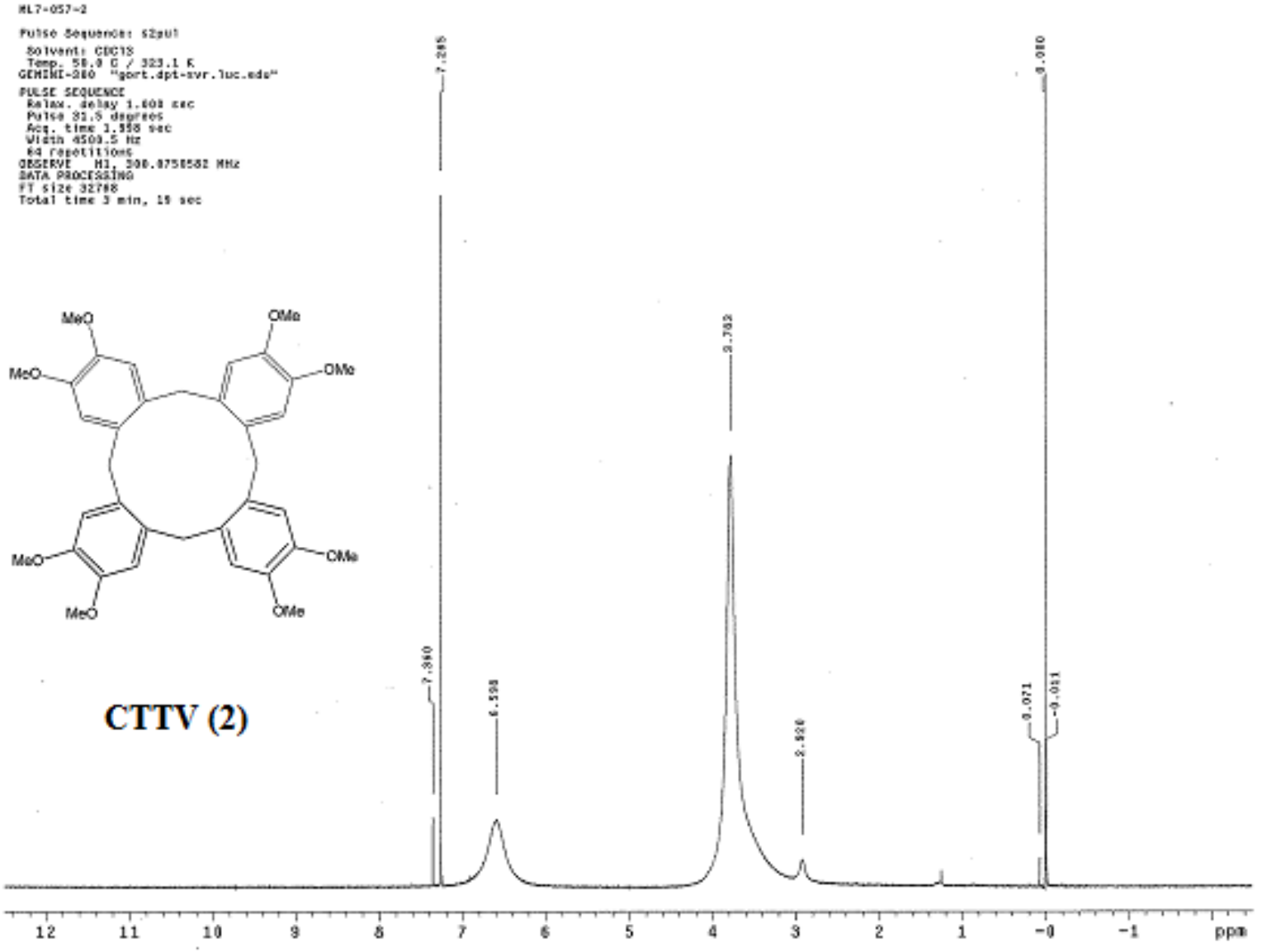
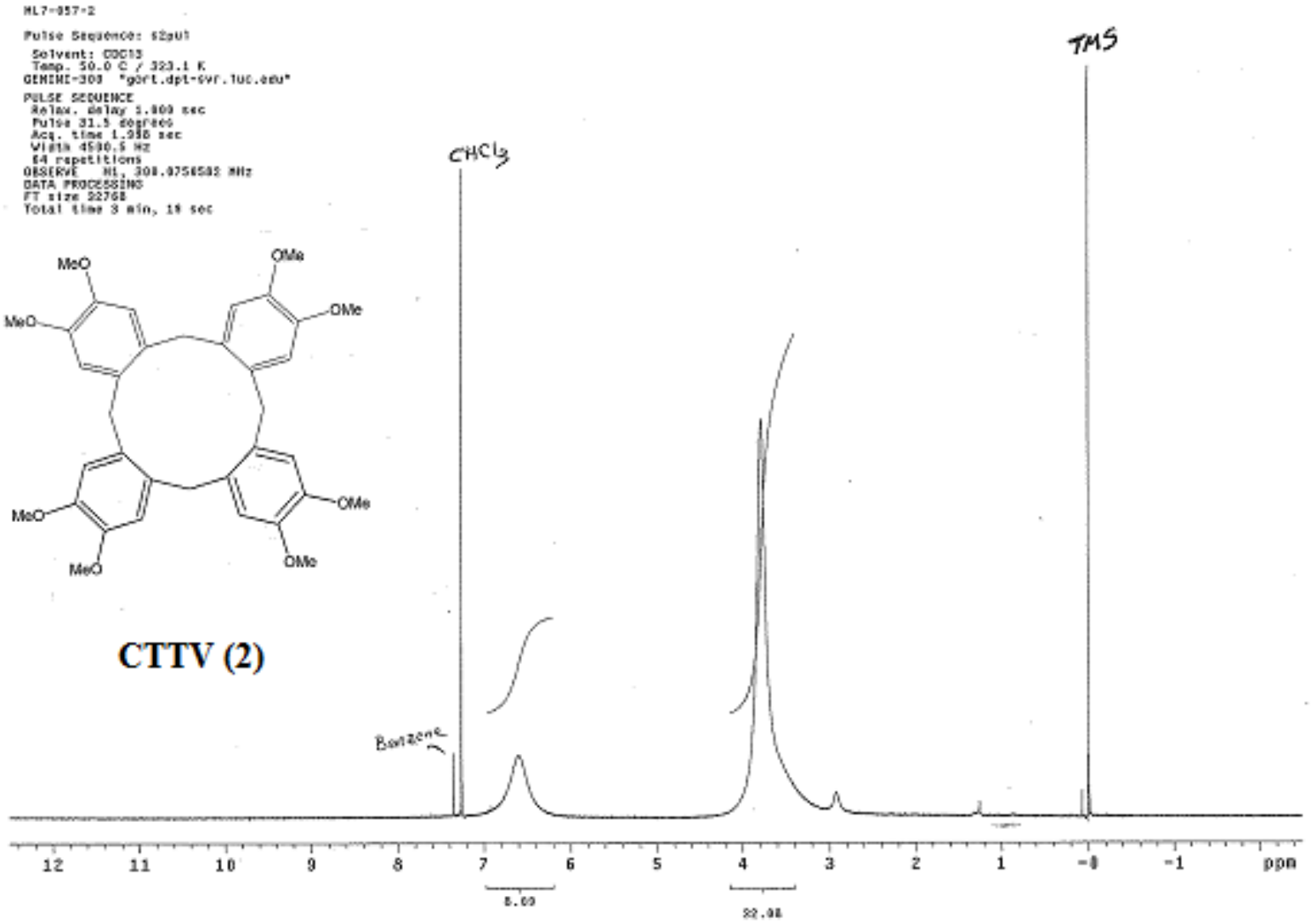
Supplementary Data

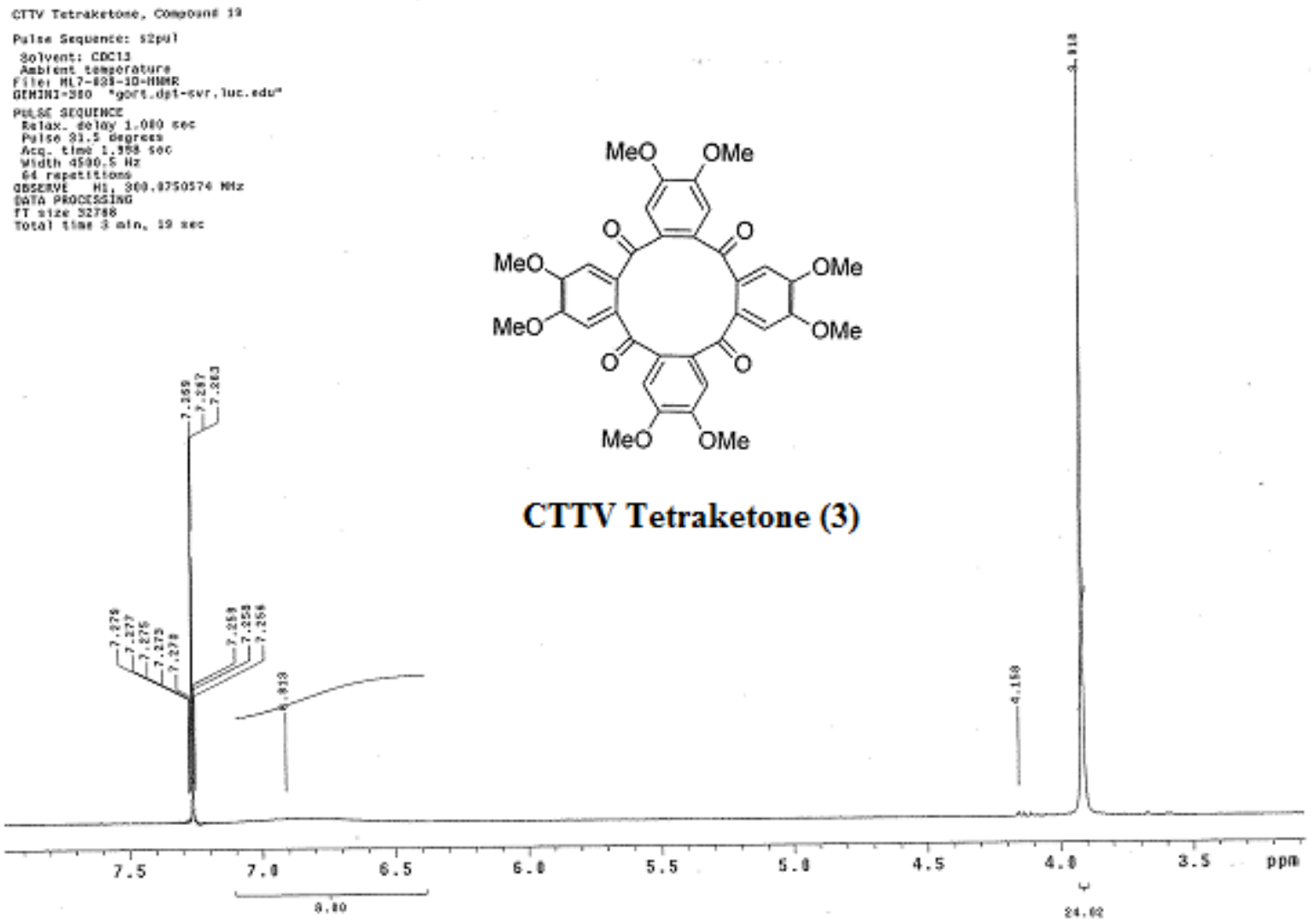
Synthesis, Crystal Structure, and Rearrangements of *ortho*-Cyclophane Cyclotetraveratrylene (CTTV) Tetraketone, a Potential Cavitand

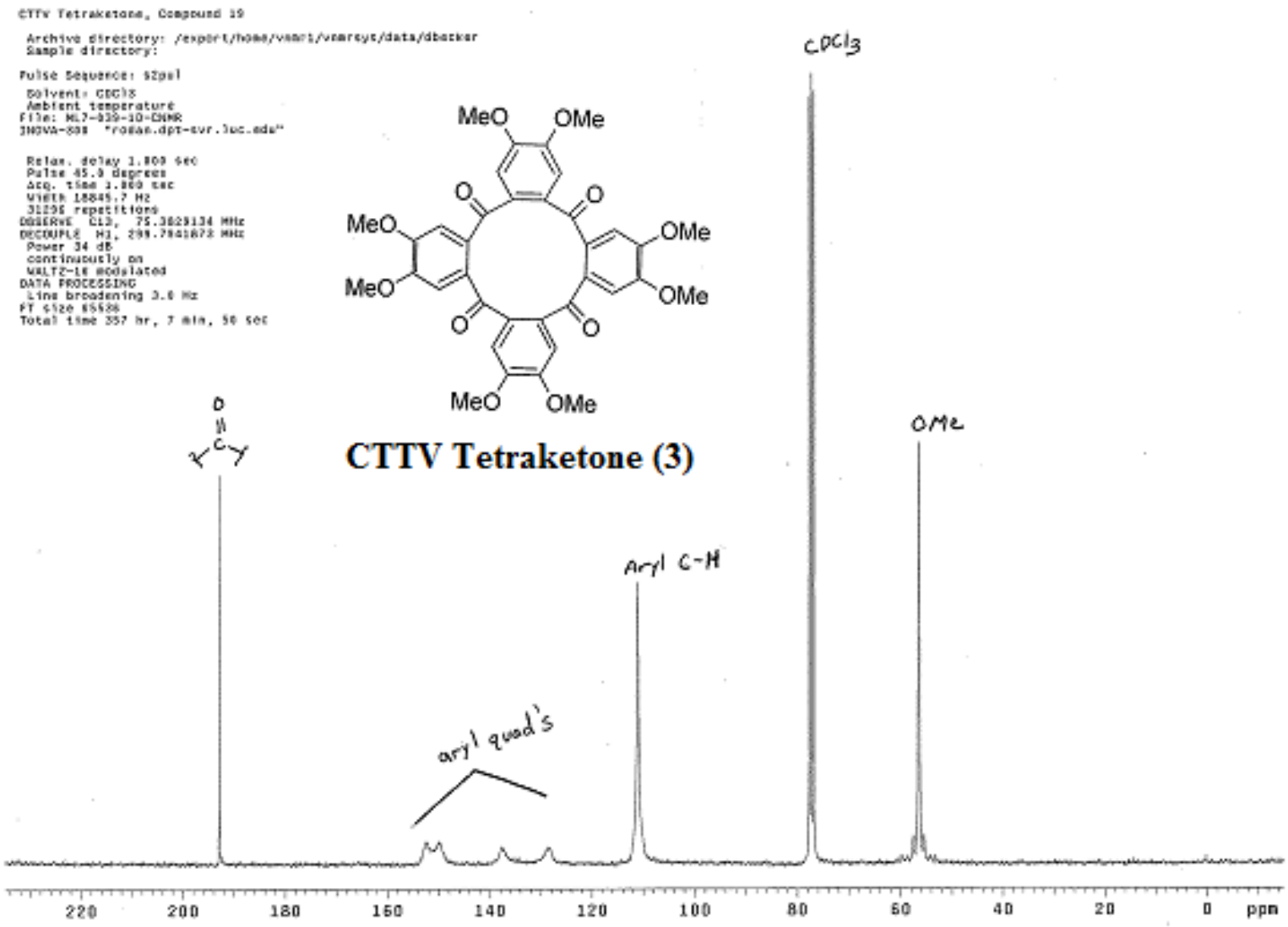
Marlon R. Lutz Jr.†, Matthias Zeller‡, Samuel Sarsah,† Artur Filipowicz†, Hailey Wouters†, and Daniel P. Becker†*

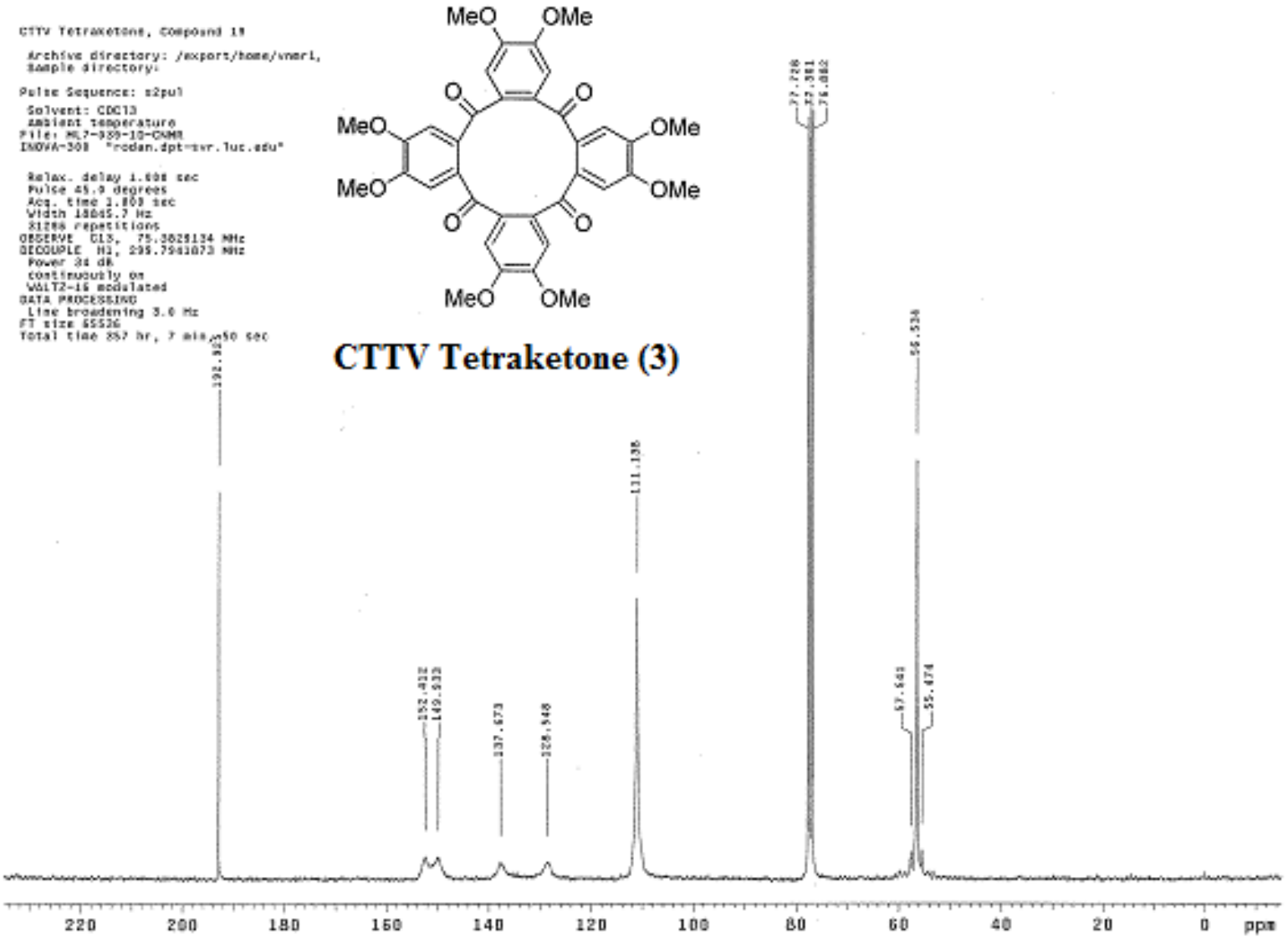
†Department of Chemistry, Loyola University Chicago, 1032 West Sheridan Road, Chicago, Illinois 60660,United States, and ‡Department of Chemistry, 1 University Plaza, Youngstown State University, Youngstown, Ohio 44555-3663, United States

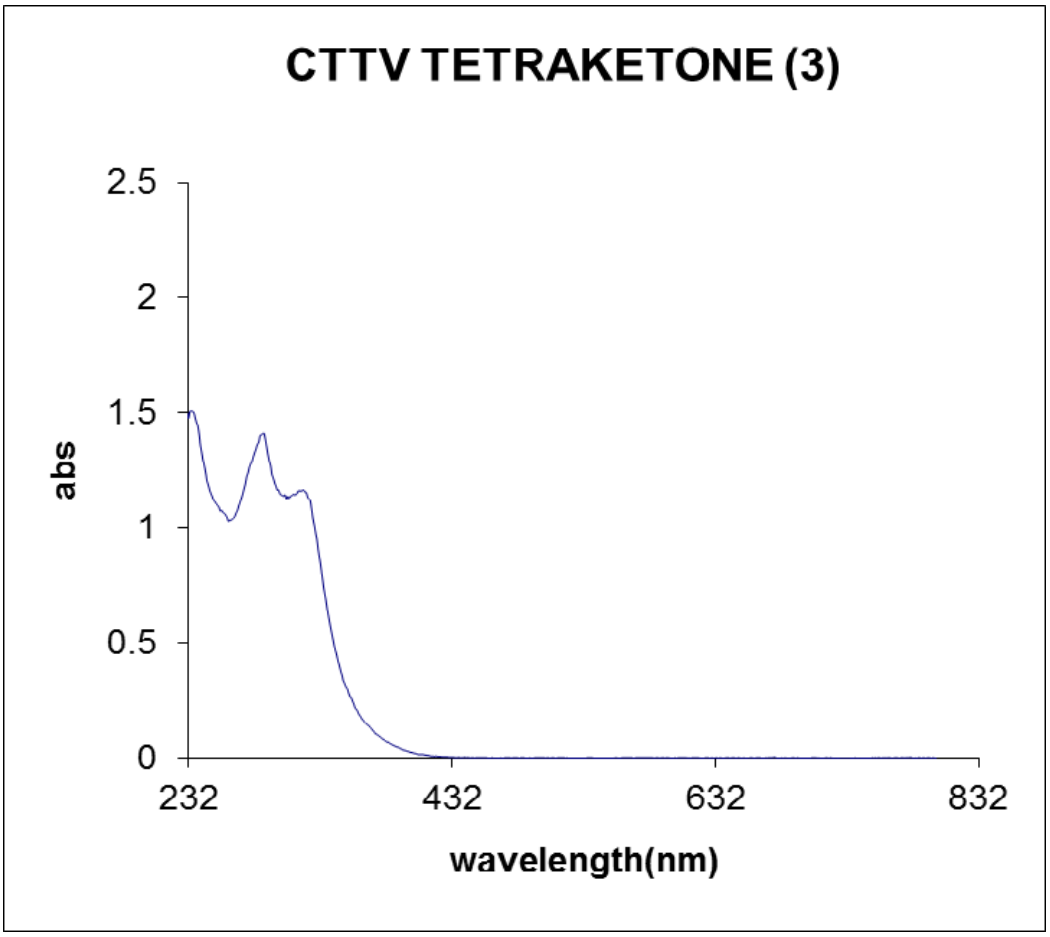

ML7-057-2
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 58.0 C / 331.1 K
GEMINI-200 "gort.dpt-svr.luc.edu"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 200.0758582 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 15 sec
MeO
OMe
CTTV (2)
7.285
7.360
6.598
3.782
2.920
0.071
0.000
-0.011
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


HL7-057-2
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 50.0 C / 323.1 K
GEMINI-300 "gort.dpt-svr.tuc.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, 300.0756582 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec
MeO
OMe
CTTV (2)
CHCl3
TMS
Benzene
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
6.00
32.08


CTTV Tetraketone, Compound 19
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: ML7-038-1D-HNMR
GEMINI-300 "gort.dpt-cvr.luc.edu"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 31.5 degrees
Acq. time 1.358 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.0750574 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 19 sec
MeO
OMe
O
CTTV Tetraketone (3)
7.359
7.297
7.283
7.278
7.277
7.275
7.273
7.270
7.259
7.258
7.256
6.933
4.150
3.918
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
8.80
24.02


CTTv Tetraketone, Compound 19
Archive directory: /export/home/vnmrj/vnmrsys/data/dbacker
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: ML7-039-1D-CNMR
INOVA-500 "rosaa.dpt-svr.luc.edu"
Relax. delay 1.800 sec
Pulse 45.0 degrees
Acq. time 1.860 sec
Width 18645.7 Hz
31256 repetitions
OBSERVE C13, 75.3829134 MHz
DECOUPLE H1, 299.7941873 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 357 hr, 7 min, 50 sec
MeO
OMe
CTTV Tetraketone (3)
CDCl3
OMe
Aryl C-H
aryl quad's
220
200
180
160
140
120
100
80
60
40
20
0
ppm

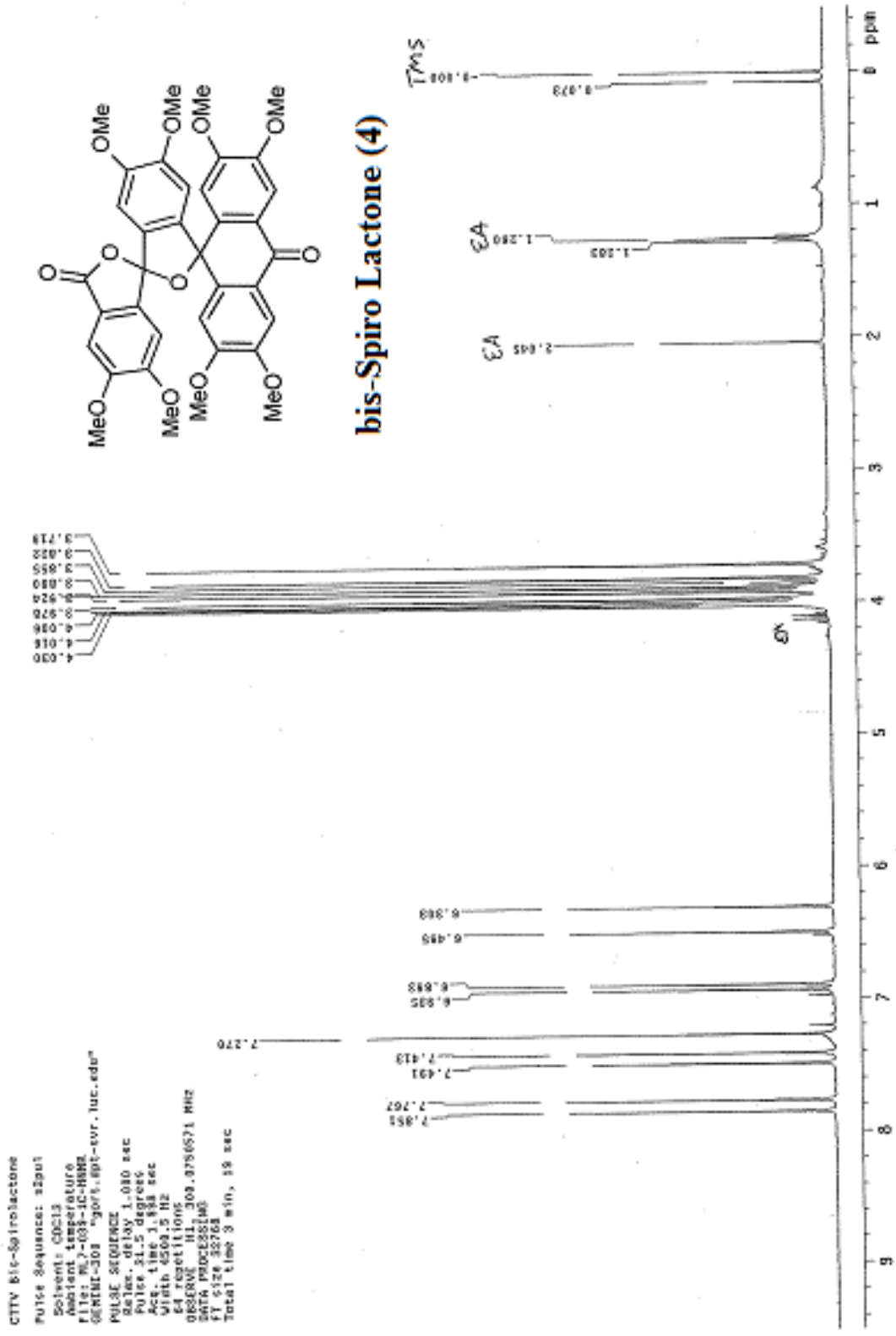

CTTV Tetraketone, Compound 18
Archive directory: /export/home/vnmrl,
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: ML7-930-10-CNMR
INOVA-300 "rodan.dpt=svr.luc.edu"
Relax. delay 1.608 sec
Pulse 45.0 degrees
Acq. time 1.869 sec
Width 18065.7 Hz
31286 repetitions
OBSERVE C13, 75.3028134 MHz
DECOUPLE H1, 299.7943073 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 857 hr, 7 min, 50 sec
MeO
OMe
CTTV Tetraketone (3)
192.903
152.432
149.533
137.673
128.548
111.136
77.720
77.381
76.882
58.534
57.641
55.474
220
200
180
160
140
120
100
80
60
40
20
0
ppm

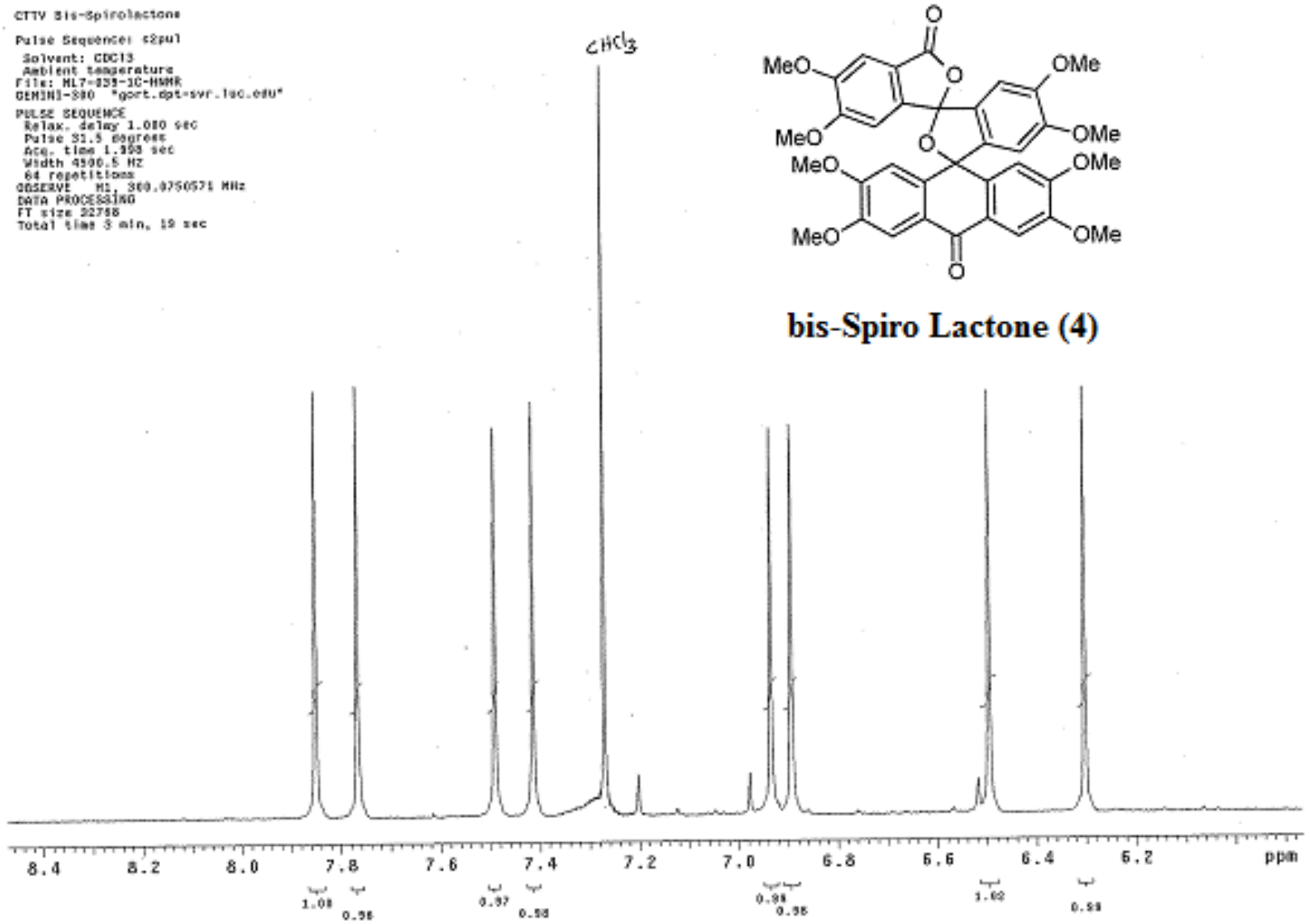


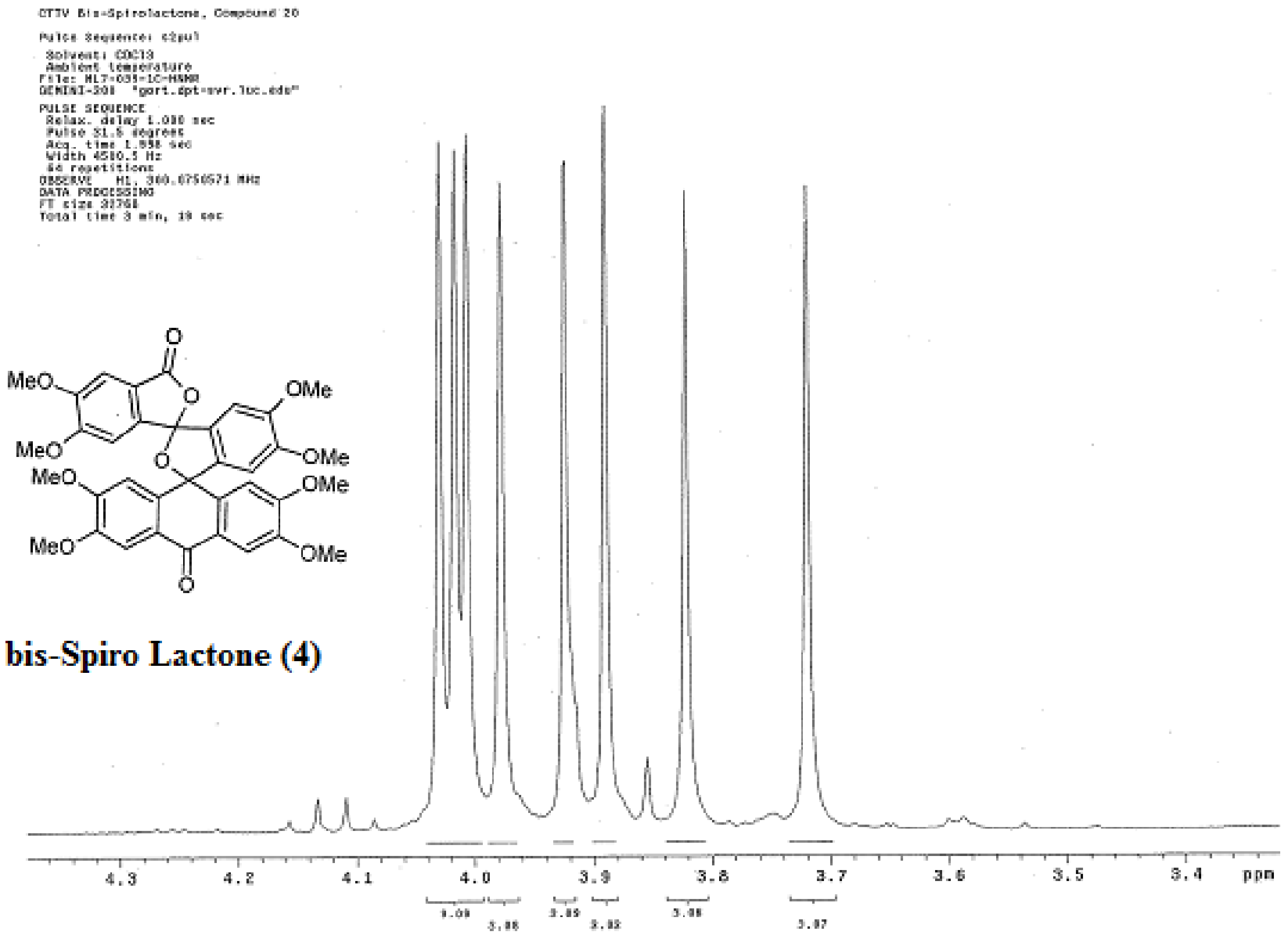
UV –absorption of CTTV-Tetraketone

CTTV-TK (2.4mg, 0.037mmol) dissolved in 10ml Dichloromethane. 1.0ml was taken and diluted to 10ml with dichloromethane to make $3.7x10^{-5}$M solution

λmax/absorbance	molar absorptivity (ε)
289nm (1.4081)	$3.81x10^{-4}$M
320nm (1.1637)	$3.15x10^{-4}$M

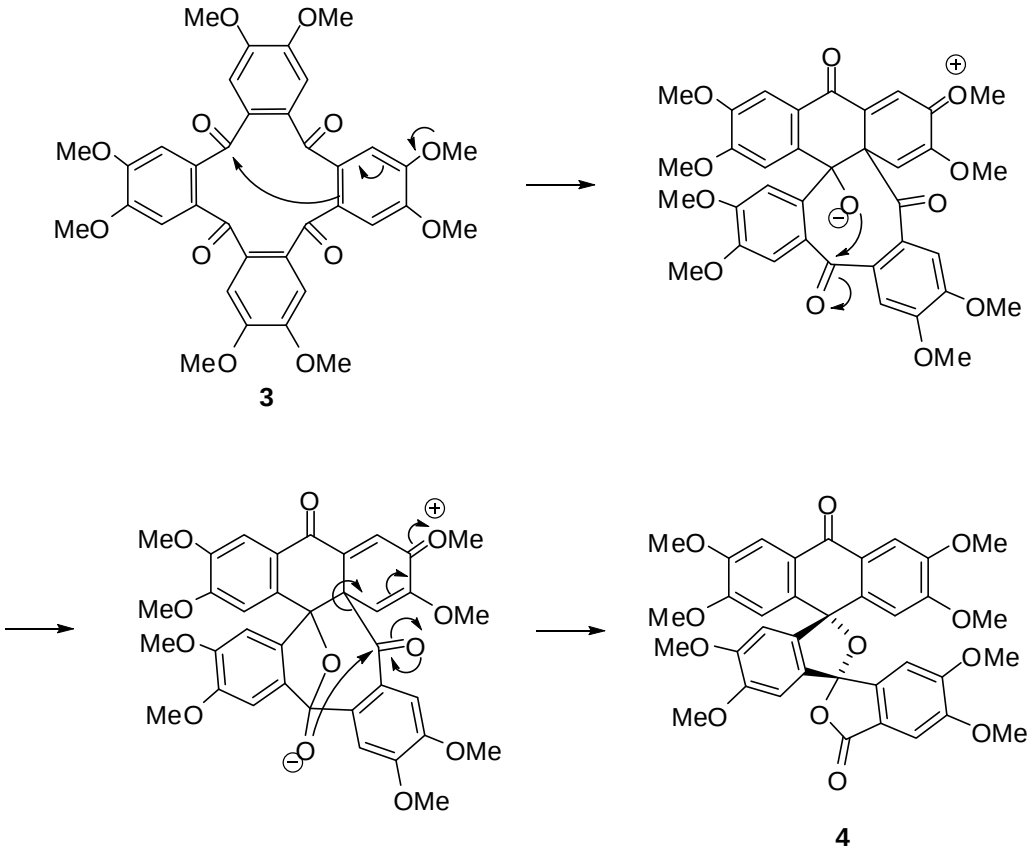

bis-Spiro Lactone (4)
OMe
MeO
TMS
EA
EA
DM
ppm

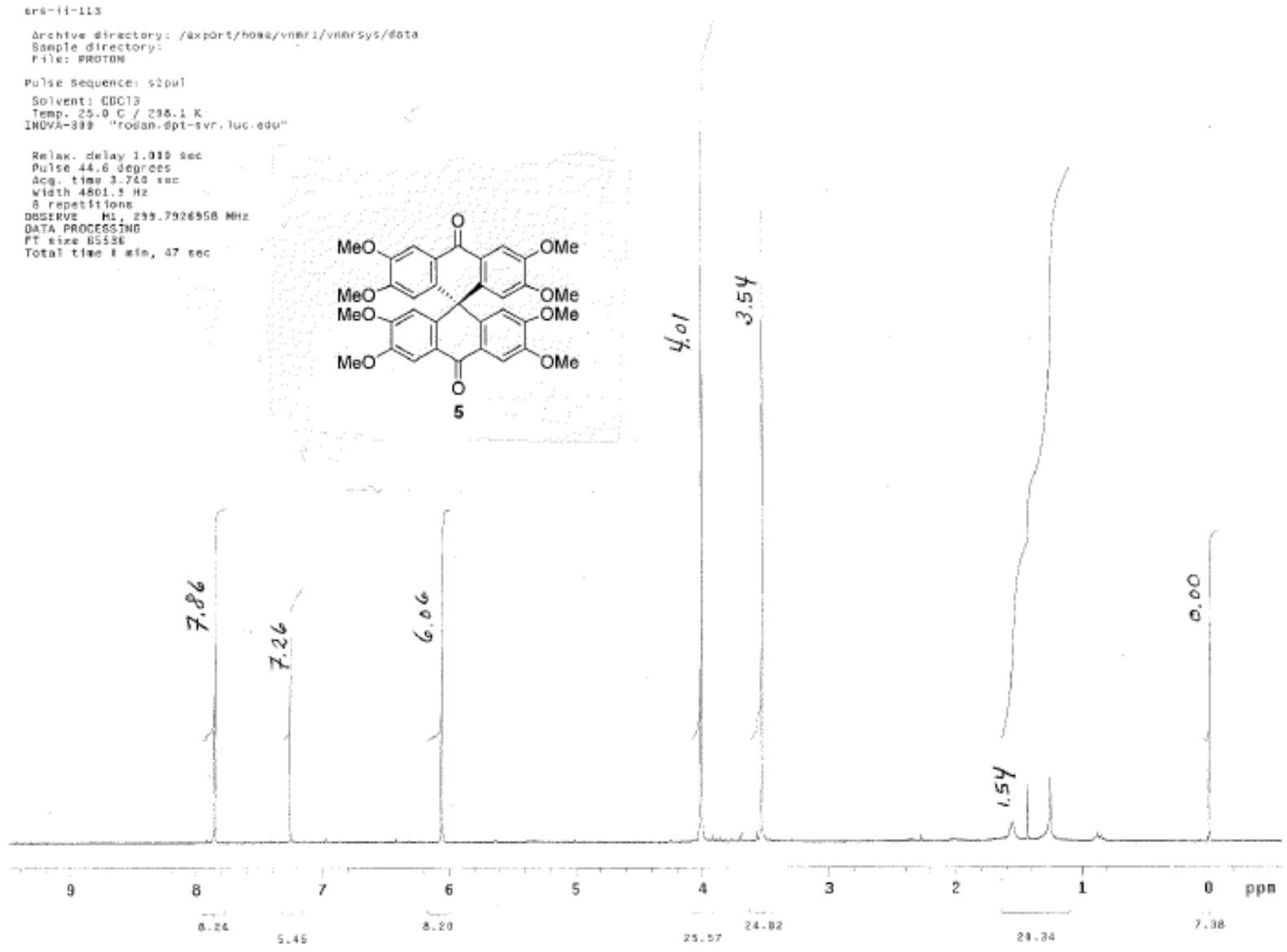

CTTV Bis-Spirolactone
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: ML7-035-1C-HNMR
GEMINI-300 "gort.dpt-svr.luc.edu"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 31.5 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
64 repetitions
OBSERVE H1, 300.0750571 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 19 sec
CHCl3
MeO
OMe
bis-Spiro Lactone (4)
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm
1.00
0.96
0.97
0.98
0.98
0.95
1.02
0.98

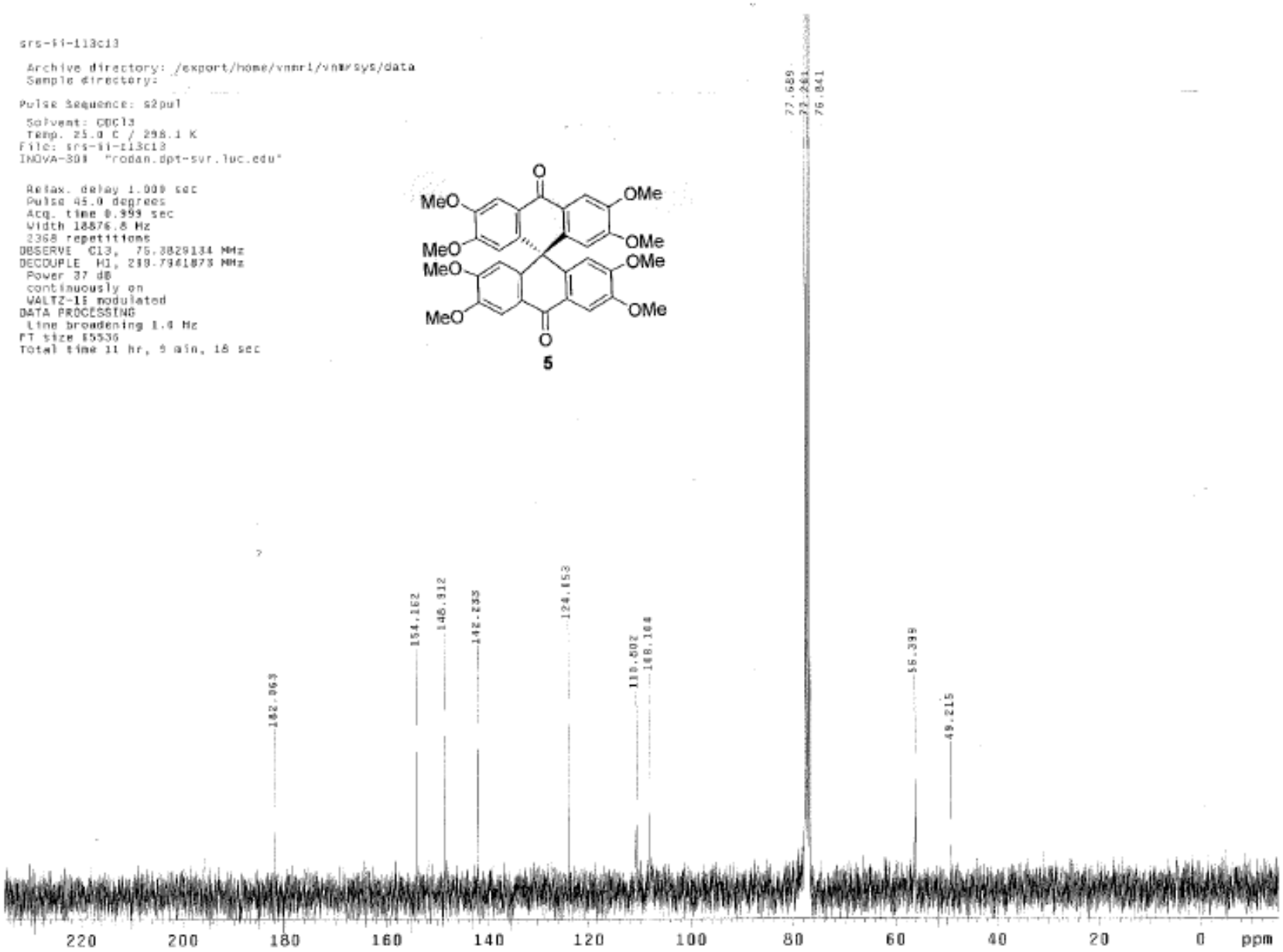


bis-Spiro Lactone (4)

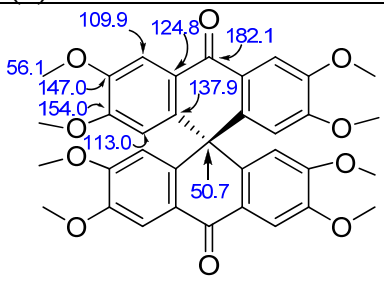
Scheme S1. Proposed Mechanism of formation of the bis-spirolactone **4** from CTTV Tetraketone **3** in *basic* conditions



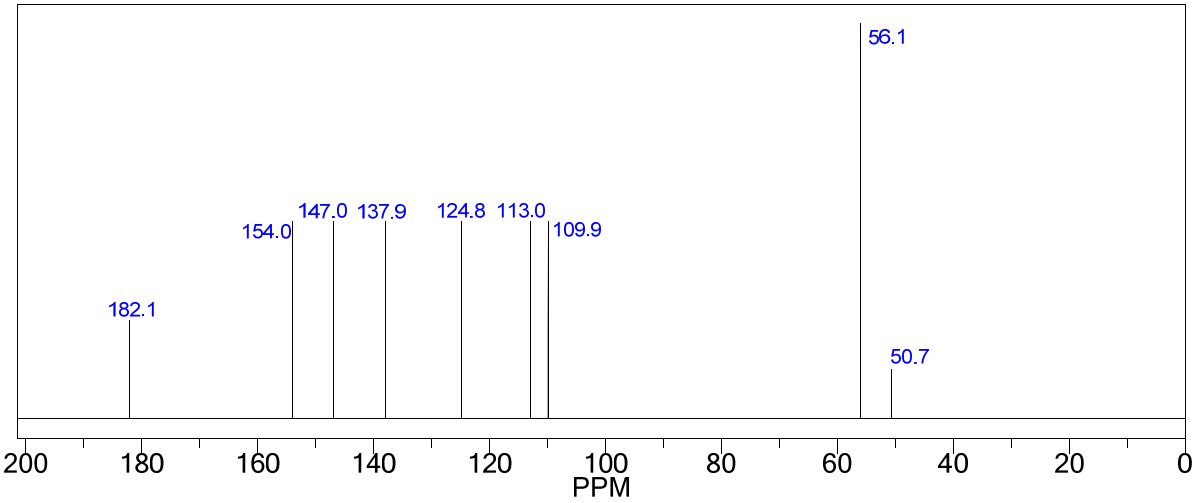

srs-ii-113
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-300 "rodan.dpt-svr.luc.edu"
Relax. delay 1.000 sec
Pulse 44.6 degrees
Acq. time 3.740 sec
width 4801.5 Hz
8 repetitions
OBSERVE H1, 299.7926958 MHz
DATA PROCESSING
FT size 65536
Total time 8 min, 47 sec
MeO
OMe
5
7.86
7.26
6.06
4.01
3.54
1.54
0.00
9
8
7
6
5
4
3
2
1
0
ppm
8.24
5.45
8.20
25.57
24.82
29.34
7.38


srs-fi-113c13
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: srs-fi-113c13
INOVA-300 "rodan.dpt-svr.luc.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.999 sec
Width 18876.8 Hz
2368 repetitions
OBSERVE C13, 75.3829134 MHz
DECOUPLE H1, 299.7961873 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.4 Hz
FT size 65536
Total time 11 hr, 9 min, 18 sec
MeO
OMe
5
77.689
77.261
76.841
182.963
154.162
146.312
142.833
124.653
110.502
108.184
56.399
49.215
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Calculated ^{13}C Spectrum for 2,2',3,3',6,6',7,7'-octamethoxy-10H,10'H-9,9'-spirobi[anthracene]-10,10'-dione (**5**) versus Observed ^{13}C Chemical Shifts

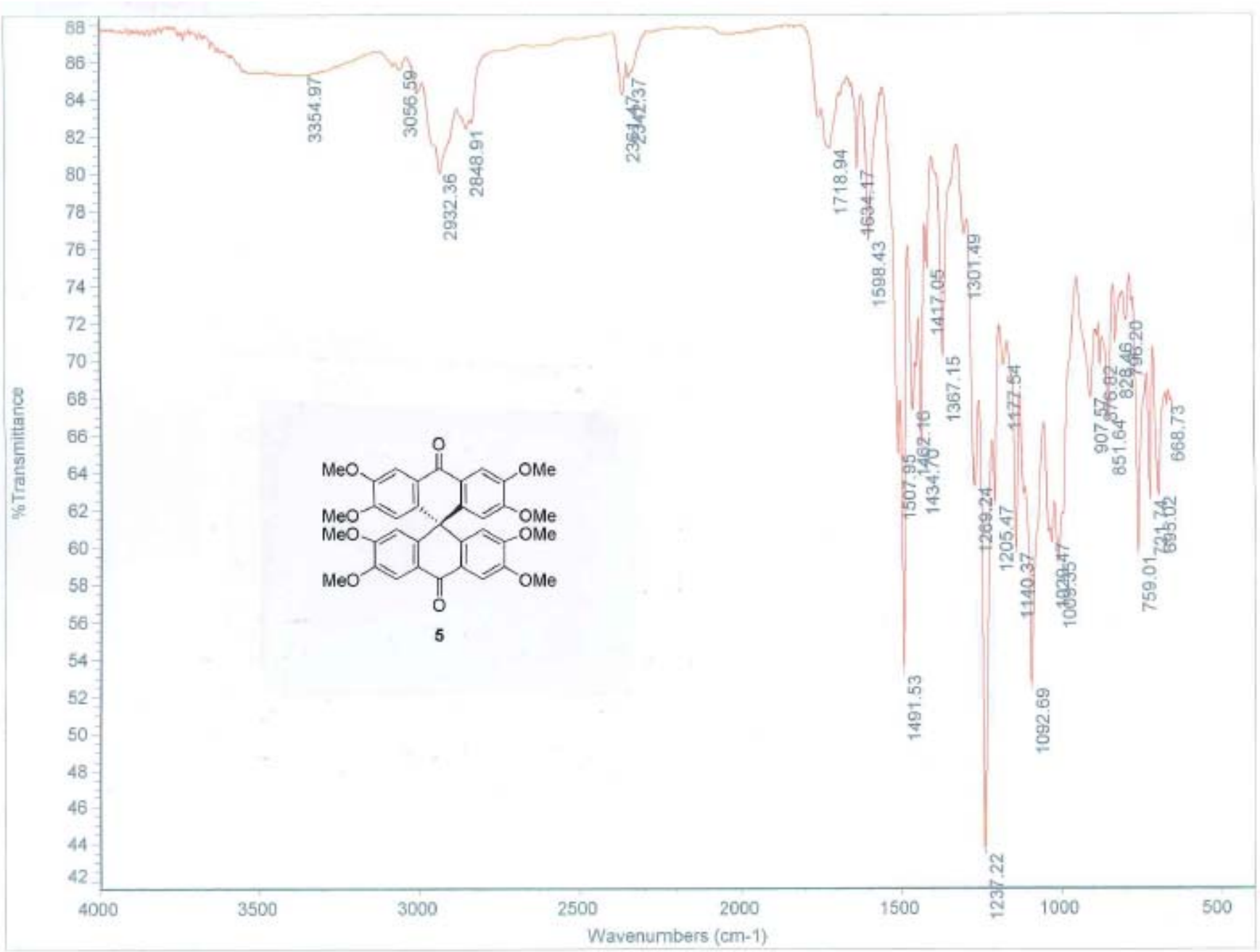


Calculated Values (ChemDraw Ultra 11.0)

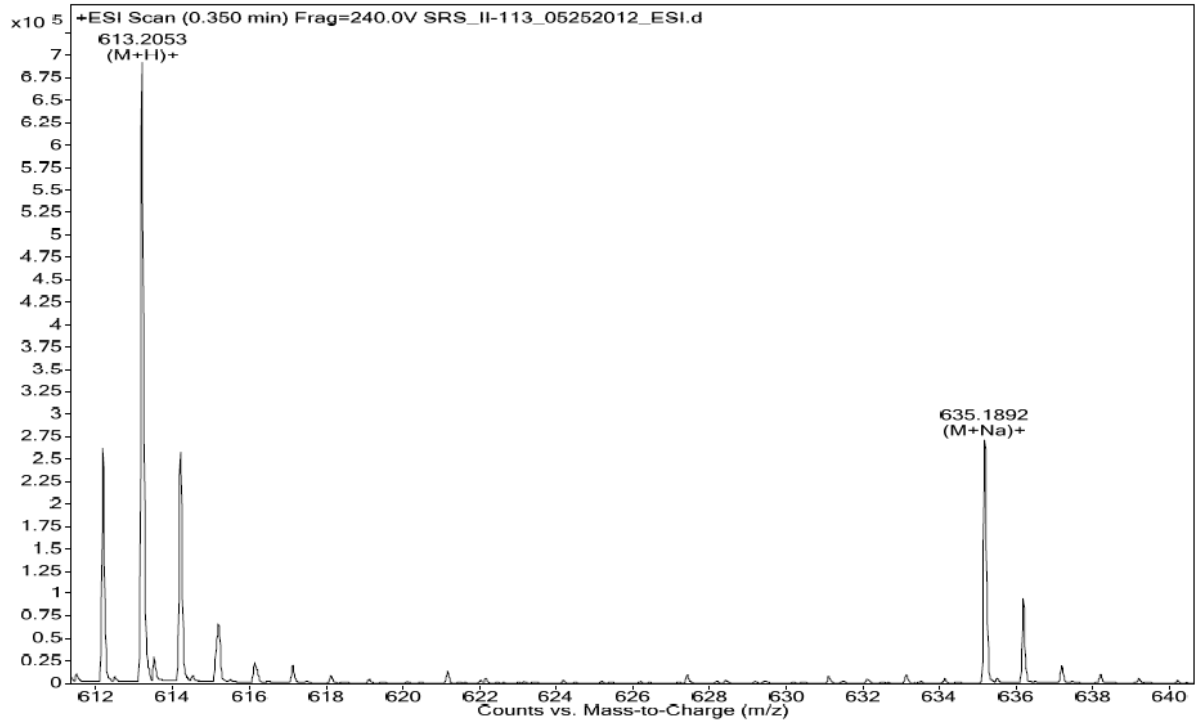


Carbon	**Calculated δ**	**Observed δ***	**Δ δ**
spiro quat	50.7	48.95	1.8
methoxy	56.1	56.14	0.0
CH ortho C=O	109.9	107.84	2.1
CH meta to spiro	113.0	110.54	2.5
arom C-C=O	124.8	123.79	1.0
arom C-quat carbon	137.9	141.97	4.1
aryl C meta C=O	147.0	148.65	1.7
aryl C meta C=O	154.0	153.9	0.1
C=O	182.1	181.8	0.3
Average Δ δ =			**1.5±1.3 ppm**

*Corrected for CDCl3 at 77.00 ppm


% Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
3354.97
3056.59
2932.36
2848.91
1718.94
1598.43
1507.95
1491.53
1462.10
1434.70
1417.05
1367.15
1301.49
1269.24
1237.22
1205.47
1177.54
1140.37
1092.69
1009.35
907.57
851.64
828.46
796.20
759.01
721.74
695.02
668.73
MeO
OMe
5

Sample Name	SRS_II-113	**Position**	P1-E5	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	SRS_II-113_05252012_	**ACQ Method**	ESI_ASL_Pos_Main_051	**Comment**		**Acquired Time**	5/25/2012 2:36:11 PM



Scheme S2. Proposed Mechanism of formation of the 2,2',3,3',6,6',7,7'-octamethoxy-10H,10'H-9,9'-spirobi[anthracene]-10,10'-dione (**5**) from CTTV Tetraketone **3** in *acidic* conditions

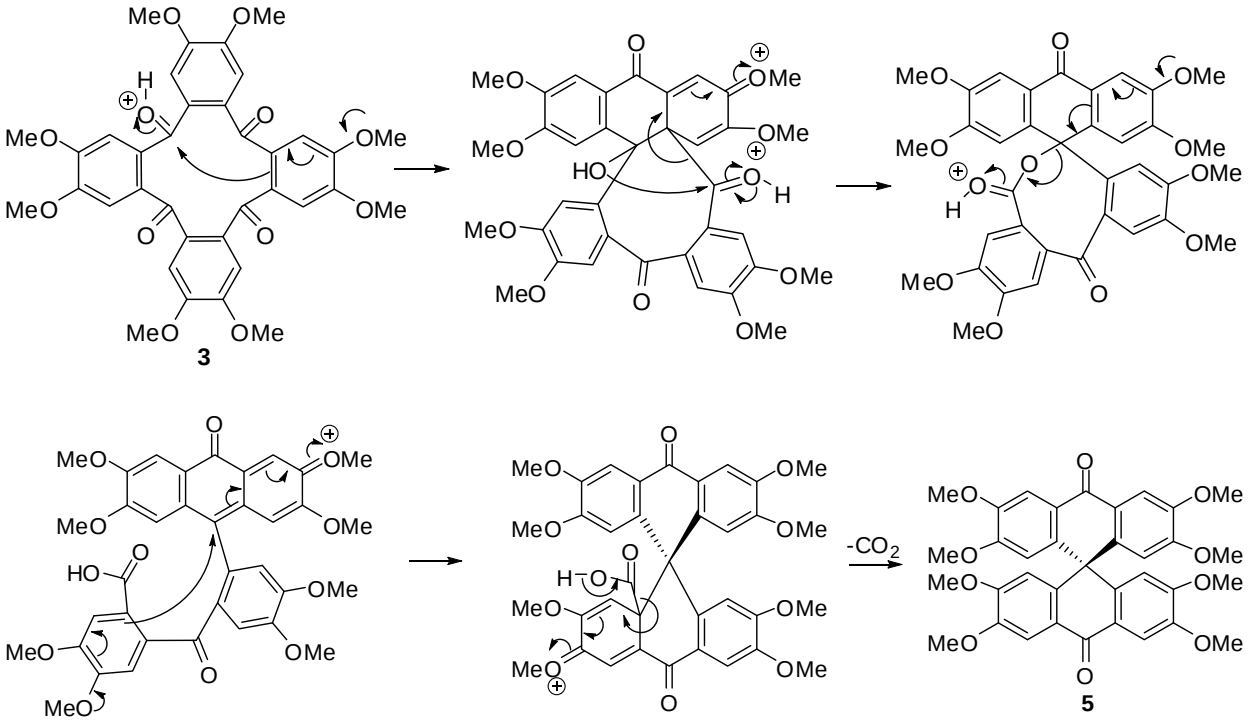


Table S1. Single Crystal Experimental details

For all structures: triclinic, $P\bar{1}$, $Z = 2$. Experiments were carried out using a Bruker AXS SMART APEX CCD diffractometer. Data collection used ω scans.

	3·3(CH_2Cl_2)	**4**
Crystal data		
Chemical formula	$C_{36}H_{32}O_{12}$·3(CH_2Cl_2)	$C_{36}H_{32}O_{12}$
M_r	911.39	656.62
Temperature (K)	100	100
a, *b*, *c* (Å)	11.9308 (7), 13.8064 (8), 14.0009 (7)	10.9038 (15), 10.9256 (15), 14.494 (2)
α, β, γ (°)	114.082 (3), 92.329 (3), 105.980 (3)	106.522 (2), 98.609 (2), 112.249 (2)
V (Å^3)	1993.17 (19)	1466.3 (3)
F(000)	940	688
D_x (Mg m^{-3})	1.519	1.487
No. of reflections for cell measurement	2777	5210
θ range (°) for cell measurement	2.2–30.2	2.2–30.5
μ (mm^{-1})	0.50	0.11
Crystal shape	Plate	Block
Colour	Colourless	Colourless
Crystal size (mm)	0.2 × 0.16 × 0.08	0.39 × 0.38 × 0.32
Data collection		
Radiation type / source	Mo *K*α, fine-focus sealed tube	Mo *K*α, fine-focus sealed tube
Monochromator	Graphite	Graphite
Absorption correction	multi-scan (Apex2, Bruker, 2008)	multi-scan (Apex2, Bruker, 2008)
T_{min}, T_{max}	0.612, 0.746	0.861, 0.965
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17017, 7022, 3759	14705, 7157, 4964
R_{int}	0.061	0.027
θ values (°)	θ_{max} = 25.0, θ_{min} = 1.6	θ_{max} = 28.3, θ_{min} = 1.5
Range of *h*, *k*, *l*	*h* = -14→14, *k* = -16→16, *l* = -16→16	*h* = -14→14, *k* = -14→14, *l* = -19→19
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.083, 0.244, 1.06	0.043, 0.126, 1.03
reflections/restraints/parameters	7022/0/441	7157/0/441
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, -0.35	0.45, -0.27

Computer programs: Apex2 v2008.2-4 (Bruker, 2008), *SHELXTL* 6.14 (Bruker, 2000-2003), *SHELXTL* 6.14.

Table S2. Selected geometric parameters (Å, º)

3			
C1–O1	1.222 (5)	C18–H18C	0.9800
C1–C30	1.487 (6)	C19–O7	1.247 (5)
C1–C2	1.500 (6)	C19–C20	1.467 (6)
C2–C3	1.385 (6)	C20–C21	1.413 (6)
C2–C7	1.405 (6)	C20–C25	1.416 (6)
C3–C4	1.401 (6)	C21–C22	1.363 (6)
C3–H3	0.9500	C21–H21	0.9500
C4–O2	1.357 (5)	C22–O8	1.364 (5)
C4–C5	1.380 (6)	C22–C23	1.436 (6)
C5–O3	1.372 (5)	C23–C24	1.361 (6)
C5–C6	1.392 (6)	C23–O9	1.378 (5)
C6–C7	1.389 (6)	C24–C25	1.400 (6)
C6–H6	0.9500	C24–H24	0.9500
C7–C10	1.528 (6)	C25–C28	1.527 (6)
C8–O2	1.398 (6)	C26–O8	1.425 (5)
C8–H8A	0.9800	C26–H26A	0.9800
C8–H8B	0.9800	C26–H26B	0.9800
C8–H8C	0.9800	C26–H26C	0.9800
C9–O3	1.448 (6)	C27–O9	1.430 (5)
C9–H9A	0.9800	C27–H27A	0.9800
C9–H9B	0.9800	C27–H27B	0.9800
C9–H9C	0.9800	C27–H27C	0.9800
C10–O4	1.196 (5)	C28–O10	1.224 (5)
C10–C11	1.501 (6)	C28–C29	1.482 (6)
C11–C12	1.388 (6)	C29–C34	1.379 (6)
C11–C16	1.390 (5)	C29–C30	1.422 (6)
C12–C13	1.397 (6)	C30–C31	1.410 (6)
C12–H12	0.9500	C31–C32	1.379 (6)
C13–O5	1.337 (5)	C31–H31	0.9500
C13–C14	1.398 (6)	C32–O12	1.356 (5)
C14–O6	1.375 (5)	C32–C33	1.375 (6)
C14–C15	1.400 (6)	C33–O11	1.382 (5)
C15–C16	1.356 (6)	C33–C34	1.405 (6)

C15–H15	0.9500	C34–H34	0.9500
C16–C19	1.517 (6)	C35–O12	1.424 (6)
C17–O5	1.441 (5)	C35–H35A	0.9800
C17–H17A	0.9800	C35–H35B	0.9800
C17–H17B	0.9800	C35–H35C	0.9800
C17–H17C	0.9800	C36–O11	1.434 (6)
C18–O6	1.450 (6)	C36–H36A	0.9800
C18–H18A	0.9800	C36–H36B	0.9800
C18–H18B	0.9800	C36–H36C	0.9800
O1–C1–C30	120.1 (4)	C21–C20–C19	117.3 (4)
O1–C1–C2	119.8 (4)	C25–C20–C19	123.6 (4)
C30–C1–C2	119.4 (4)	C22–C21–C20	120.5 (4)
C3–C2–C7	120.1 (4)	C22–C21–H21	119.8
C3–C2–C1	115.9 (4)	C20–C21–H21	119.8
C7–C2–C1	124.0 (4)	C21–C22–O8	126.0 (4)
C2–C3–C4	120.2 (4)	C21–C22–C23	120.1 (4)
C2–C3–H3	119.9	O8–C22–C23	113.9 (4)
C4–C3–H3	119.9	C24–C23–O9	124.4 (4)
O2–C4–C5	116.9 (4)	C24–C23–C22	119.9 (4)
O2–C4–C3	123.1 (4)	O9–C23–C22	115.7 (4)
C5–C4–C3	120.0 (4)	C23–C24–C25	120.6 (4)
O3–C5–C4	114.2 (4)	C23–C24–H24	119.7
O3–C5–C6	126.1 (4)	C25–C24–H24	119.7
C4–C5–C6	119.7 (4)	C24–C25–C20	120.0 (4)
C7–C6–C5	121.1 (4)	C24–C25–C28	113.9 (3)
C7–C6–H6	119.4	C20–C25–C28	126.0 (4)
C5–C6–H6	119.4	O8–C26–H26A	109.5
C6–C7–C2	118.9 (4)	O8–C26–H26B	109.5
C6–C7–C10	113.0 (4)	H26A–C26–H26B	109.5
C2–C7–C10	128.2 (4)	O8–C26–H26C	109.5
O2–C8–H8A	109.5	H26A–C26–H26C	109.5
O2–C8–H8B	109.5	H26B–C26–H26C	109.5
H8A–C8–H8B	109.5	O9–C27–H27A	109.5
O2–C8–H8C	109.5	O9–C27–H27B	109.5
H8A–C8–H8C	109.5	H27A–C27–H27B	109.5
H8B–C8–H8C	109.5	O9–C27–H27C	109.5

O3–C9–H9A	109.5	H27A–C27–H27C	109.5
O3–C9–H9B	109.5	H27B–C27–H27C	109.5
H9A–C9–H9B	109.5	O10–C28–C29	120.4 (4)
O3–C9–H9C	109.5	O10–C28–C25	117.7 (4)
H9A–C9–H9C	109.5	C29–C28–C25	121.3 (4)
H9B–C9–H9C	109.5	C34–C29–C30	119.6 (4)
O4–C10–C11	121.1 (4)	C34–C29–C28	116.2 (4)
O4–C10–C7	120.9 (4)	C30–C29–C28	124.0 (4)
C11–C10–C7	117.7 (3)	C31–C30–C29	118.1 (4)
C12–C11–C16	118.6 (4)	C31–C30–C1	115.2 (4)
C12–C11–C10	115.5 (3)	C29–C30–C1	126.6 (4)
C16–C11–C10	125.9 (4)	C32–C31–C30	120.7 (4)
C11–C12–C13	122.2 (4)	C32–C31–H31	119.7
C11–C12–H12	118.9	C30–C31–H31	119.7
C13–C12–H12	118.9	O12–C32–C33	116.0 (4)
O5–C13–C12	125.6 (4)	O12–C32–C31	122.7 (4)
O5–C13–C14	117.3 (4)	C33–C32–C31	121.2 (4)
C12–C13–C14	117.1 (4)	C32–C33–O11	117.4 (3)
O6–C14–C13	114.7 (4)	C32–C33–C34	118.7 (4)
O6–C14–C15	124.3 (4)	O11–C33–C34	123.5 (4)
C13–C14–C15	120.9 (4)	C29–C34–C33	121.1 (4)
C16–C15–C14	120.1 (4)	C29–C34–H34	119.4
C16–C15–H15	119.9	C33–C34–H34	119.4
C14–C15–H15	119.9	O12–C35–H35A	109.5
C15–C16–C11	121.0 (4)	O12–C35–H35B	109.5
C15–C16–C19	111.2 (4)	H35A–C35–H35B	109.5
C11–C16–C19	127.6 (4)	O12–C35–H35C	109.5
O5–C17–H17A	109.5	H35A–C35–H35C	109.5
O5–C17–H17B	109.5	H35B–C35–H35C	109.5
H17A–C17–H17B	109.5	O11–C36–H36A	109.5
O5–C17–H17C	109.5	O11–C36–H36B	109.5
H17A–C17–H17C	109.5	H36A–C36–H36B	109.5
H17B–C17–H17C	109.5	O11–C36–H36C	109.5
O6–C18–H18A	109.5	H36A–C36–H36C	109.5
O6–C18–H18B	109.5	H36B–C36–H36C	109.5
H18A–C18–H18B	109.5	C4–O2–C8	118.7 (3)
O6–C18–H18C	109.5	C5–O3–C9	114.7 (4)

H18A–C18–H18C	109.5	C13–O5–C17	118.5 (3)
H18B–C18–H18C	109.5	C14–O6–C18	117.3 (3)
O7–C19–C20	119.8 (4)	C22–O8–C26	116.0 (3)
O7–C19–C16	118.1 (4)	C23–O9–C27	117.3 (4)
C20–C19–C16	122.0 (3)	C33–O11–C36	115.4 (3)
C21–C20–C25	118.9 (4)	C32–O12–C35	116.9 (3)
O1–C1–C2–C3	-0.8 (6)	C21–C22–C23–C24	4.2 (7)
C30–C1–C2–C3	-170.9 (4)	O8–C22–C23–C24	-178.1 (4)
O1–C1–C2–C7	178.2 (4)	C21–C22–C23–O9	-175.4 (4)
C30–C1–C2–C7	8.1 (6)	O8–C22–C23–O9	2.3 (6)
C7–C2–C3–C4	-0.1 (6)	O9–C23–C24–C25	176.4 (4)
C1–C2–C3–C4	179.0 (4)	C22–C23–C24–C25	-3.1 (7)
C2–C3–C4–O2	176.4 (4)	C23–C24–C25–C20	1.0 (7)
C2–C3–C4–C5	-2.7 (6)	C23–C24–C25–C28	177.7 (4)
O2–C4–C5–O3	2.0 (6)	C21–C20–C25–C24	0.1 (6)
C3–C4–C5–O3	-178.9 (4)	C19–C20–C25–C24	-175.5 (4)
O2–C4–C5–C6	-176.4 (4)	C21–C20–C25–C28	-176.1 (4)
C3–C4–C5–C6	2.7 (6)	C19–C20–C25–C28	8.3 (7)
O3–C5–C6–C7	-178.3 (4)	C24–C25–C28–O10	82.1 (5)
C4–C5–C6–C7	-0.1 (6)	C20–C25–C28–O10	-101.5 (5)
C5–C6–C7–C2	-2.6 (6)	C24–C25–C28–C29	-89.1 (5)
C5–C6–C7–C10	176.0 (4)	C20–C25–C28–C29	87.3 (6)
C3–C2–C7–C6	2.6 (6)	O10–C28–C29–C34	-2.6 (6)
C1–C2–C7–C6	-176.3 (4)	C25–C28–C29–C34	168.4 (4)
C3–C2–C7–C10	-175.7 (4)	O10–C28–C29–C30	-178.2 (4)
C1–C2–C7–C10	5.3 (7)	C25–C28–C29–C30	-7.2 (6)
C6–C7–C10–O4	84.4 (5)	C34–C29–C30–C31	-0.9 (6)
C2–C7–C10–O4	-97.1 (5)	C28–C29–C30–C31	174.6 (4)
C6–C7–C10–C11	-89.2 (5)	C34–C29–C30–C1	178.1 (4)
C2–C7–C10–C11	89.3 (5)	C28–C29–C30–C1	-6.5 (7)
O4–C10–C11–C12	-3.1 (6)	O1–C1–C30–C31	-80.2 (5)
C7–C10–C11–C12	170.4 (4)	C2–C1–C30–C31	89.9 (5)
O4–C10–C11–C16	177.5 (4)	O1–C1–C30–C29	100.9 (6)
C7–C10–C11–C16	-9.0 (6)	C2–C1–C30–C29	-89.0 (5)
C16–C11–C12–C13	0.2 (6)	C29–C30–C31–C32	1.2 (6)
C10–C11–C12–C13	-179.2 (4)	C1–C30–C31–C32	-177.9 (4)

C11–C12–C13–O5	179.2 (4)	C30–C31–C32–O12	179.0 (4)
C11–C12–C13–C14	-0.3 (6)	C30–C31–C32–C33	3.5 (6)
O5–C13–C14–O6	-0.6 (6)	O12–C32–C33–O11	2.1 (6)
C12–C13–C14–O6	178.9 (4)	C31–C32–C33–O11	177.9 (4)
O5–C13–C14–C15	-179.7 (4)	O12–C32–C33–C34	175.9 (4)
C12–C13–C14–C15	-0.1 (6)	C31–C32–C33–C34	-8.3 (6)
O6–C14–C15–C16	-178.2 (4)	C30–C29–C34–C33	-4.0 (6)
C13–C14–C15–C16	0.7 (7)	C28–C29–C34–C33	-179.9 (4)
C14–C15–C16–C11	-0.9 (7)	C32–C33–C34–C29	8.6 (6)
C14–C15–C16–C19	-177.3 (4)	O11–C33–C34–C29	-177.9 (4)
C12–C11–C16–C15	0.4 (6)	C5–C4–O2–C8	174.6 (4)
C10–C11–C16–C15	179.8 (4)	C3–C4–O2–C8	-4.5 (6)
C12–C11–C16–C19	176.2 (4)	C4–C5–O3–C9	178.0 (4)
C10–C11–C16–C19	-4.5 (7)	C6–C5–O3–C9	-3.8 (6)
C15–C16–C19–O7	-89.3 (5)	C12–C13–O5–C17	2.6 (6)
C11–C16–C19–O7	94.6 (5)	C14–C13–O5–C17	-177.9 (4)
C15–C16–C19–C20	86.8 (5)	C13–C14–O6–C18	-177.0 (4)
C11–C16–C19–C20	-89.3 (5)	C15–C14–O6–C18	2.0 (6)
O7–C19–C20–C21	6.5 (6)	C21–C22–O8–C26	-1.4 (6)
C16–C19–C20–C21	-169.5 (4)	C23–C22–O8–C26	-179.0 (4)
O7–C19–C20–C25	-177.9 (4)	C24–C23–O9–C27	-2.0 (6)
C16–C19–C20–C25	6.2 (6)	C22–C23–O9–C27	177.5 (4)
C25–C20–C21–C22	1.0 (6)	C32–C33–O11–C36	-179.2 (4)
C19–C20–C21–C22	176.9 (4)	C34–C33–O11–C36	7.3 (6)
C20–C21–C22–O8	179.5 (4)	C33–C32–O12–C35	-175.1 (4)
C20–C21–C22–C23	-3.1 (7)	C31–C32–O12–C35	9.2 (6)
4			
C1–O8	1.4752 (19)	C19–C24	1.373 (2)
C1–C19	1.522 (2)	C19–C20	1.395 (2)
C1–C14	1.523 (2)	C20–C21	1.389 (2)
C1–C2	1.526 (2)	C20–H20	0.9500
C2–C7	1.389 (2)	C21–O6	1.367 (2)
C2–C3	1.400 (2)	C21–C22	1.421 (2)
C3–C4	1.385 (2)	C22–O7	1.359 (2)
C3–H3	0.9500	C22–C23	1.388 (2)
C4–O1	1.361 (2)	C23–C24	1.396 (2)

C4–C5	1.412 (2)	C23–H23	0.9500
C5–O2	1.362 (2)	C24–C25	1.500 (2)
C5–C6	1.375 (2)	C25–O8	1.405 (2)
C6–C7	1.409 (2)	C25–O12	1.4876 (19)
C6–H6	0.9500	C25–C26	1.511 (2)
C7–C8	1.474 (2)	C26–C31	1.375 (2)
C8–O3	1.228 (2)	C26–C27	1.393 (2)
C8–C9	1.480 (2)	C27–C28	1.386 (2)
C9–C14	1.386 (2)	C27–H27	0.9500
C9–C10	1.407 (2)	C28–O9	1.357 (2)
C10–C11	1.370 (2)	C28–C29	1.423 (2)
C10–H10	0.9500	C29–O10	1.355 (2)
C11–O4	1.3707 (19)	C29–C30	1.380 (2)
C11–C12	1.414 (2)	C30–C31	1.394 (2)
C12–O5	1.3578 (19)	C30–H30	0.9500
C12–C13	1.389 (2)	C31–C32	1.460 (2)
C13–C14	1.398 (2)	C32–O11	1.203 (2)
C13–H13	0.9500	C32–O12	1.374 (2)
C15–O1	1.424 (2)	C33–O6	1.425 (2)
C15–H15A	0.9800	C33–H33A	0.9800
C15–H15B	0.9800	C33–H33B	0.9800
C15–H15C	0.9800	C33–H33C	0.9800
C16–O2	1.426 (2)	C34–O7	1.433 (2)
C16–H16A	0.9800	C34–H34A	0.9800
C16–H16B	0.9800	C34–H34B	0.9800
C16–H16C	0.9800	C34–H34C	0.9800
C17–O4	1.427 (2)	C35–O9	1.426 (2)
C17–H17A	0.9800	C35–H35A	0.9800
C17–H17B	0.9800	C35–H35B	0.9800
C17–H17C	0.9800	C35–H35C	0.9800
C18–O5	1.429 (2)	C36–O10	1.421 (2)
C18–H18A	0.9800	C36–H36A	0.9800
C18–H18B	0.9800	C36–H36B	0.9800
C18–H18C	0.9800	C36–H36C	0.9800
O8–C1–C19	101.93 (12)	C19–C20–H20	121.0
O8–C1–C14	109.27 (12)	O6–C21–C20	124.36 (15)

C19–C1–C14	109.61 (13)	O6–C21–C22	114.57 (15)
O8–C1–C2	111.22 (13)	C20–C21–C22	121.04 (15)
C19–C1–C2	111.03 (13)	O7–C22–C23	124.80 (15)
C14–C1–C2	113.18 (14)	O7–C22–C21	114.99 (15)
C7–C2–C3	118.92 (15)	C23–C22–C21	120.15 (15)
C7–C2–C1	121.25 (15)	C22–C23–C24	117.56 (15)
C3–C2–C1	119.56 (14)	C22–C23–H23	121.2
C4–C3–C2	120.51 (15)	C24–C23–H23	121.2
C4–C3–H3	119.7	C19–C24–C23	122.57 (15)
C2–C3–H3	119.7	C19–C24–C25	109.04 (14)
O1–C4–C3	124.86 (15)	C23–C24–C25	128.38 (15)
O1–C4–C5	114.78 (14)	O8–C25–O12	108.97 (12)
C3–C4–C5	120.30 (15)	O8–C25–C24	105.16 (13)
O2–C5–C6	125.51 (15)	O12–C25–C24	108.29 (13)
O2–C5–C4	115.17 (14)	O8–C25–C26	115.02 (14)
C6–C5–C4	119.32 (15)	O12–C25–C26	102.03 (13)
C5–C6–C7	120.18 (15)	C24–C25–C26	117.06 (14)
C5–C6–H6	119.9	C31–C26–C27	120.20 (16)
C7–C6–H6	119.9	C31–C26–C25	109.30 (15)
C2–C7–C6	120.65 (15)	C27–C26–C25	130.24 (15)
C2–C7–C8	121.89 (15)	C28–C27–C26	118.10 (16)
C6–C7–C8	117.42 (15)	C28–C27–H27	120.9
O3–C8–C7	121.53 (15)	C26–C27–H27	120.9
O3–C8–C9	121.51 (16)	O9–C28–C27	125.07 (16)
C7–C8–C9	116.95 (14)	O9–C28–C29	113.89 (15)
C14–C9–C10	120.40 (15)	C27–C28–C29	121.02 (16)
C14–C9–C8	122.27 (15)	O10–C29–C30	125.13 (16)
C10–C9–C8	117.32 (15)	O10–C29–C28	114.66 (15)
C11–C10–C9	120.85 (16)	C30–C29–C28	120.20 (16)
C11–C10–H10	119.6	C29–C30–C31	117.36 (15)
C9–C10–H10	119.6	C29–C30–H30	121.3
C10–C11–O4	124.98 (15)	C31–C30–H30	121.3
C10–C11–C12	119.20 (15)	C26–C31–C30	122.89 (16)
O4–C11–C12	115.81 (14)	C26–C31–C32	109.06 (15)
O5–C12–C13	125.09 (15)	C30–C31–C32	128.05 (16)
O5–C12–C11	115.20 (14)	O11–C32–O12	121.74 (16)
C13–C12–C11	119.71 (15)	O11–C32–C31	130.45 (16)

C12–C13–C14	121.04 (15)	O12–C32–C31	107.80 (14)
C12–C13–H13	119.5	O6–C33–H33A	109.5
C14–C13–H13	119.5	O6–C33–H33B	109.5
C9–C14–C13	118.80 (15)	H33A–C33–H33B	109.5
C9–C14–C1	121.20 (14)	O6–C33–H33C	109.5
C13–C14–C1	119.66 (14)	H33A–C33–H33C	109.5
O1–C15–H15A	109.5	H33B–C33–H33C	109.5
O1–C15–H15B	109.5	O7–C34–H34A	109.5
H15A–C15–H15B	109.5	O7–C34–H34B	109.5
O1–C15–H15C	109.5	H34A–C34–H34B	109.5
H15A–C15–H15C	109.5	O7–C34–H34C	109.5
H15B–C15–H15C	109.5	H34A–C34–H34C	109.5
O2–C16–H16A	109.5	H34B–C34–H34C	109.5
O2–C16–H16B	109.5	O9–C35–H35A	109.5
H16A–C16–H16B	109.5	O9–C35–H35B	109.5
O2–C16–H16C	109.5	H35A–C35–H35B	109.5
H16A–C16–H16C	109.5	O9–C35–H35C	109.5
H16B–C16–H16C	109.5	H35A–C35–H35C	109.5
O4–C17–H17A	109.5	H35B–C35–H35C	109.5
O4–C17–H17B	109.5	O10–C36–H36A	109.5
H17A–C17–H17B	109.5	O10–C36–H36B	109.5
O4–C17–H17C	109.5	H36A–C36–H36B	109.5
H17A–C17–H17C	109.5	O10–C36–H36C	109.5
H17B–C17–H17C	109.5	H36A–C36–H36C	109.5
O5–C18–H18A	109.5	H36B–C36–H36C	109.5
O5–C18–H18B	109.5	C4–O1–C15	117.40 (13)
H18A–C18–H18B	109.5	C5–O2–C16	116.87 (13)
O5–C18–H18C	109.5	C11–O4–C17	115.36 (13)
H18A–C18–H18C	109.5	C12–O5–C18	116.36 (13)
H18B–C18–H18C	109.5	C21–O6–C33	116.52 (14)
C24–C19–C20	120.59 (15)	C22–O7–C34	116.43 (13)
C24–C19–C1	110.17 (14)	C25–O8–C1	112.09 (12)
C20–C19–C1	129.20 (15)	C28–O9–C35	116.50 (14)
C21–C20–C19	118.06 (15)	C29–O10–C36	116.50 (14)
C21–C20–H20	121.0	C32–O12–C25	111.06 (12)
O8–C1–C2–C7	-144.20 (15)	C21–C22–C23–C24	1.4 (2)

C19–C1–C2–C7	103.04 (17)	C20–C19–C24–C23	-0.4 (2)
C14–C1–C2–C7	-20.7 (2)	C1–C19–C24–C23	177.51 (15)
O8–C1–C2–C3	41.9 (2)	C20–C19–C24–C25	178.54 (14)
C19–C1–C2–C3	-70.87 (19)	C1–C19–C24–C25	-3.56 (18)
C14–C1–C2–C3	165.36 (14)	C22–C23–C24–C19	-1.2 (2)
C7–C2–C3–C4	-1.5 (2)	C22–C23–C24–C25	-179.87 (15)
C1–C2–C3–C4	172.51 (15)	C19–C24–C25–O8	10.27 (17)
C2–C3–C4–O1	-178.92 (15)	C23–C24–C25–O8	-170.89 (15)
C2–C3–C4–C5	-1.7 (2)	C19–C24–C25–O12	-106.11 (15)
O1–C4–C5–O2	1.0 (2)	C23–C24–C25–O12	72.7 (2)
C3–C4–C5–O2	-176.50 (15)	C19–C24–C25–C26	139.35 (15)
O1–C4–C5–C6	-179.10 (15)	C23–C24–C25–C26	-41.8 (2)
C3–C4–C5–C6	3.4 (2)	O8–C25–C26–C31	-126.51 (15)
O2–C5–C6–C7	178.02 (15)	O12–C25–C26–C31	-8.72 (17)
C4–C5–C6–C7	-1.9 (2)	C24–C25–C26–C31	109.26 (16)
C3–C2–C7–C6	3.1 (2)	O8–C25–C26–C27	59.4 (2)
C1–C2–C7–C6	-170.86 (15)	O12–C25–C26–C27	177.23 (17)
C3–C2–C7–C8	-174.49 (15)	C24–C25–C26–C27	-64.8 (2)
C1–C2–C7–C8	11.6 (2)	C31–C26–C27–C28	-1.2 (2)
C5–C6–C7–C2	-1.4 (2)	C25–C26–C27–C28	172.34 (17)
C5–C6–C7–C8	176.30 (16)	C26–C27–C28–O9	178.50 (16)
C2–C7–C8–O3	179.10 (17)	C26–C27–C28–C29	-2.9 (3)
C6–C7–C8–O3	1.4 (3)	O9–C28–C29–O10	3.5 (2)
C2–C7–C8–C9	0.8 (2)	C27–C28–C29–O10	-175.23 (16)
C6–C7–C8–C9	-176.86 (15)	O9–C28–C29–C30	-175.76 (15)
O3–C8–C9–C14	179.27 (17)	C27–C28–C29–C30	5.5 (3)
C7–C8–C9–C14	-2.4 (2)	O10–C29–C30–C31	177.01 (16)
O3–C8–C9–C10	-2.3 (3)	C28–C29–C30–C31	-3.8 (3)
C7–C8–C9–C10	175.97 (15)	C27–C26–C31–C30	2.8 (3)
C14–C9–C10–C11	-0.3 (2)	C25–C26–C31–C30	-171.93 (16)
C8–C9–C10–C11	-178.76 (15)	C27–C26–C31–C32	-177.33 (15)
C9–C10–C11–O4	-178.78 (15)	C25–C26–C31–C32	7.92 (19)
C9–C10–C11–C12	0.7 (2)	C29–C30–C31–C26	-0.3 (3)
C10–C11–C12–O5	179.45 (15)	C29–C30–C31–C32	179.92 (16)
O4–C11–C12–O5	-1.1 (2)	C26–C31–C32–O11	175.35 (18)
C10–C11–C12–C13	-0.7 (2)	C30–C31–C32–O11	-4.8 (3)
O4–C11–C12–C13	178.76 (14)	C26–C31–C32–O12	-3.67 (19)

O5–C12–C13–C14	-179.72 (15)	C30–C31–C32–O12	176.17 (16)
C11–C12–C13–C14	0.5 (2)	C3–C4–O1–C15	-0.2 (2)
C10–C9–C14–C13	0.1 (2)	C5–C4–O1–C15	-177.54 (14)
C8–C9–C14–C13	178.41 (15)	C6–C5–O2–C16	-0.9 (2)
C10–C9–C14–C1	173.28 (15)	C4–C5–O2–C16	178.96 (15)
C8–C9–C14–C1	-8.4 (2)	C10–C11–O4–C17	-3.3 (2)
C12–C13–C14–C9	-0.1 (2)	C12–C11–O4–C17	177.28 (14)
C12–C13–C14–C1	-173.47 (15)	C13–C12–O5–C18	0.6 (2)
O8–C1–C14–C9	143.63 (15)	C11–C12–O5–C18	-179.63 (14)
C19–C1–C14–C9	-105.45 (17)	C20–C21–O6–C33	-12.8 (2)
C2–C1–C14–C9	19.1 (2)	C22–C21–O6–C33	165.53 (14)
O8–C1–C14–C13	-43.21 (19)	C23–C22–O7–C34	-3.5 (2)
C19–C1–C14–C13	67.71 (18)	C21–C22–O7–C34	179.40 (14)
C2–C1–C14–C13	-167.75 (14)	O12–C25–O8–C1	102.57 (14)
O8–C1–C19–C24	-4.15 (16)	C24–C25–O8–C1	-13.34 (16)
C14–C1–C19–C24	-119.84 (15)	C26–C25–O8–C1	-143.63 (14)
C2–C1–C19–C24	114.38 (15)	C19–C1–O8–C25	11.06 (16)
O8–C1–C19–C20	173.51 (15)	C14–C1–O8–C25	126.99 (14)
C14–C1–C19–C20	57.8 (2)	C2–C1–O8–C25	-107.33 (15)
C2–C1–C19–C20	-68.0 (2)	C27–C28–O9–C35	-13.0 (3)
C24–C19–C20–C21	1.6 (2)	C29–C28–O9–C35	168.28 (16)
C1–C19–C20–C21	-175.83 (15)	C30–C29–O10–C36	-5.1 (2)
C19–C20–C21–O6	176.85 (14)	C28–C29–O10–C36	175.69 (15)
C19–C20–C21–C22	-1.3 (2)	O11–C32–O12–C25	178.68 (16)
O6–C21–C22–O7	-1.3 (2)	C31–C32–O12–C25	-2.19 (18)
C20–C21–C22–O7	177.04 (14)	O8–C25–O12–C32	128.56 (14)
O6–C21–C22–C23	-178.56 (14)	C24–C25–O12–C32	-117.56 (14)
C20–C21–C22–C23	-0.2 (2)	C26–C25–O12–C32	6.52 (17)
O7–C22–C23–C24	-175.53 (15)		