Unexpected Solid State Photochemistry of an α-Thiophenyl-α'-Thiophenyl-S,S-dioxo Substituted Ketone

*Marino J. E. Resendiz, Jennifer Taing, Saeed I. Khan and Miguel A. Garcia-Garibay**

Department of Chemistry and Biochemistry, University of California–Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095-1569. E-mail: mgg@chem.ucla.edu; Fax: 310-825-6707; Tel: 310-825-3159.

Table of Contents

Materials and Photolysis Procedures…….. 2 - 3

IR, UV-vis, ^{1}H , ^{13}C and ^{13}C CP-MAS NMR spectra for **2**……..…… 4 - 6

IR, UV-vis, ^{1}H and ^{13}C NMR spectra for **5**…… 6 - 8

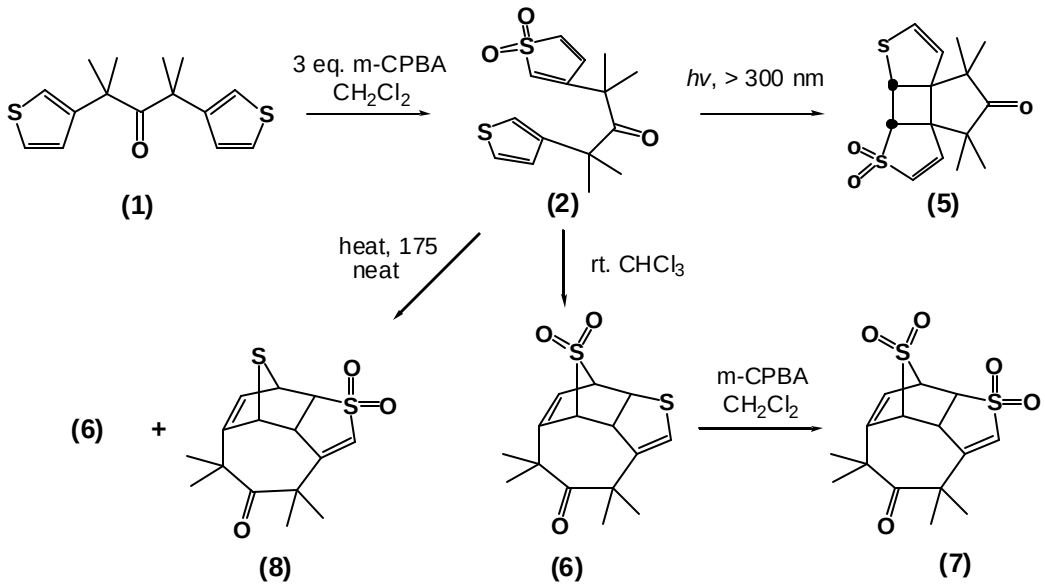
IR, UV-vis, ^{1}H and ^{13}C NMR spectra and DSC trace for **6**…… 8 - 10

IR, UV-vis, ^{1}H , ^{13}C and ^{13}C CP-MAS NMR spectra, DSC trace and ORTEP for **7**…… 10 - 12

Transformation of **2** to **6** followed by ^{1}H NMR…….. 13

Thermal cycloaddition of **2** to **6** + **8** by ^{1}H NMR…… 14

Supporting Information



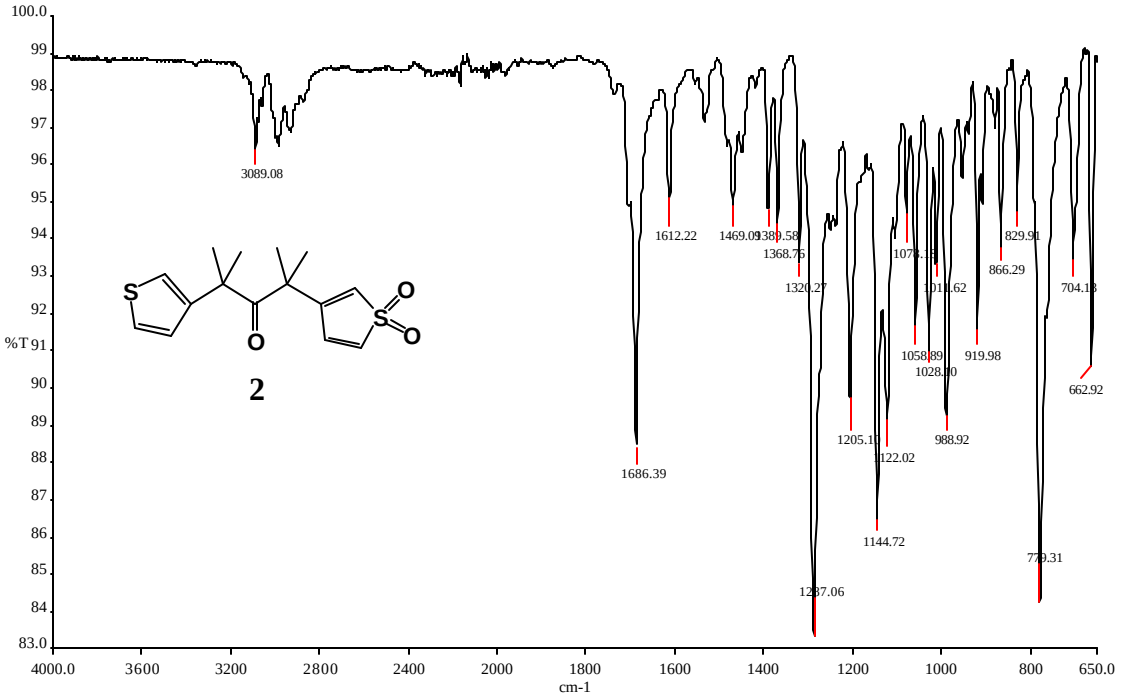
Experimental

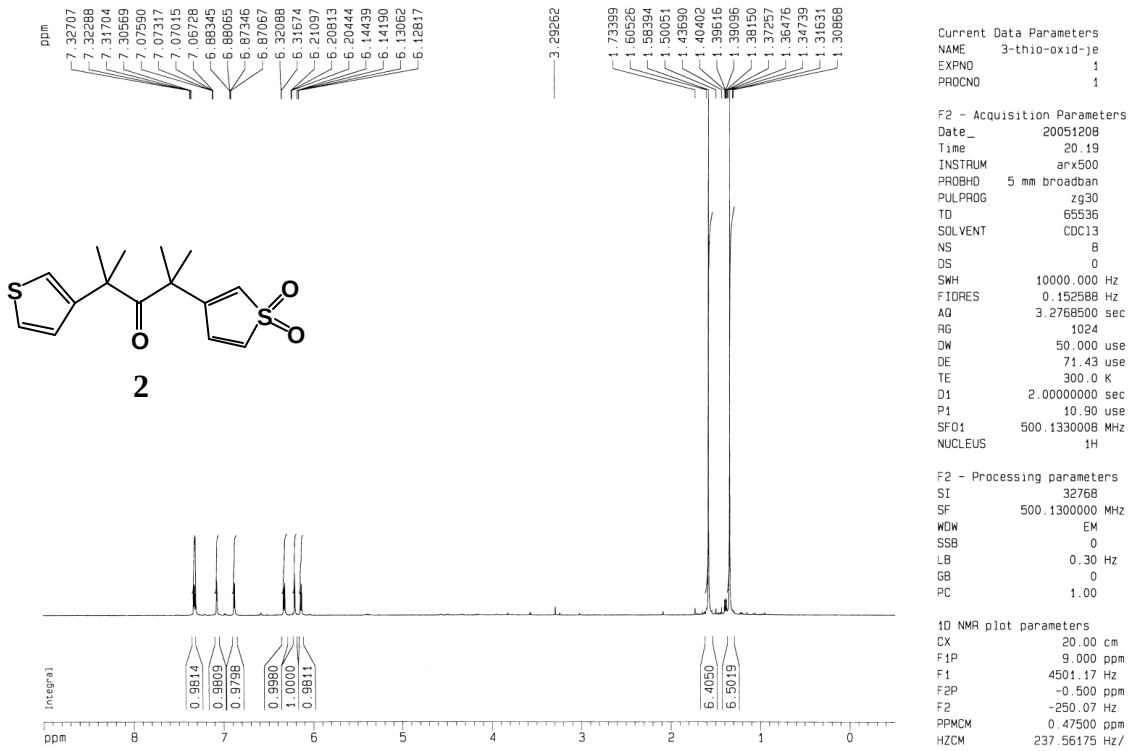
Materials. Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone, CH_2Cl_2 was dried by distillation from CaH_2. All other reagents were commercial products that were used without further purification.

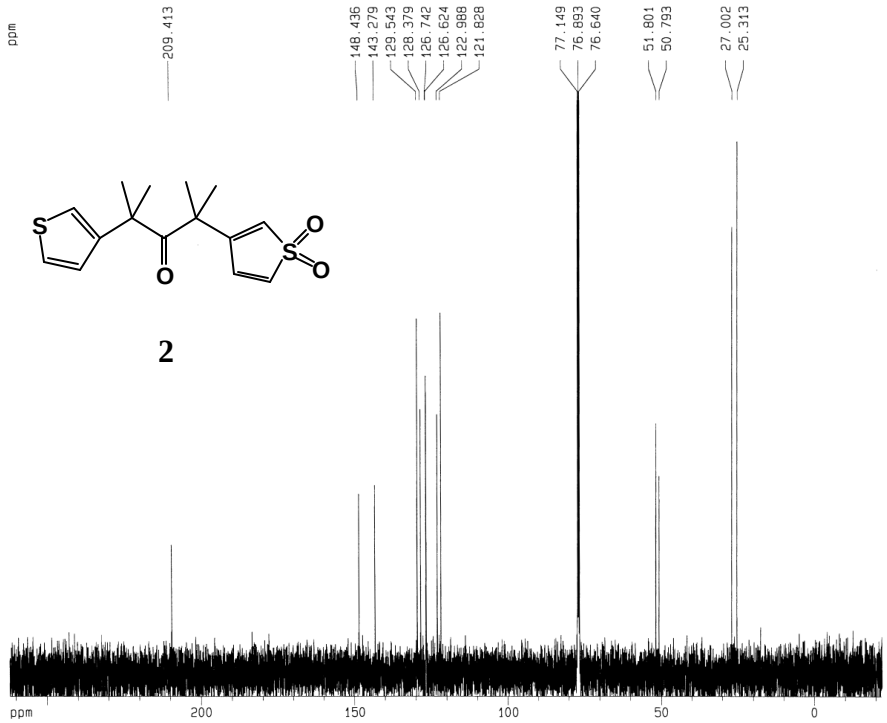
General Procedure for Photolysis in Solution. Compound **2** was dissolved in deuterated benzene, deuterated acetone or cyclohexane (ca. 3.2×10^{-3}M, 3 mg,0.009 mmol, in 3mL) and deoxygenated by bubbling Argon for 30 min. Photolysis occurred by placing the mixtures at a distance (~ 10 cm) from a medium-pressure Hg Hanovia lamp. Samples were taken at different time intervals and monitored by NMR until disappearance of the starting material to yield exclusively the 2 +2 photocycloaddition adduct **5**.

General Procedure for Photolysis in the Solid State. Finely powdered solid samples of **2** (~ 60 mg) were placed evenly on a Petri dish at a distance (~ 10 cm) from a medium-

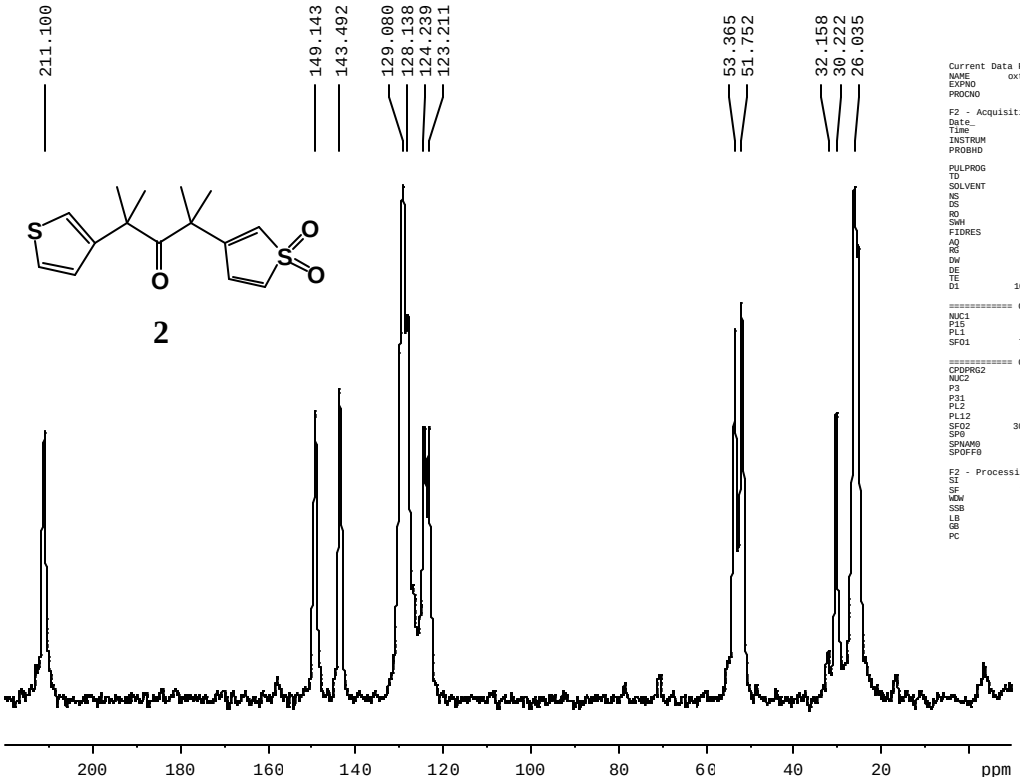
pressure Hg Hanovia lamp. During the course of irradiation, small amounts of each sample were removed at various times and analyzed by NMR and X-RPD.


%T
cm-1
3089.08
1686.39
1612.22
1469.09
1389.58
1368.76
1320.27
1287.06
1205.11
1144.72
1122.02
1074.33
1058.89
1028.10
1014.62
988.92
919.98
866.29
829.91
779.31
704.13
662.92
2

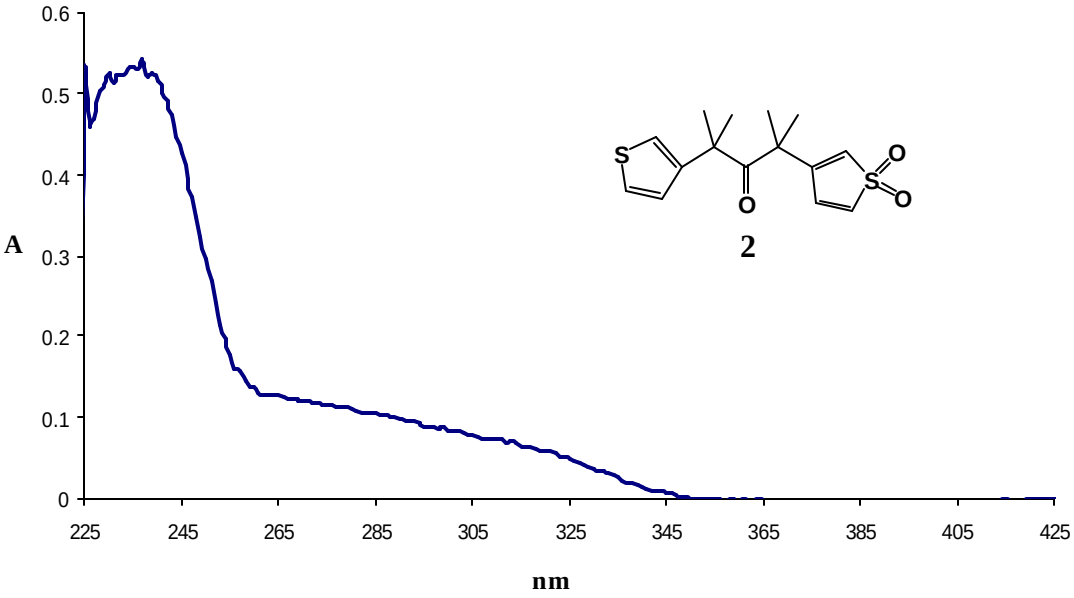

ppm
7.32707
7.32288
7.31704
7.30569
7.07590
7.07317
7.07015
7.06728
6.88345
6.88065
6.87346
6.87067
6.32088
6.31674
6.21097
6.20813
6.20444
6.14439
6.14190
6.13062
6.12817
3.29262
1.73399
1.60526
1.58394
1.50051
1.43690
1.40402
1.39616
1.39096
1.38150
1.37257
1.36476
1.34739
1.31631
1.30868
Integral
0.9814
0.9809
0.9798
0.9980
1.0000
0.9811
6.4050
6.5019
2
Current Data Parameters
NAME 3-thio-oxid-je
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051208
Time 20.19
INSTRUM arx500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 1024
DW 50.000 use
DE 71.43 use
TE 300.0 K
D1 2.00000000 sec
P1 10.90 use
SFO1 500.1330008 MHz
NUCLEUS 1H
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.47500 ppm
HZCM 237.56175 Hz/

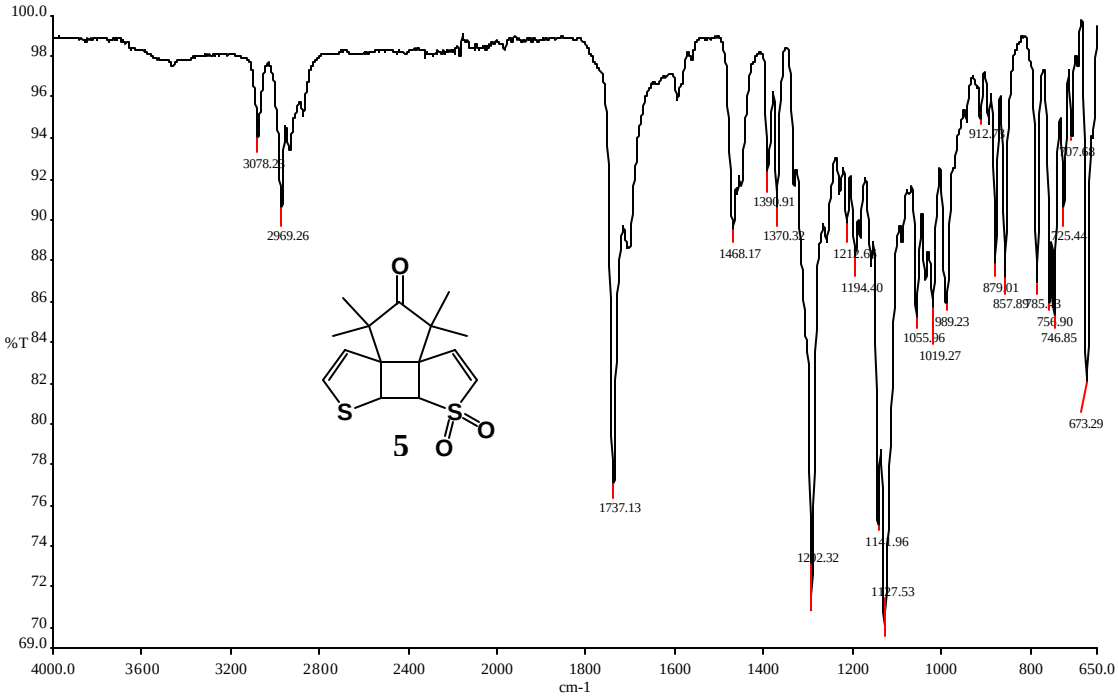


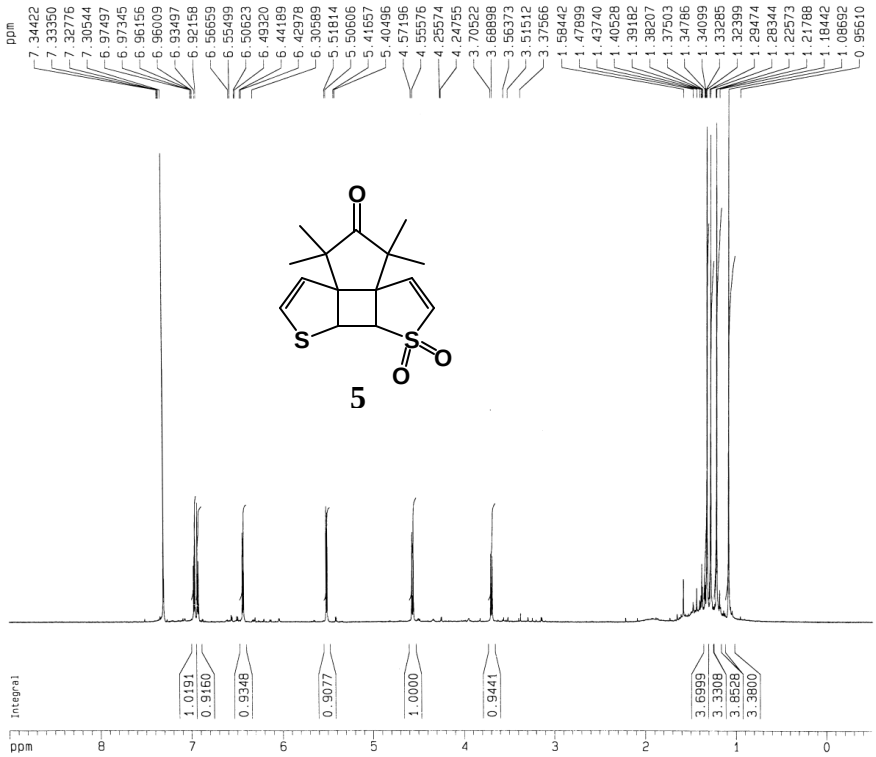

```
Current Data Parameters
NAME      3-thio-oxid-je
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051208
Time               20.47
INSTRUM          arx500
PROBHD    5 mm broadban
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  197
DS                    0
SWH           35714.285 Hz
FIDRES         0.544957 Hz
AQ           0.9175540 sec
RG                32768
DW               14.000 usec
DE               20.00 usec
TE               300.0 K
D12           0.0000200 sec
DL5               17.70 dB
CPDPRG          waltz16
P31              100.00 usec
D1           4.00000000 sec
P1                7.00 usec
SFO1        125.7728999 MHz
NUCLEUS             13C
D11           0.0300000 sec

F2 - Processing parameters
SI                32768
SF          125.7578090 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              261.996 ppm
F1             32948.08 Hz
F2P              -21.996 ppm
F2            -2766.20 Hz
PPMCM           14.19963 ppm/cm
HZCM         1785.71436 Hz/cm
```



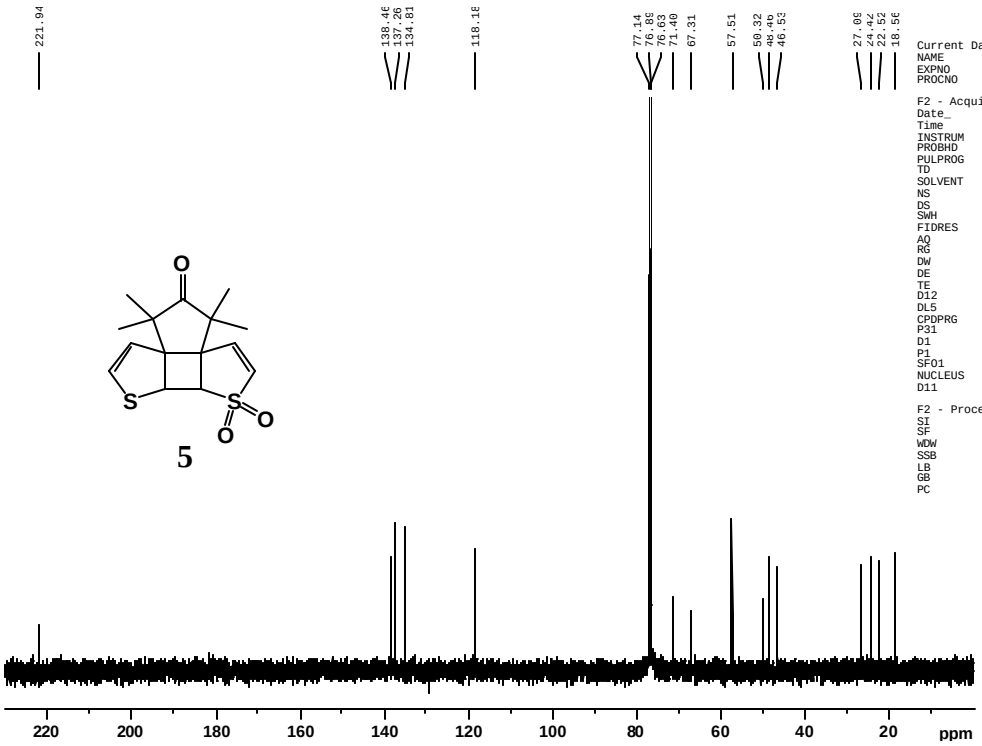

```
Current Data Parameters
NAME        oxthiophenyl
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060304
Time               12.07
INSTRUM        avance300
PROBHD        4 mm MAS

PULPROG        cpva_tppm
TD                  4096
SOLVENT             NONE
NS                   128
DS                     0
RG                 10000
SWH            31152.648 Hz
FIDRES          7.605627 Hz
AQ             0.0658869 sec
RG                 32768
DW                16.050 usec
DE                 4.50 usec
TE                296.0 K
D1            10.00000000 sec

============ CHANNEL f1 ============
NUC1                 13C
P15               5000.00 usec
PL1                14.00 dB
SFO1           75.4763978 MHz

============ CHANNEL f2 ============
CPDPRG2           tppm15
NUC2                  1H
P3                  4.50 usec
P31                 6.70 usec
PL2                11.85 dB
PL12               10.50 dB
SFO2          300.1301000 MHz
SP0                11.55 dB
SPNAM0           ramp.64
SPOFF0              0.00 Hz

F2 - Processing parameters
SI                 32768
SF            75.4675671 MHz
WDW                   EM
SSB                    0
LB                 20.00 Hz
GB                     0
PC                  1.40
```


A
nm
2

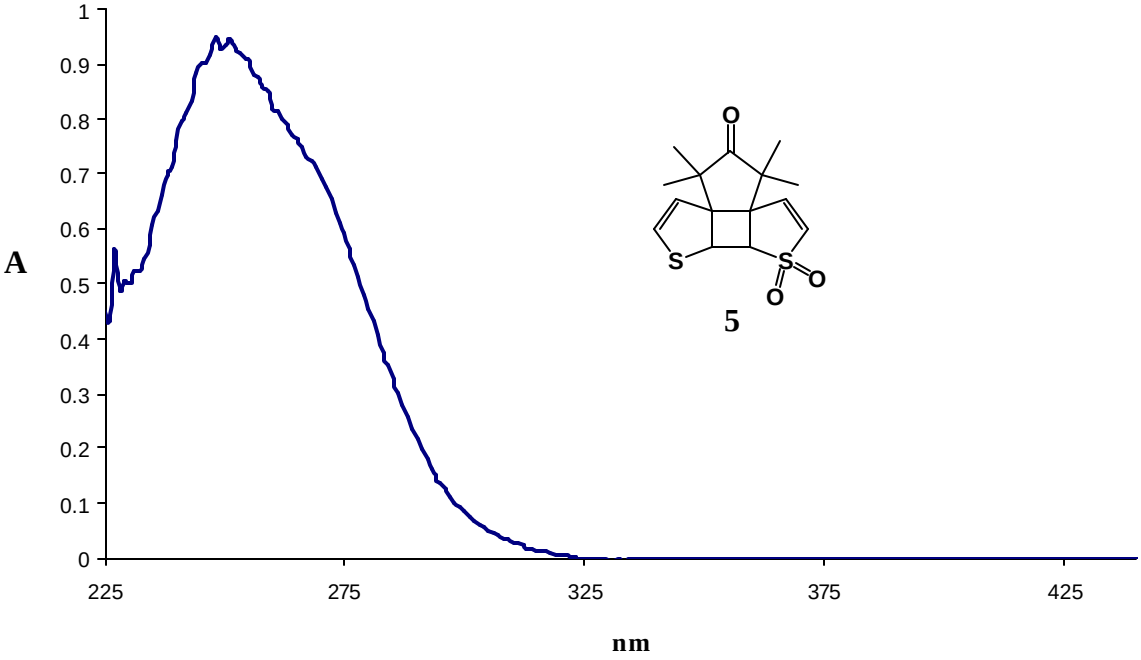

%T
cm-1
5
3078.23
2969.26
1737.13
1468.17
1390.91
1370.32
1292.32
1212.64
1194.40
1141.96
1127.53
1055.96
1019.27
989.23
912.70
879.01
857.87
785.73
756.90
746.85
725.44
707.68
673.29

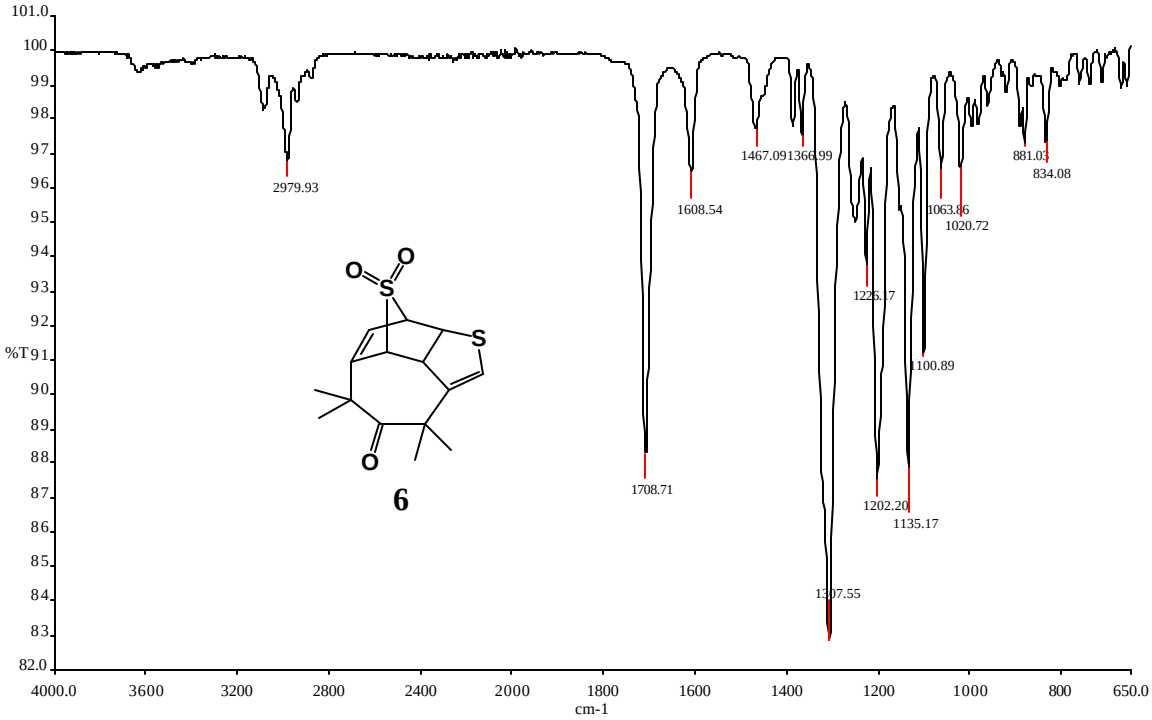


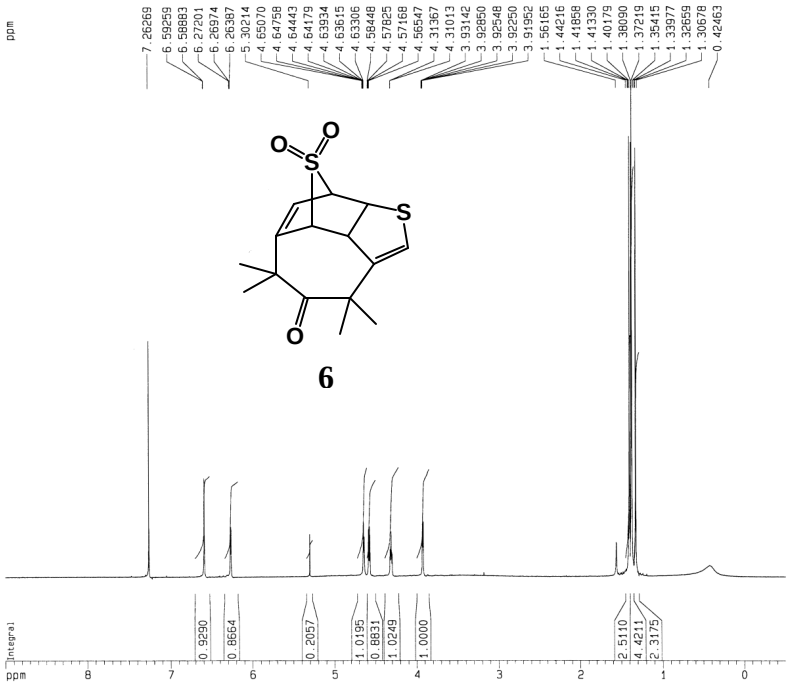

```
Current Data Parameters
NAME        hv-3-thio-jen
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20051209
Time                18.55
INSTRUM           arx500
PROBHD     5 mm broadban
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2768500 sec
RG                  2048
DW                50.000 use
DE                 71.43 use
TE                 300.0 K
D1            2.00000000 sec
P1                 10.90 use
SFO1         500.1330008 MHz
NUCLEUS               1H

F2 - Processing parameters
SI                  32768
SF           500.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                  9.000 ppm
F1                 4501.17 Hz
F2P                 -0.500 ppm
F2                -250.07 Hz
PPMCM             0.47500 ppm
HZCM            237.56175 Hz/
```




```
Current Data Parameters
NAME        hv-3-thio-jen
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20051209
Time                19.18
INSTRUM           arx500
PROBHD     5 mm broadban
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                  1656
DS                     0
SWH            35714.285 Hz
FIDRES          0.544957 Hz
AQ             0.9175540 sec
RG                 32768
DW                14.000 usec
DE                 20.00 usec
TE                 300.0 K
D12            0.0000200 sec
DL5                17.70 dB
CPDPRG            waltz16
P31               100.00 usec
D1             4.00000000 sec
P1                  7.00 usec
SFO1          125.7728999 MHz
NUCLEUS               13C
D11            0.0300000 sec

F2 - Processing parameters
SI                  32768
SF           125.7578090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

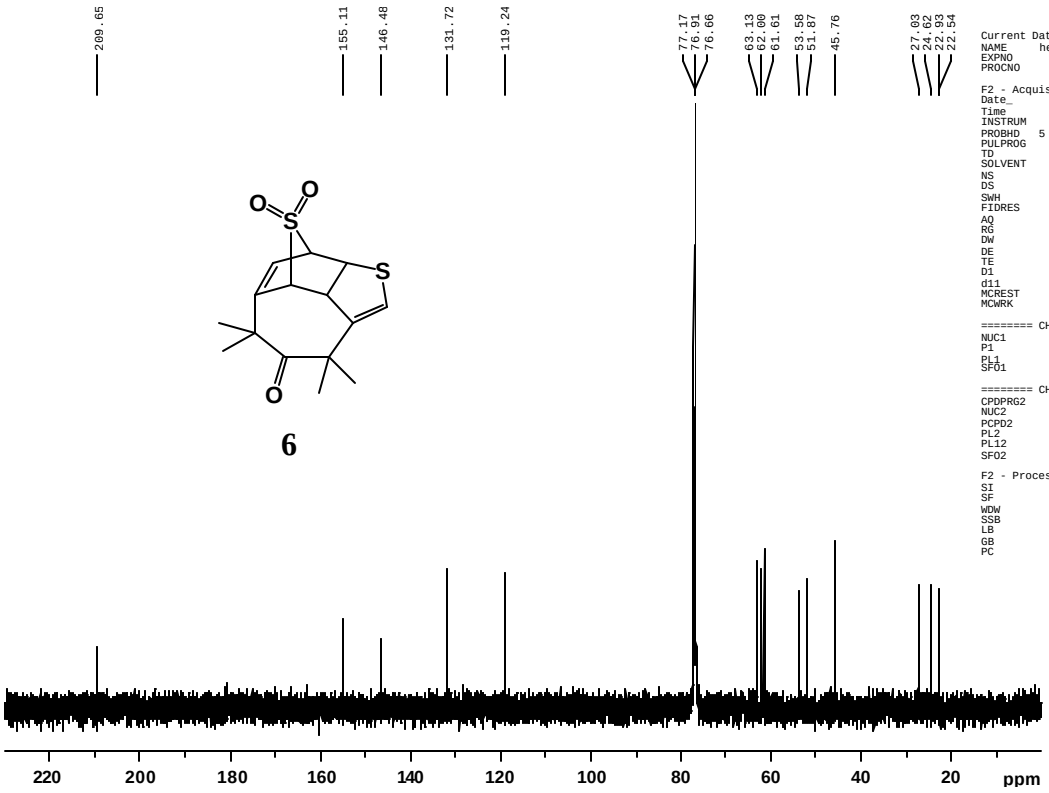

A
nm
5


%T
cm-1
2979.93
1708.71
1608.54
1467.09
1366.99
1307.55
1226.17
1202.20
1135.17
1100.89
1063.86
1020.72
881.03
834.08
6



6

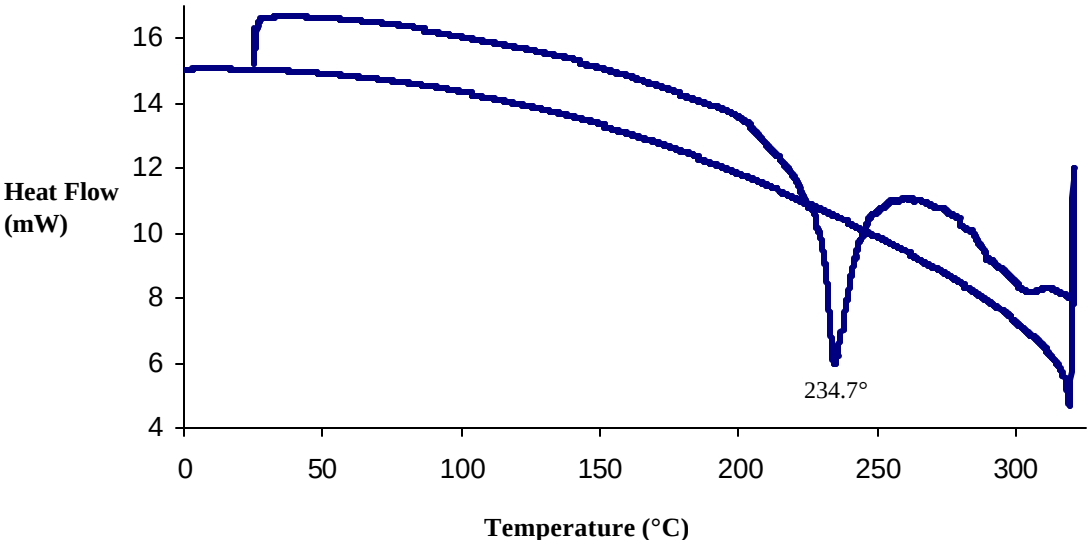
```
Current Data Parameters
NAME      heptanone-spot4
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20060315
Time              20.56
INSTRUM       avance500
PROBHD   5 mm bb-Z Z800
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2769001 sec
RG                  181
DW               50.000 usec
DE                6.00 usec
TE               294.5 K
D1            2.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.75 usec
PL1                0.00 dB
SFO1        500.3330020 MHz

F2 - Processing parameters
SI                 32768
SF          500.3300220 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4502.97 Hz
F2P               -0.500 ppm
F2               -250.17 Hz
PPMCM            0.47500 ppm/cm
HZCM           237.65675 Hz/cm
```



6

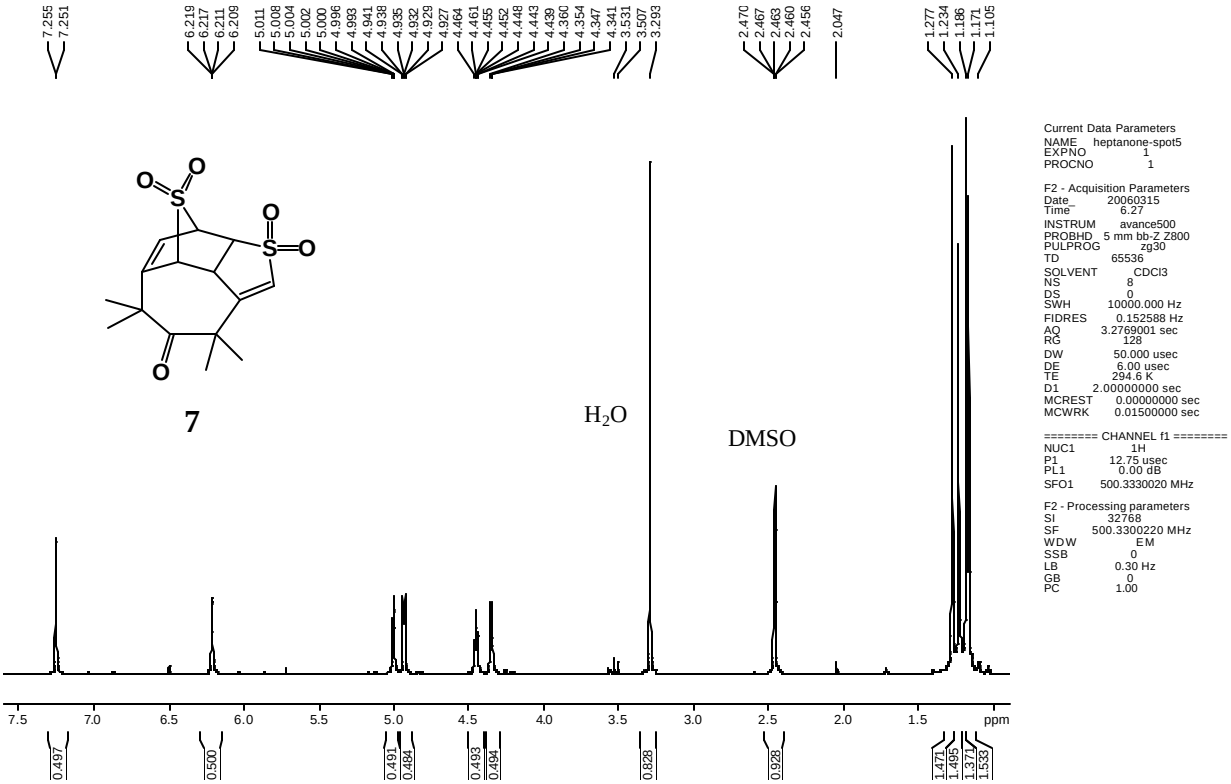
```
Current Data Parameters
NAME      heptanone-spot4
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20060315
Time               6.04
INSTRUM       avance500
PROBHD   5 mm bb-Z Z800
PULPROG         zgdc30
TD                65536
SOLVENT           CDCl3
NS                  233
DS                    0
SWH           32679.738 Hz
FIDRES         0.498653 Hz
AQ            1.0027661 sec
RG                 3251
DW               15.300 usec
DE                6.00 usec
TE               295.0 K
D1            4.00000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 5.50 usec
PL1                0.00 dB
SFO1        125.8231939 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                0.00 dB
PL12              16.10 dB
SFO2        500.3320013 MHz

F2 - Processing parameters
SI                 65536
SF          125.8080969 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

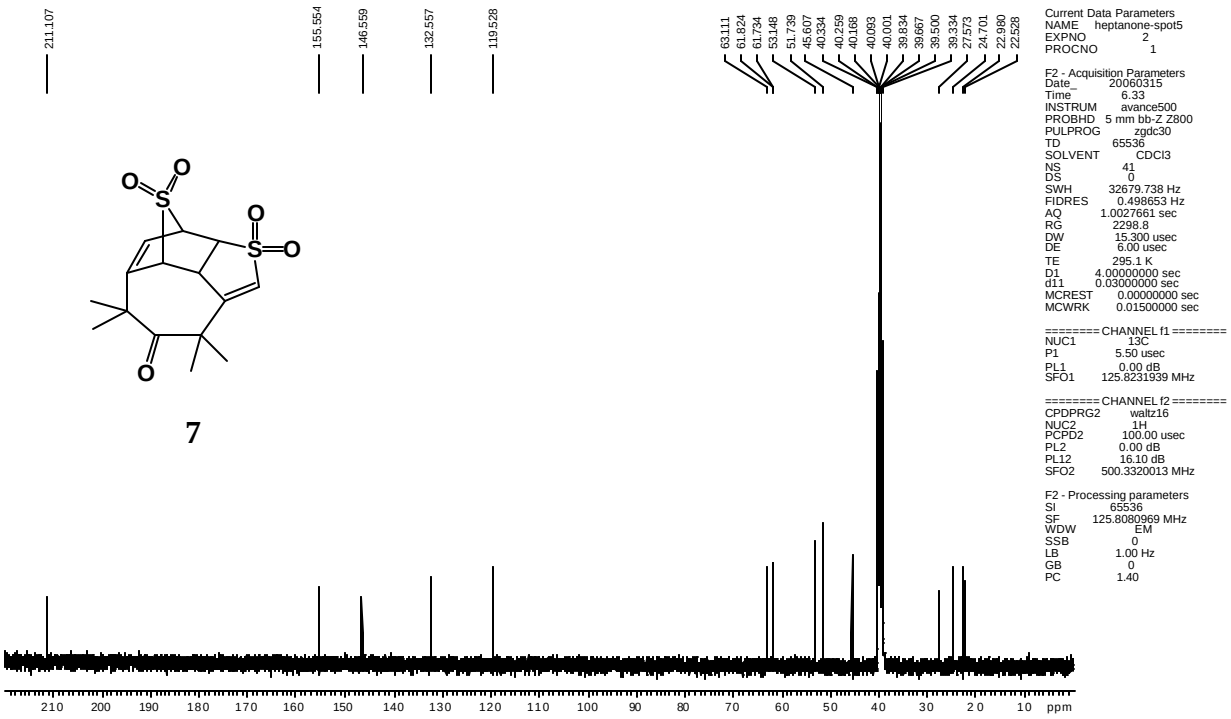
DSC trace for 6

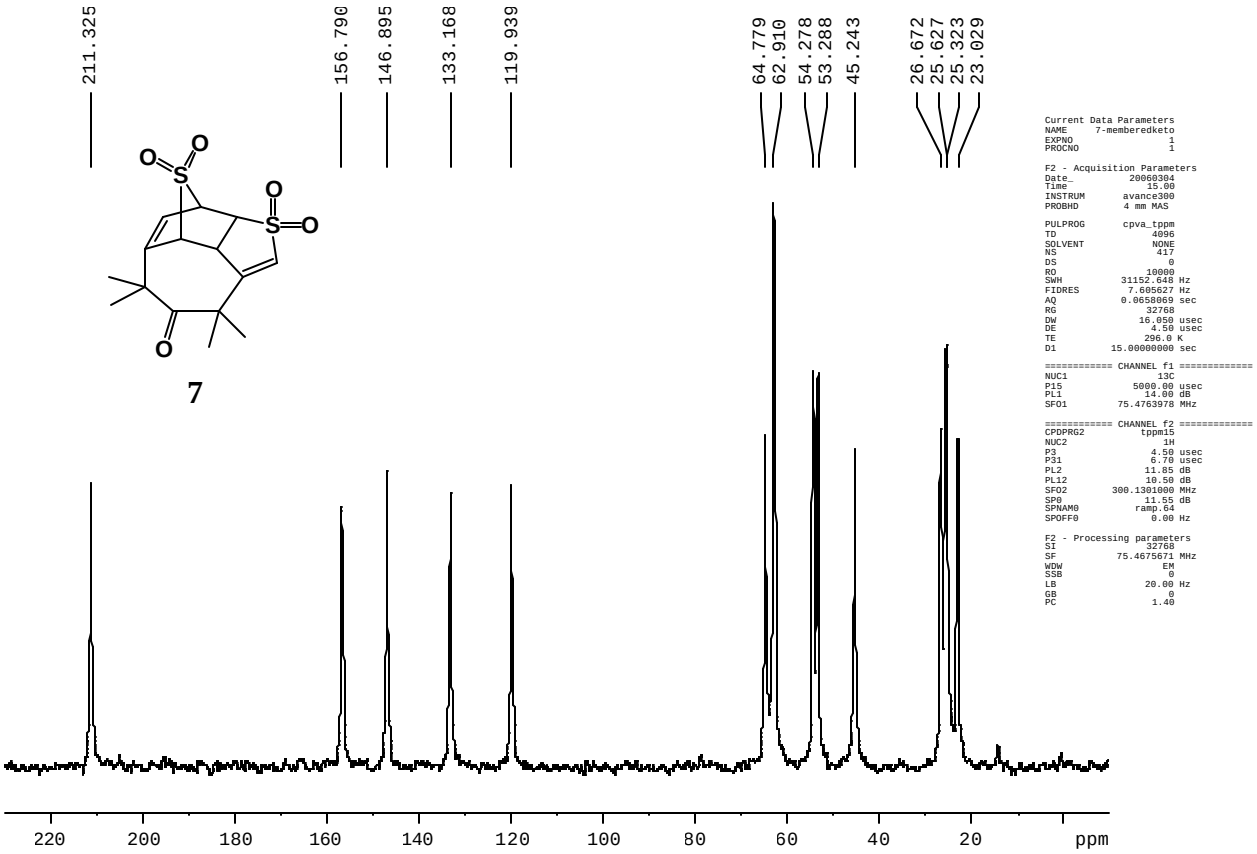


Parameters used: Hold for 2.0 min at 25.0° C; Heat from 25.0° to 320.0° at 10.0°/min; Hold 1.0 min at 320.0°; Cool to 0.0° at 10.0°/min; Hold 1.0 min at 0°.

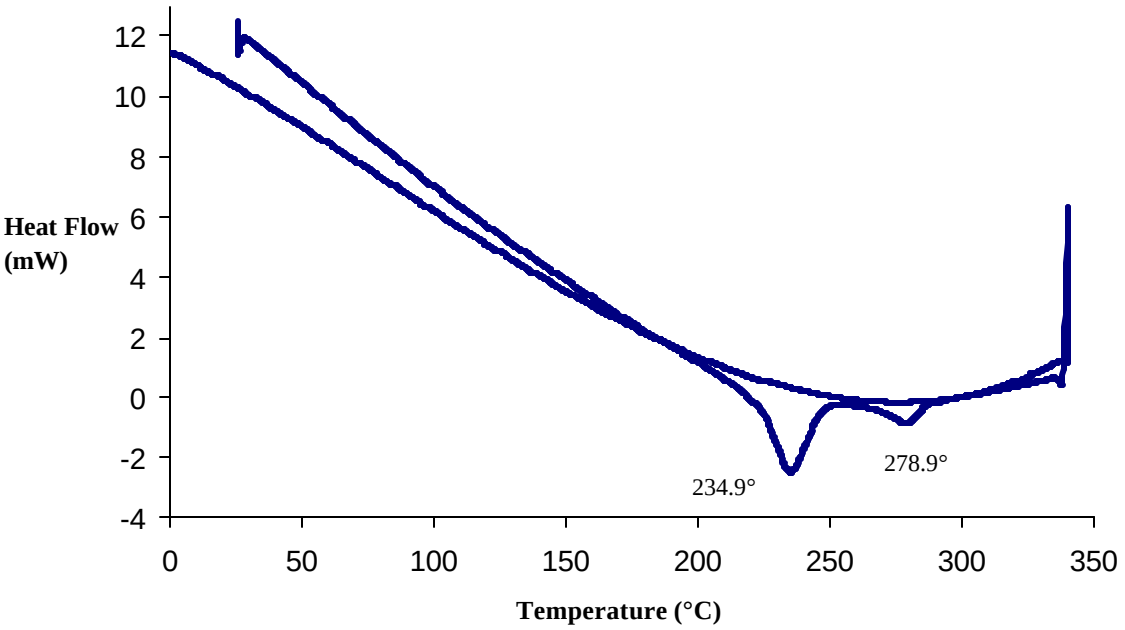
DSC experiments on **6** showing a melting and decomposition transitions. NMR spectra of the samples after heating showed a mixture of several unidentified products.




211.107
155.554
146.559
132.557
119.528
63.111
61.824
61.734
53.148
51.739
45.607
40.334
40.259
40.168
40.093
40.001
39.834
39.667
39.500
39.334
27.573
24.701
22.980
22.528
7
Current Data Parameters
NAME heptanone-spot5
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060315
Time 6.33
INSTRUM avance500
PROBHD 5 mm bb-Z Z800
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 41
DS 0
SWH 32679.738 Hz
FIDRES 0.498653 Hz
AQ 1.0027661 sec
RG 2298.8
DW 15.300 usec
DE 6.00 usec
TE 295.1 K
D1 4.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 0.00 dB
SFO1 125.8231939 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 0.00 dB
PL12 16.10 dB
SFO2 500.3320013 MHz
F2 - Processing parameters
SI 65536
SF 125.8080969 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

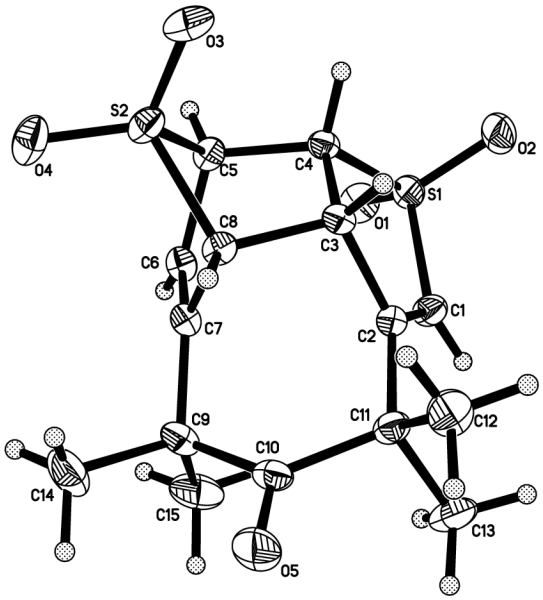

211.325
156.790
146.895
133.168
119.939
64.779
62.910
54.278
53.288
45.243
26.672
25.627
25.323
23.029
7
Current Data Parameters
NAME 7-memberedketo
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060304
Time 15.00
INSTRUM avance300
PROBHD 4 mm MAS
PULPROG cpva_tppm
TD 4096
SOLVENT NONE
NS 417
DS 0
RG 10000
SWH 31152.648 Hz
FIDRES 7.605627 Hz
AQ 0.0658069 sec
RG 32768
DW 16.050 usec
DE 4.50 usec
TE 296.0 K
D1 15.00000000 sec
========== CHANNEL f1 ==========
NUC1 13C
P15 5000.00 usec
PL1 14.00 dB
SFO1 75.4763978 MHz
========== CHANNEL f2 ==========
CPDPRG2 tppm15
NUC2 1H
P3 4.50 usec
P31 6.70 usec
PL2 11.85 dB
PL12 10.50 dB
SFO2 300.1301000 MHz
SP0 11.55 dB
SPNAM0 ramp.64
SPOFF0 0.00 Hz
F2 - Processing parameters
SI 32768
SF 75.4675671 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40
220 200 180 160 140 120 100 80 60 40 20 ppm

DSC trace for 7

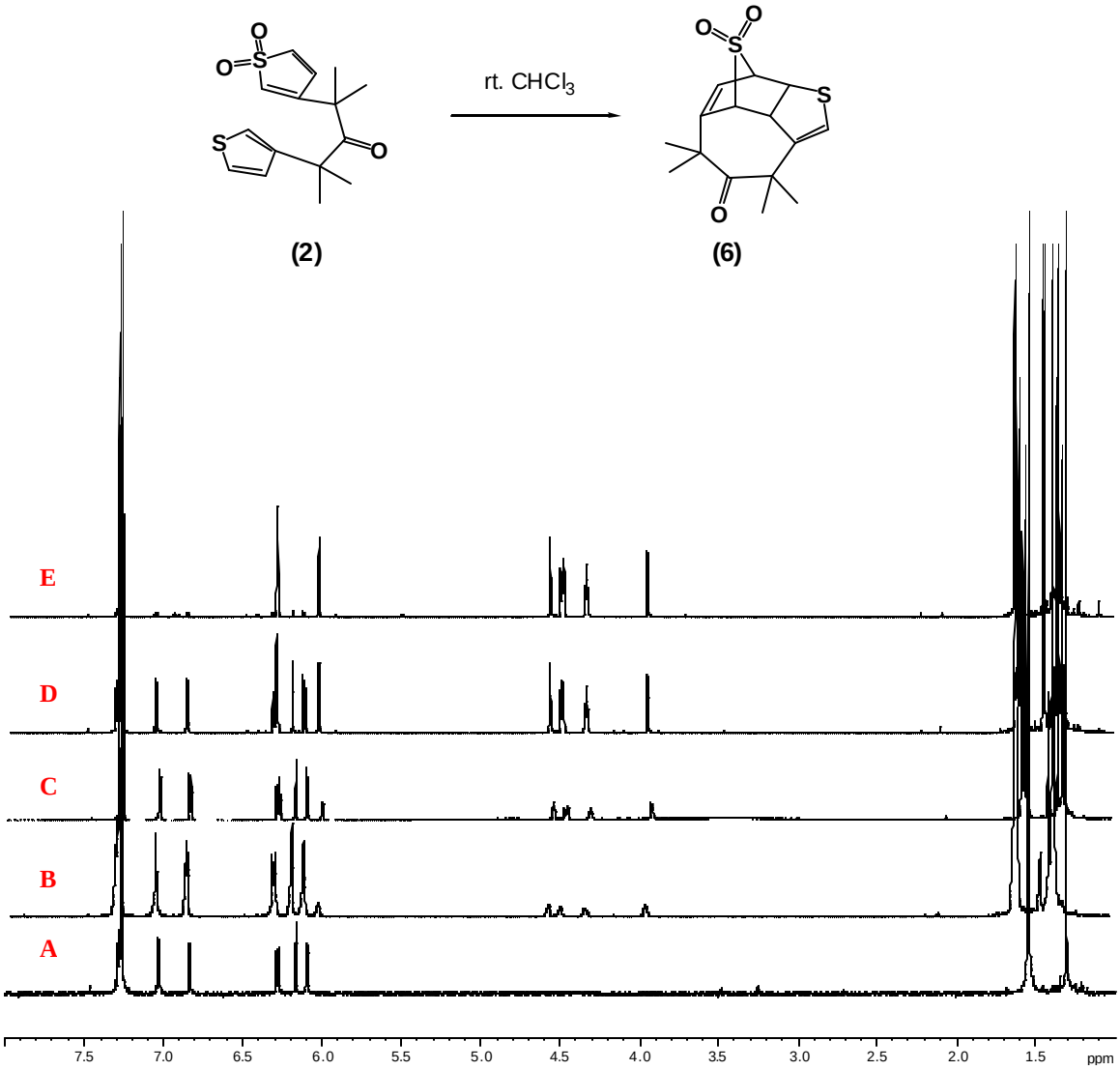


Parameters used: Hold for 2.0 min at 25.0° C; Heat from 25.0° to 340.0° at 10.0°/min; Hold 1.0 min at 340.0°; Cool to 0.0° at 10.0°/min; Hold 1.0 min at 0°.

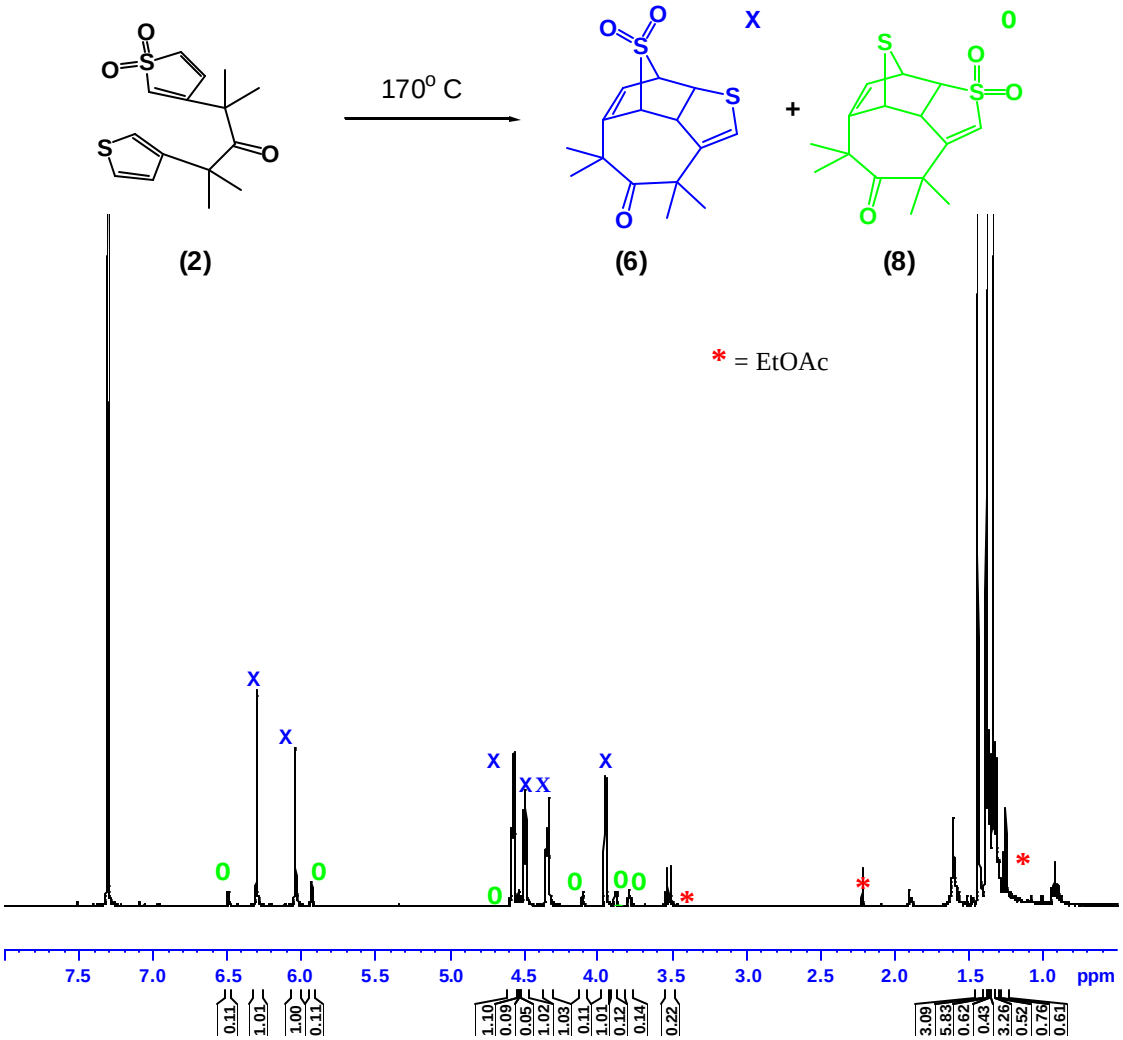
DSC experiments on **7** show melting and decomposition at 234° and 278° C. NMR spectra of the samples after heating showed a mixture of several unidentified products.

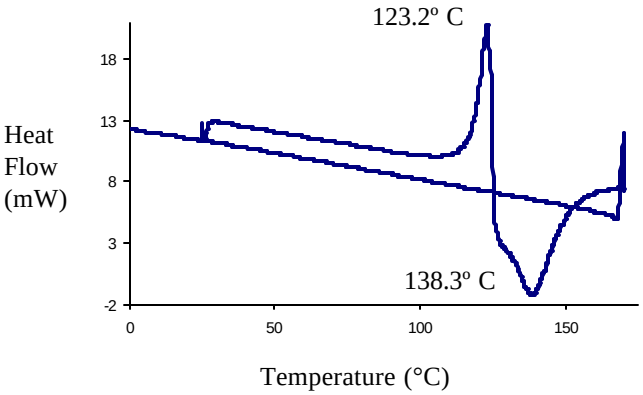


Ortep diagram of 7.



500 MHz ^{1}H NMR spectra following the 4+2 cycloaddition of 2 to 6. The figure shows the NMRs of 2 (A) after purification, (B) after 2 days (14% conv.), (C) after 5 days (36% conv.), (D) after 19 days (59% conv.) and (E) after 62 days (94% conv.).





Transformation **2** to **6** + **8** was achieved by heating 6.2 mg of **2** to 170°C at 10°/min with cooling to 0° at the same rate (left). Conversion ratios of 90:10 (**6**:**8**) were obtained as measured by NMR (top).