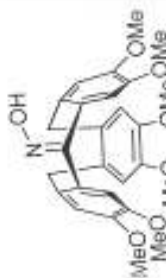


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclonon-5-oxime, CTV  
Oxime Crown (3) <sup>1</sup>H NMR Spectrum

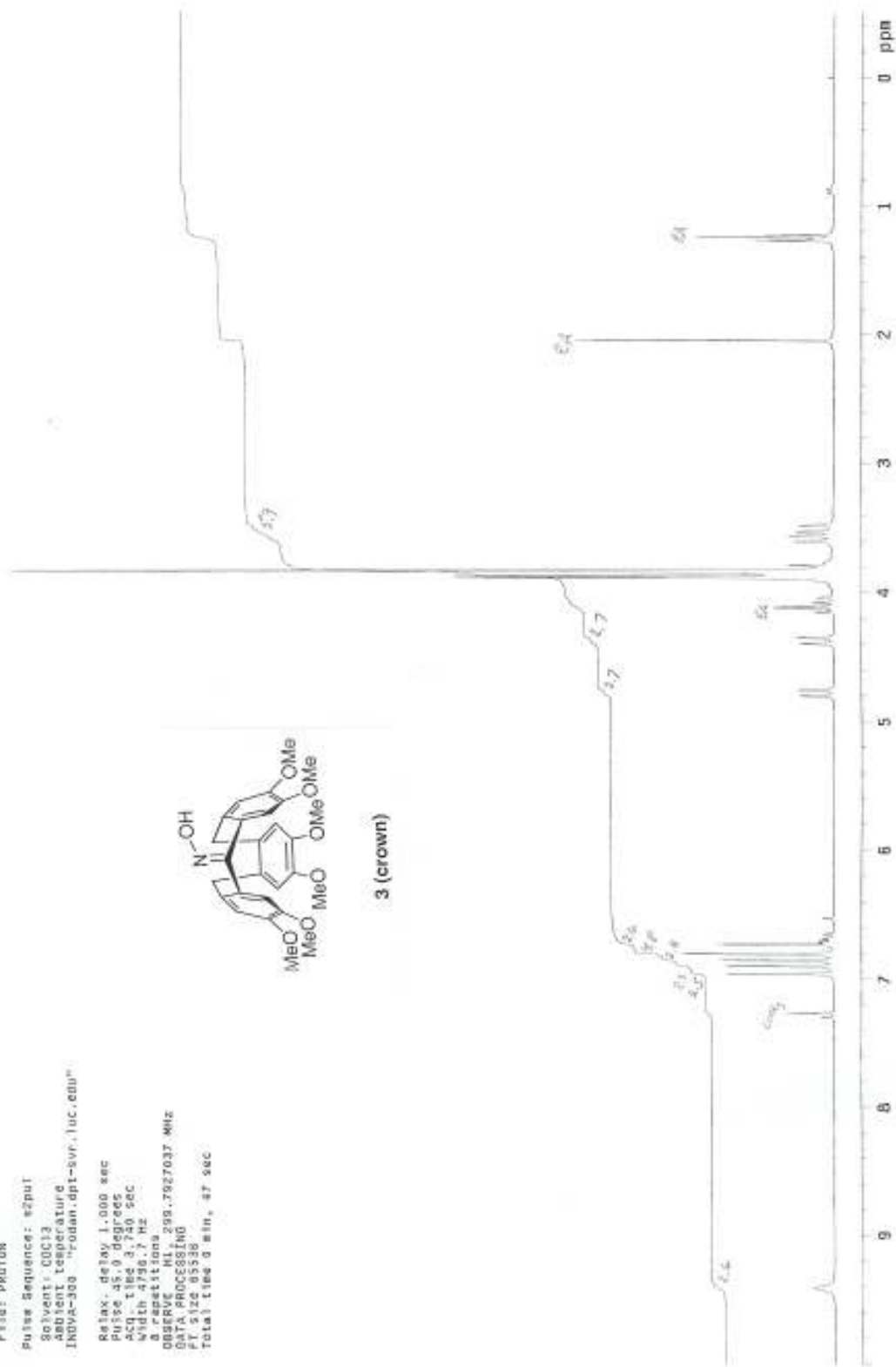
MLA-73-D  
Archive directory: /export/home/vmar1/vnairsys/data/dbecker  
Sample directory:  
File: PROTON

Pulse sequence: zgpg30  
Solvent: CDCl3  
Ambient temperature  
INOVA-300 <sup>1</sup>Hadam.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)



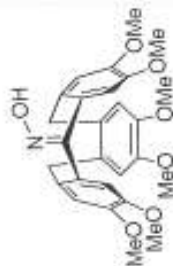
10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclonon-5-oxime, CTV Oxime Crown (3) <sup>1</sup>H NMR Spectrum

ML4-74-0

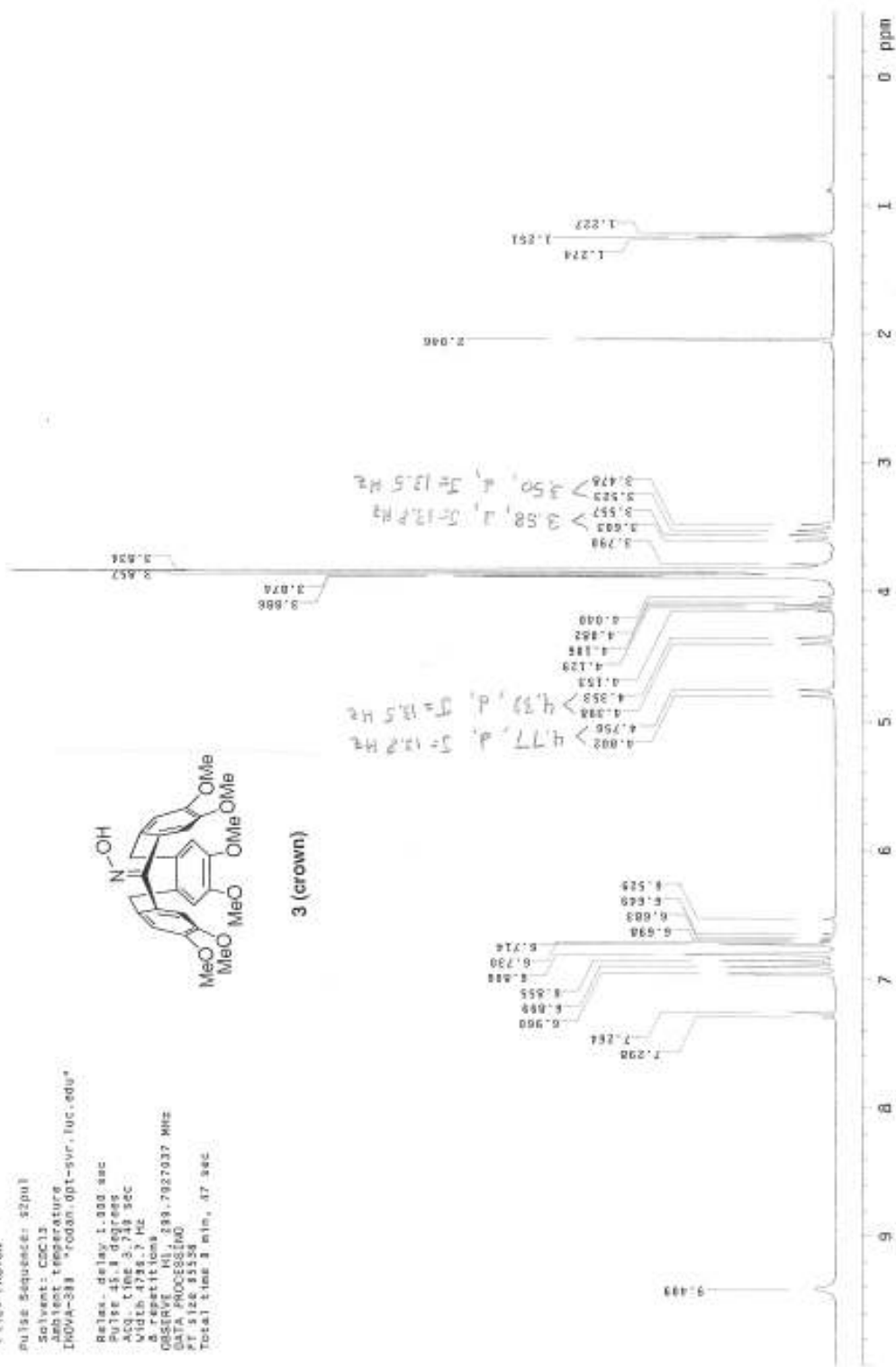
Archive directory: /export/home/vmerli/vmerlys/data/dbecker  
 Sample directory:  
 File: PROTON

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)

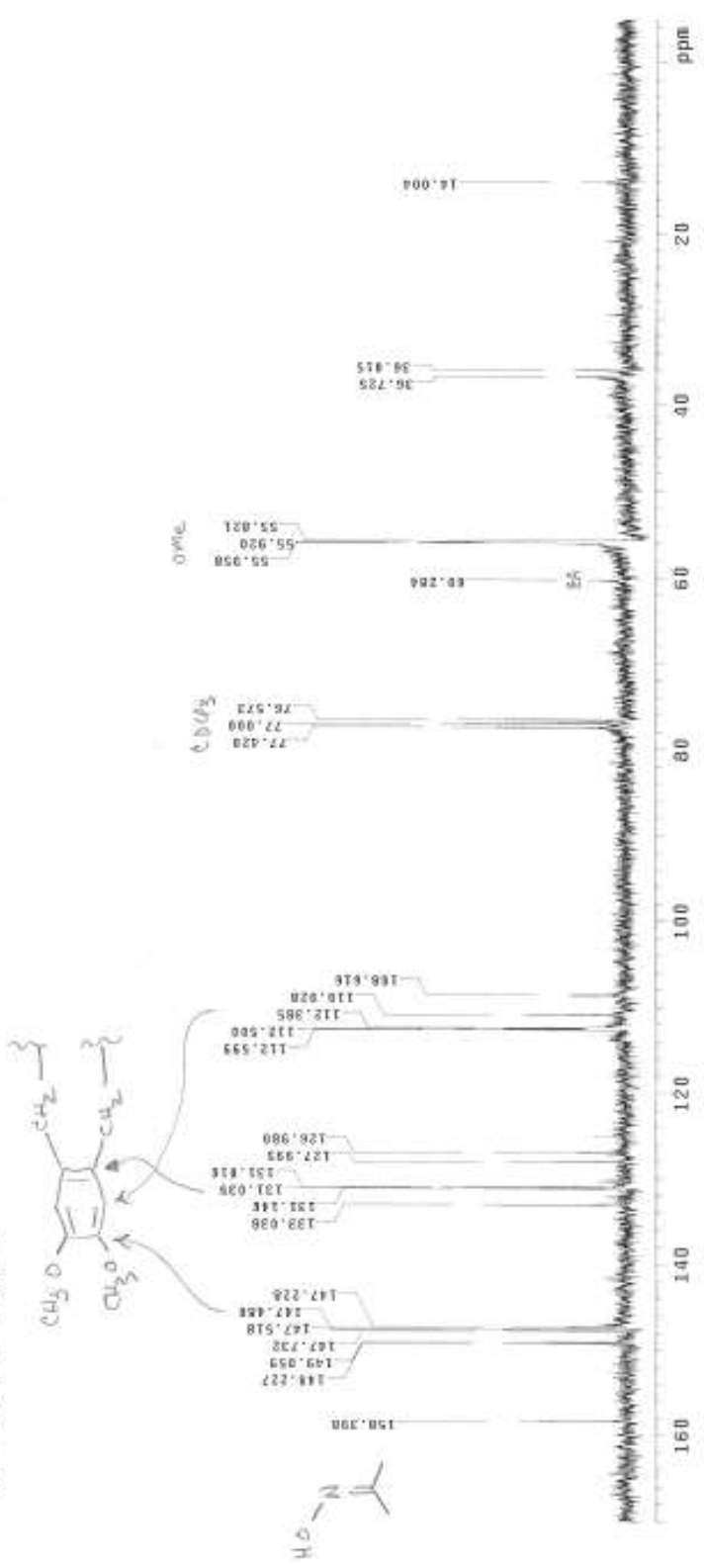
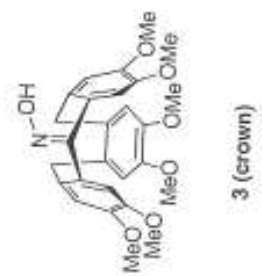


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclonon-5-oxime, CTV Oxime Crown (3) <sup>13</sup>C NMR Spectrum

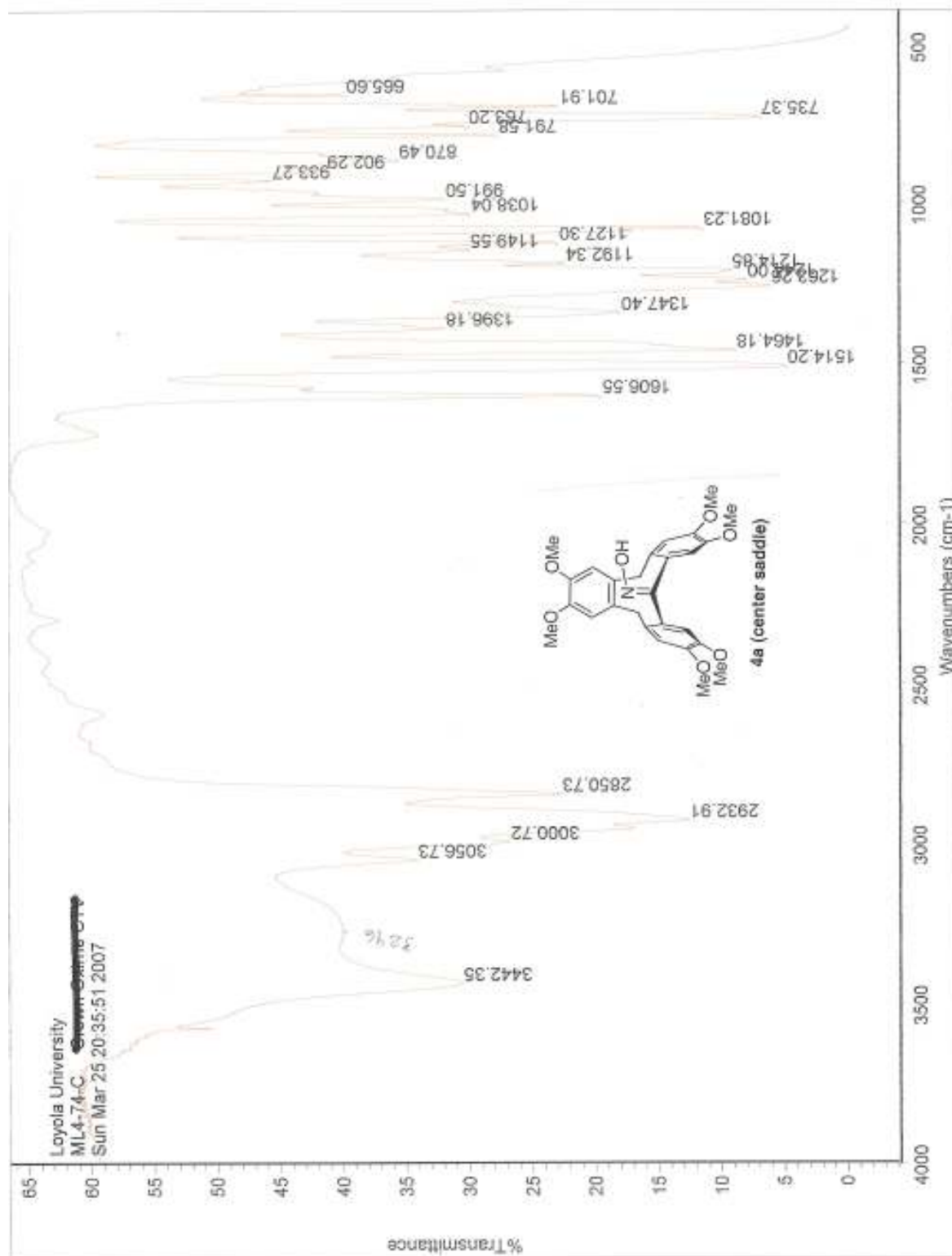
ML4-74-B  
 Archive directory: /export/home/vnarr1/vnarrays/data/dbecker  
 Sample directory:

Pulse sequence: zgpg30  
 Solvent: CDCl3  
 Ambient temperature  
 File: ML4-74-B-CNMR  
 INOVA-300 -prodan.dpt-svr.luc.edu

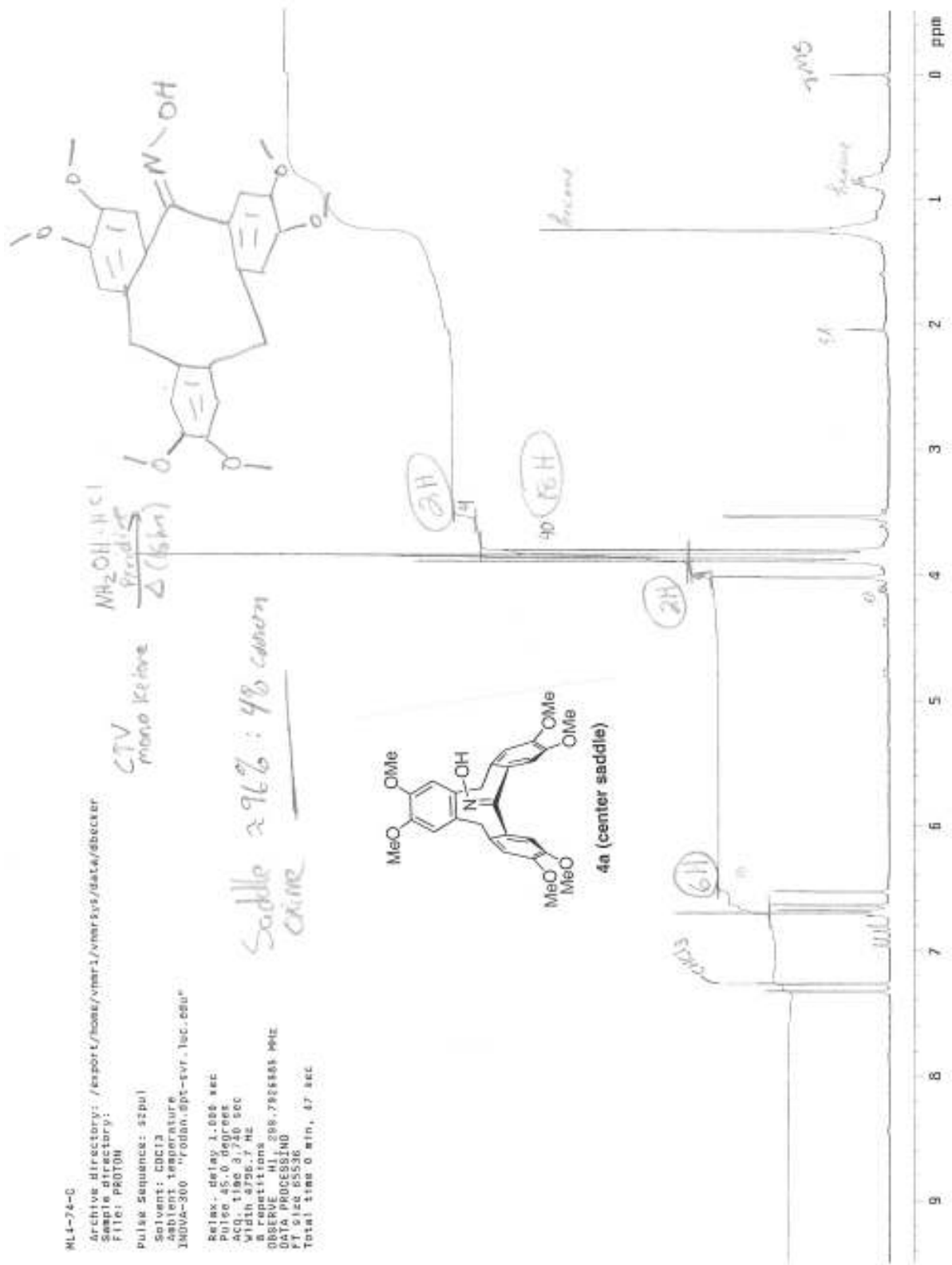
Relax. delay 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time 1.900 sec  
 Width 18895.7 Hz  
 Observed frequency 382851.7 MHz  
 DECOUPLE CH1: 239.7641873 MHz  
 power 33 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.0 Hz  
 FT size 65236  
 Total time 2 hr, 17 min, 8 sec



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) <sup>1</sup>H NMR Spectrum

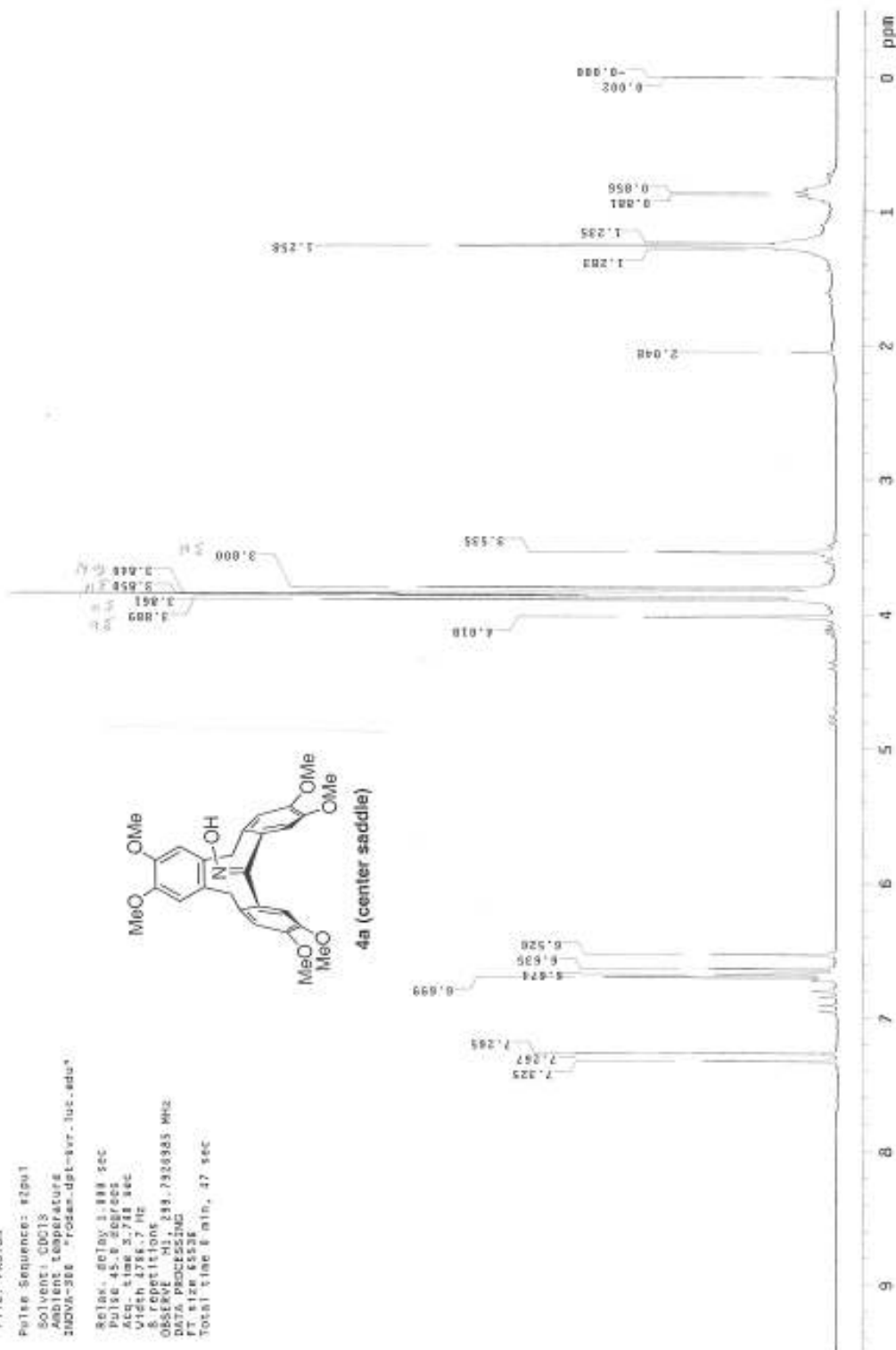
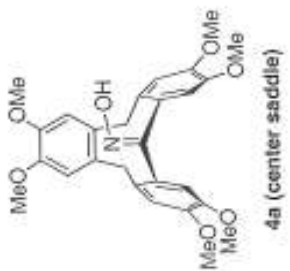


10,15-Dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[a,d,g]cyclononen-5-oxime, CTV Oxime Saddle (4) <sup>1</sup>H NMR Spectrum

MLF-74-C  
 Archive directory: /export/home/vmr1/vmr1sys/data/dbecker  
 Sample directory:  
 File: PK0101

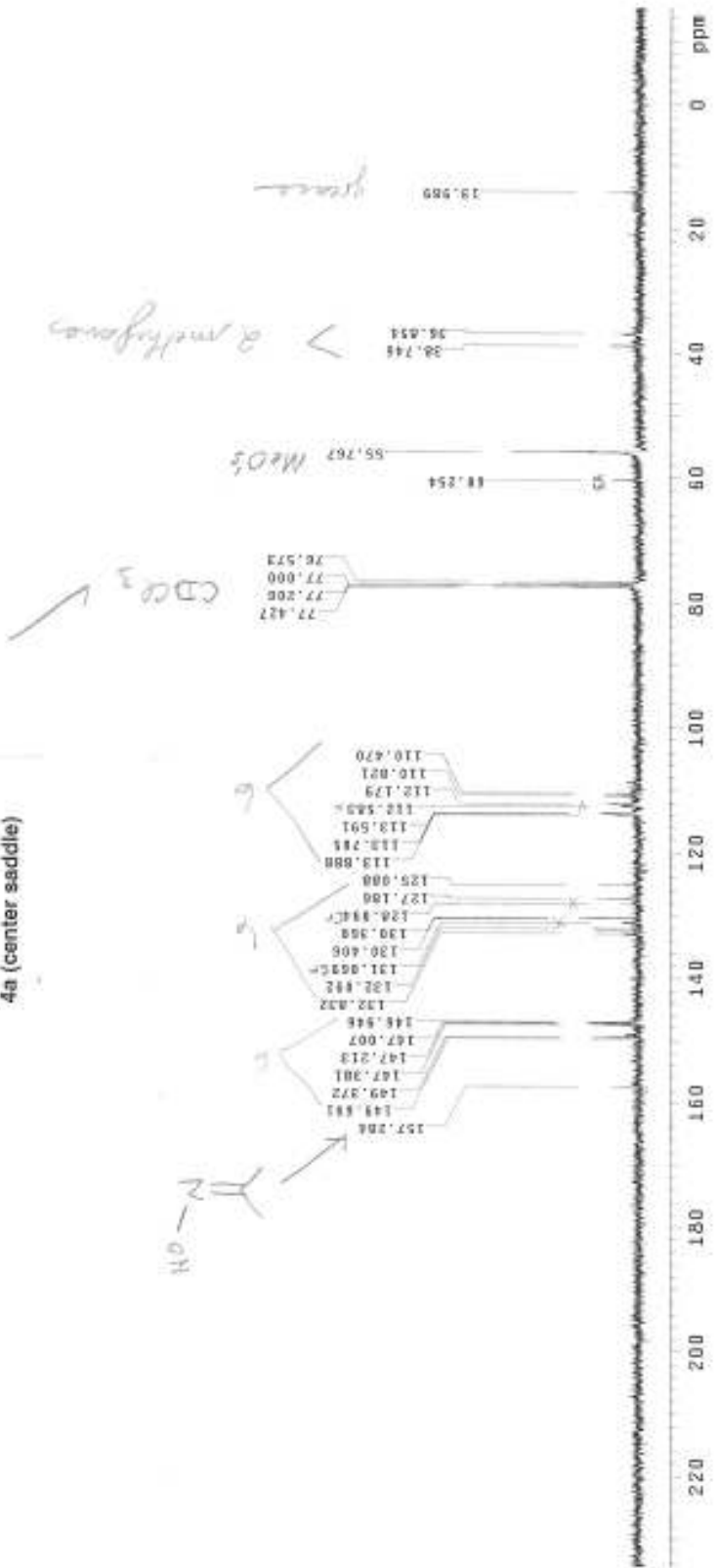
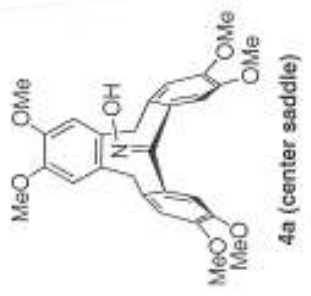
Pulse Sequence: zgpg30  
 Solvent: CDCl3  
 Ambient temperature  
 INOVA-300 P00001-dpt-avr-luc.edu\*

Relax. delay: 1.000 sec  
 Pulse 45.0 degrees  
 Acq. time: 7.41 sec  
 SFO: 125.761 MHz  
 SFO2: 400.141 MHz  
 OBSERVE: H1, 299.7328985 MHz  
 DATA PROCESSING  
 FT size 65536  
 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) <sup>13</sup>C NMR Spectrum

ML3-31-C  
 Archive directory: /export/home/vnsf1/vnsr/sys/data/dbecker  
 Sample directory:  
 FILE: C00000  
 Pulse sequence: eFpu1  
 Solvent: CDCl3  
 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 8358  
 Total time 2 hr, 17 min, 8 sec



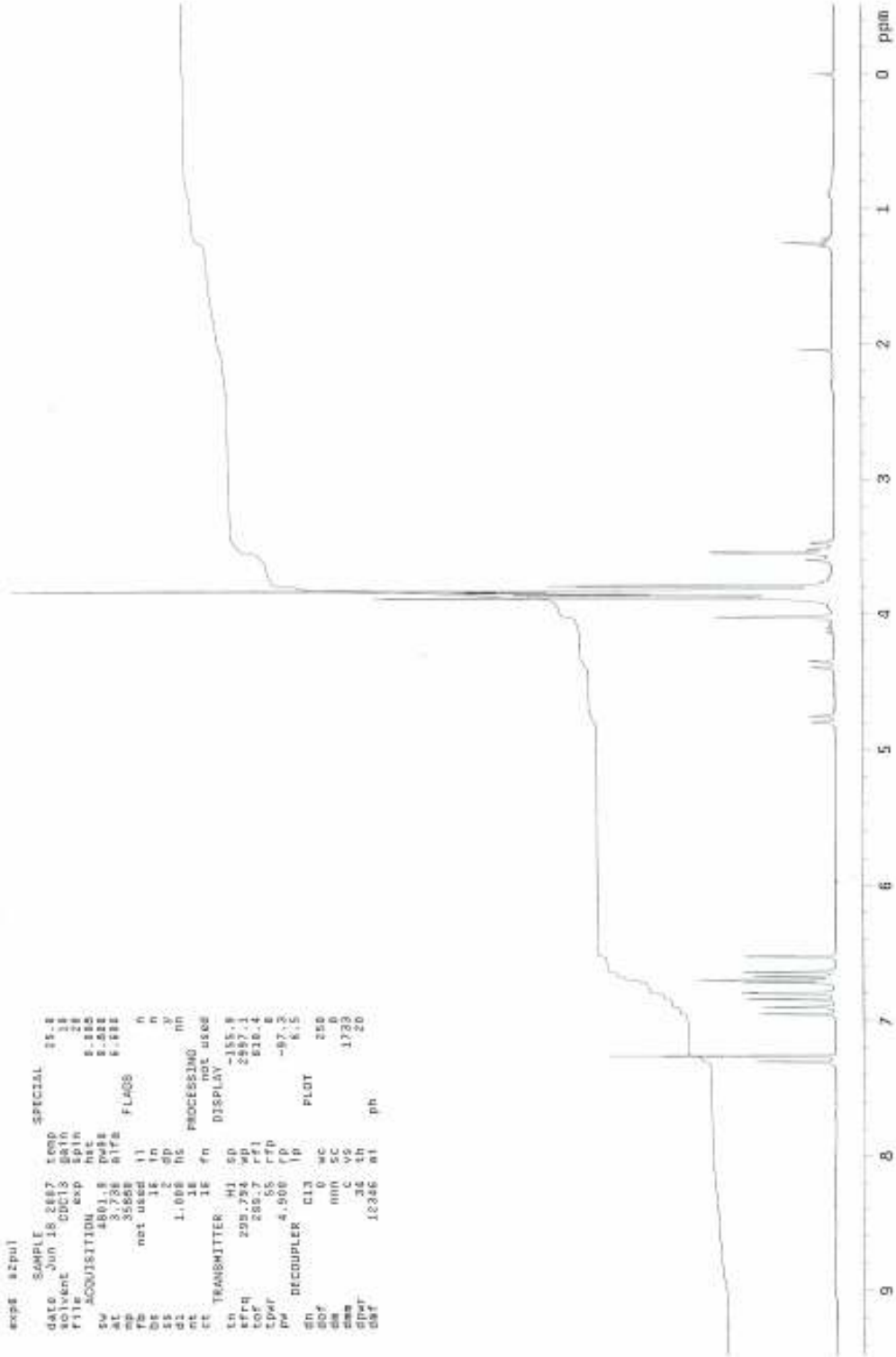
CTV oxime saddle and crown equilibrium mixture in CDCl<sub>3</sub> at 25°C for 7 days:  
saddle to crown = 48:52

CTV oxime saddle and crown equilibrium mixture  
in CDCl<sub>3</sub> at 25°C for 7 days  
saddle to crown = 48:52

STANDARD JH OBSERVE

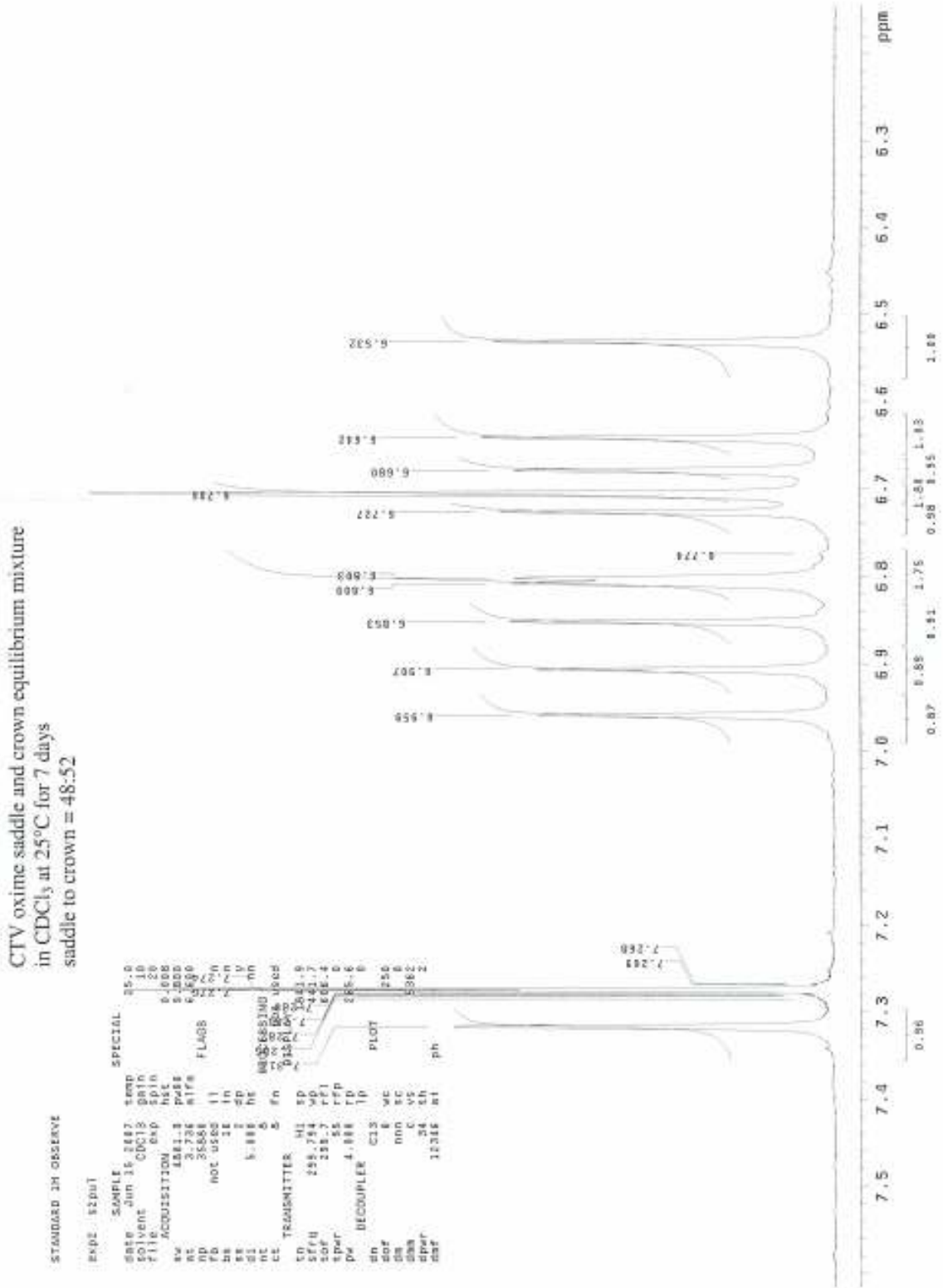
```

exp# 82pu1
-----
SAMPLE      SPECIAL  11.8
DATE  Jun 18 2007  1000
solvent  CDCl3  S110  18
File      exp  S110  28
ACQUISITION  exp  S110  28
SW  250 J  R  DASH  0.200
AL  3268  S110  0.200
TS  not used  11  FL408  0
BE  1E  1n  0
SE  1E  2D  0
SI  1.000  15  0
ET  1E  1E  0
CT  1E  1E  0
-----
CT TRANSMITTER  H1  5D  not used
Ln  200.75  2897.1  155.8
F0F1  250.75  2897.1  155.8
F0F2  250.75  2897.1  155.8
F0F4  250.75  2897.1  155.8
EDWT  55  155.8  155.8
PM  4.500  10  -97.2
DC DECOUPLER  CL3  10  8.5
-----
SN  0
SOF  0  WC  250
SA  0  MM  5C  0
SMA  3E  VS  1728
SPPW  3E  1h  20
SST  10266  01  0h
  
```





CTV oxime saddle and crown equilibrium mixture in CDCl<sub>3</sub> at 25°C for 7 days:  
 saddle to crown = 48:52



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

CTV oxime saddle and crown equilibrium mixture  
in *dmso-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 2005  temp
solvent  DMSO  DMSO    20
file  /export/home/~sp1n  28
nmr3/vmr3s/data/~hst  8.885
/vmr3/ctv_oxime.t~  Pasa  8.888
105.250.F15  n1rs  8.888
ACQUISITION
sv  4861.2  11  n
at  3.28  10  n
td  3.00  10  n
ts  3.00  10  n
bb  not used  nc  PROCESSING  nn
ss  2  2  fn  not used
ds  1.888  2  fn  DISPLAY
nc  1.888  5D  -152.2
cc  125  125  5D  8635.5
    TRANSMITTER  n1  rfp  3257.3
    srfq  288.74  1D  744.5
    cor  295.4  1D  -113.8
    pow  4.818  1D  PLOT  258
    pw  DECOUPLER  C13  VS  3824
    dn  nnn  e  th
    da  nnn  at  ph
    ga  c
    spw  84
    sw  12348
  
```



CTV oxime saddle to crown interconversion in  $\text{CDCl}_3$  kinetics data at 25°C

Exponential data analysis:

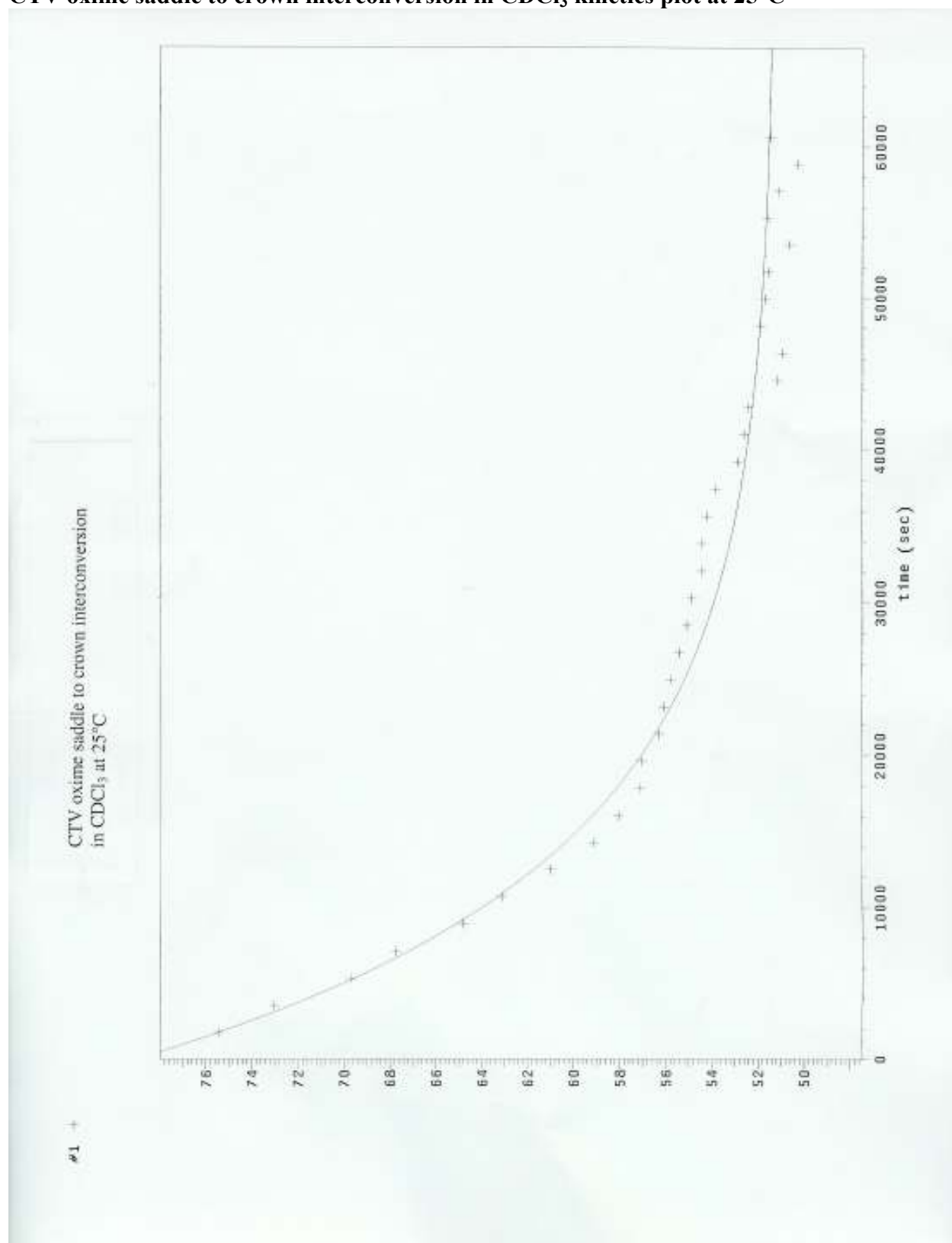
CTV oxime saddle to crown interconversion  
in  $\text{CDCl}_3$  at 25°C

peak	tau	error
1	1.275e+04	640.7

peak number 1

tau =	time	observed	error =	calculated	641 difference
1.28e+04	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 $\text{CDCl}_3$ kinetics plot at $25^\circ\text{C}$



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-d<sub>6</sub> kinetics plot at 25°C

#1 +

