Electronic Supplementary Information

for:

Quantitative preparation of 3,4-di(methylene)tetrahydrothiophene-1,1-dioxide by Zn-induced 1,4-debromination. A valuable 6-C reactive diene in [4+2] cycloadditions with DMAD and [60]fullerene

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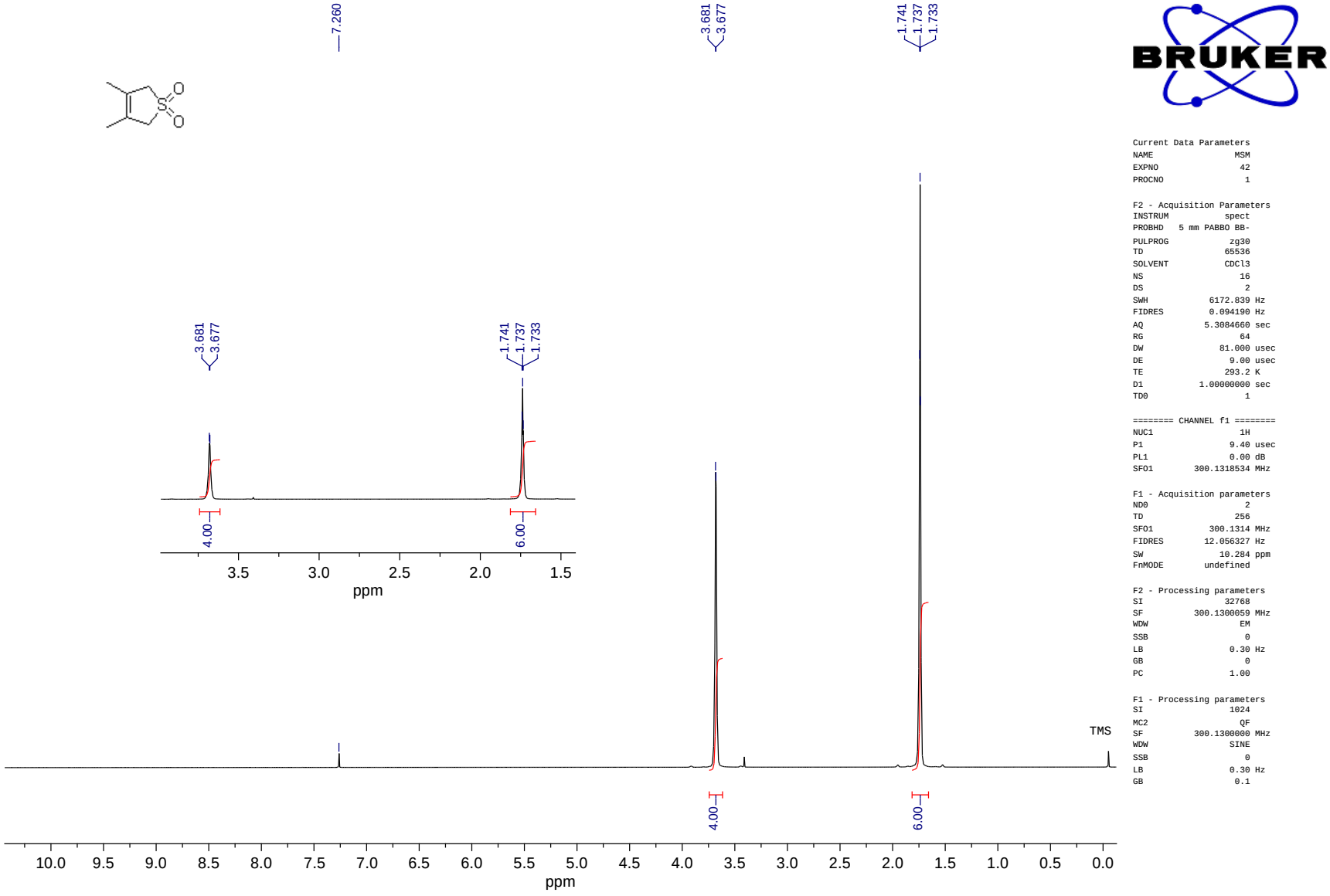
1. X-ray Crystallography

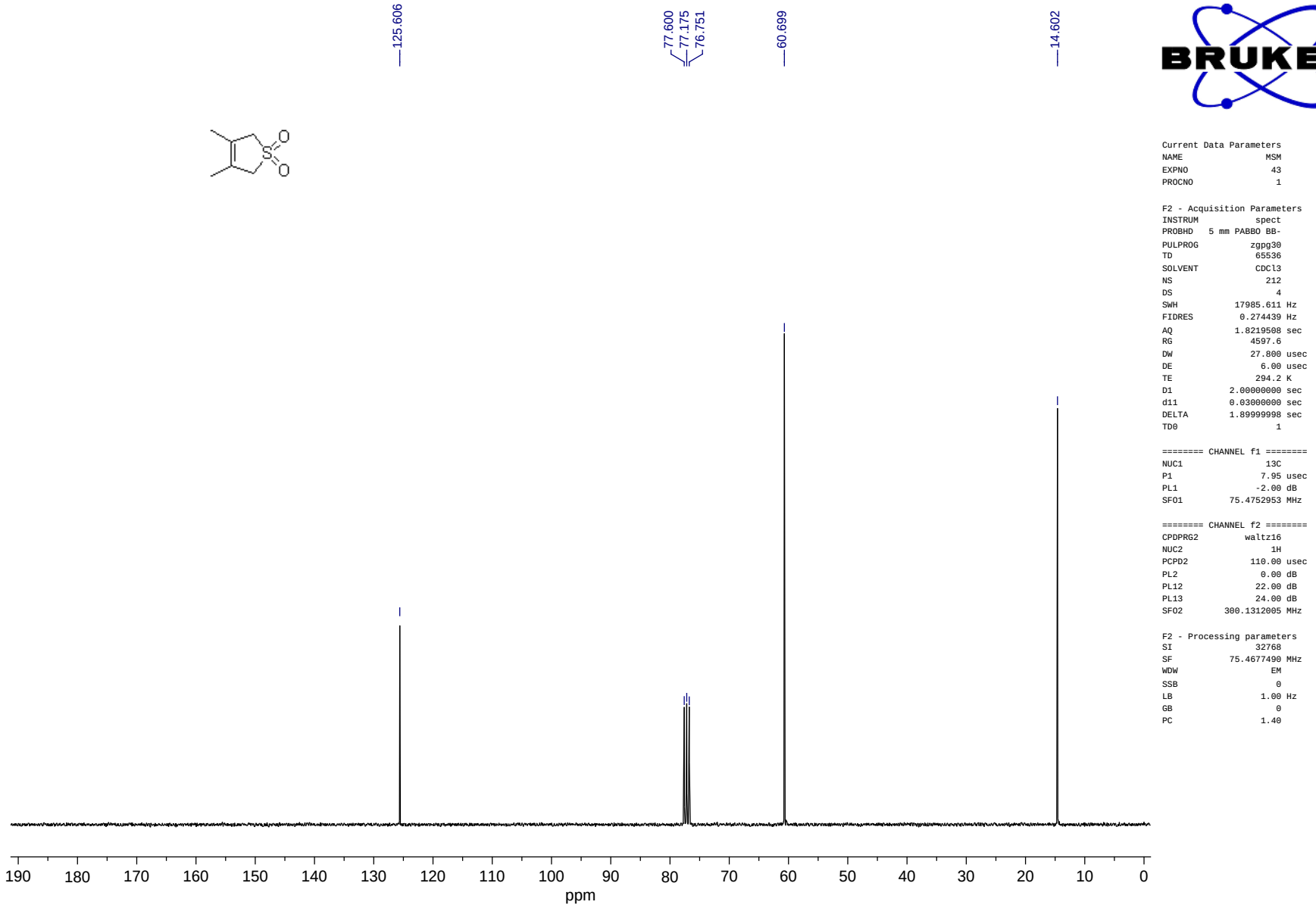
Crystallographic data were collected on an Oxford-Diffraction Supernova diffractometer, equipped with a CCD area detector utilizing Mo-Kα radiation (λ = 0.71073 Å). A suitable crystal was attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.[1] The structures were solved by direct methods using SIR92[2] and refined on F^2 using full-matrix least squares using SHELXL97.[3] Software packages used: CrysAlis CCD[1] for data collection, CrysAlis RED[1] for cell refinement and data reduction, WINGX for geometric calculations[4] and MERCURY[5] for molecular graphics. The non-H atoms were treated anisotropically. The hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. Selected crystallographic data for compounds **3** and **10** are shown in Table S1. CCDC 868567 and 868568 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

2. ^{1}H NMR and ^{13}C NMR spectra

^{1}H NMR spectrum of 7 (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of 7 (75 MHz, $CDCl_3$)

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PROCNO                  1

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DE                   6.00 usec
TE                  294.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                     1

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P1                    7.95 usec
PL1                  -2.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               110.00 usec
PL2                   0.00 dB
PL12                 22.00 dB
PL13                 24.00 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
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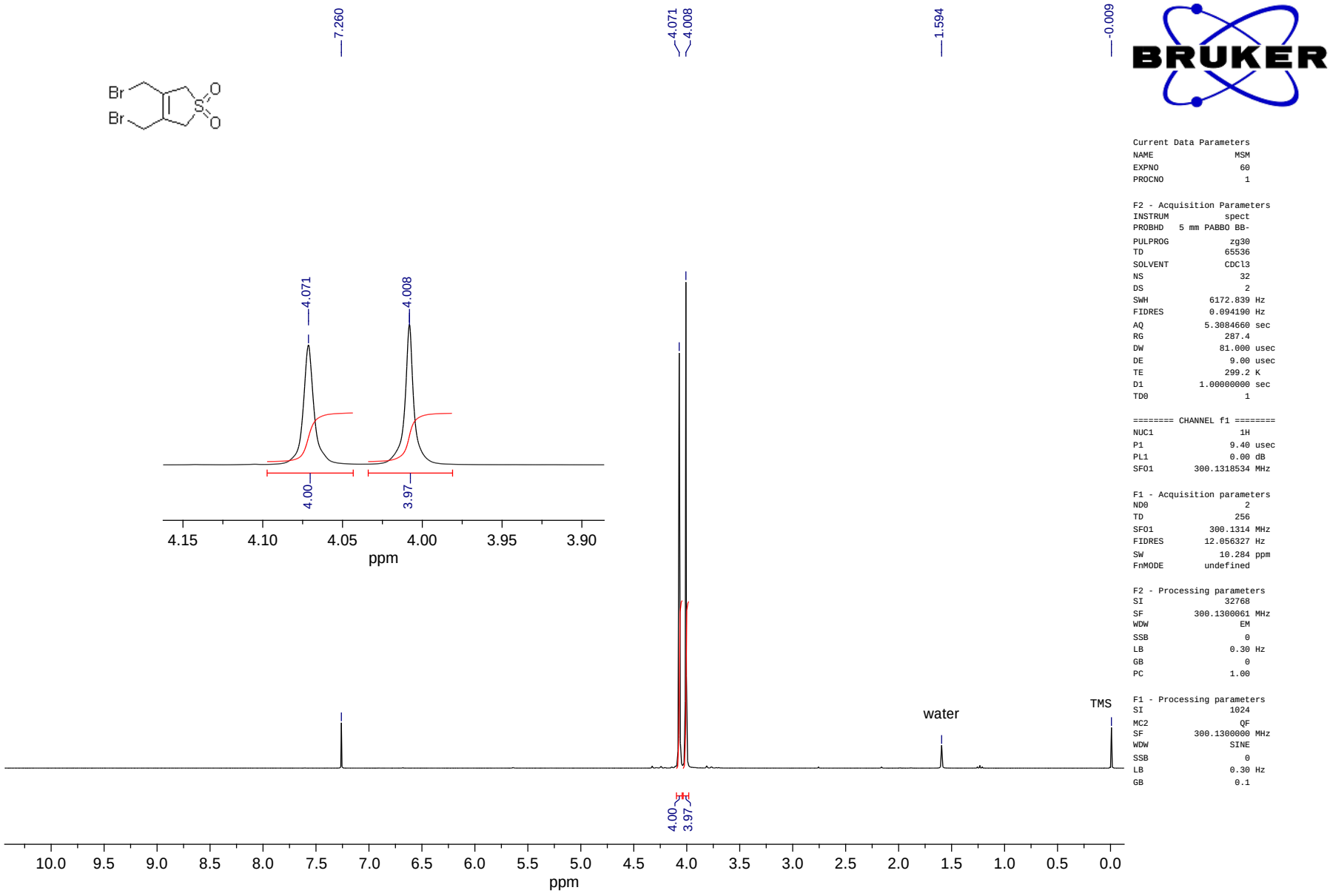
^{1}H NMR spectrum of 3 (300 MHz, $CDCl_3$)

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F1 - Acquisition parameters
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FnMODE          undefined

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F1 - Processing parameters
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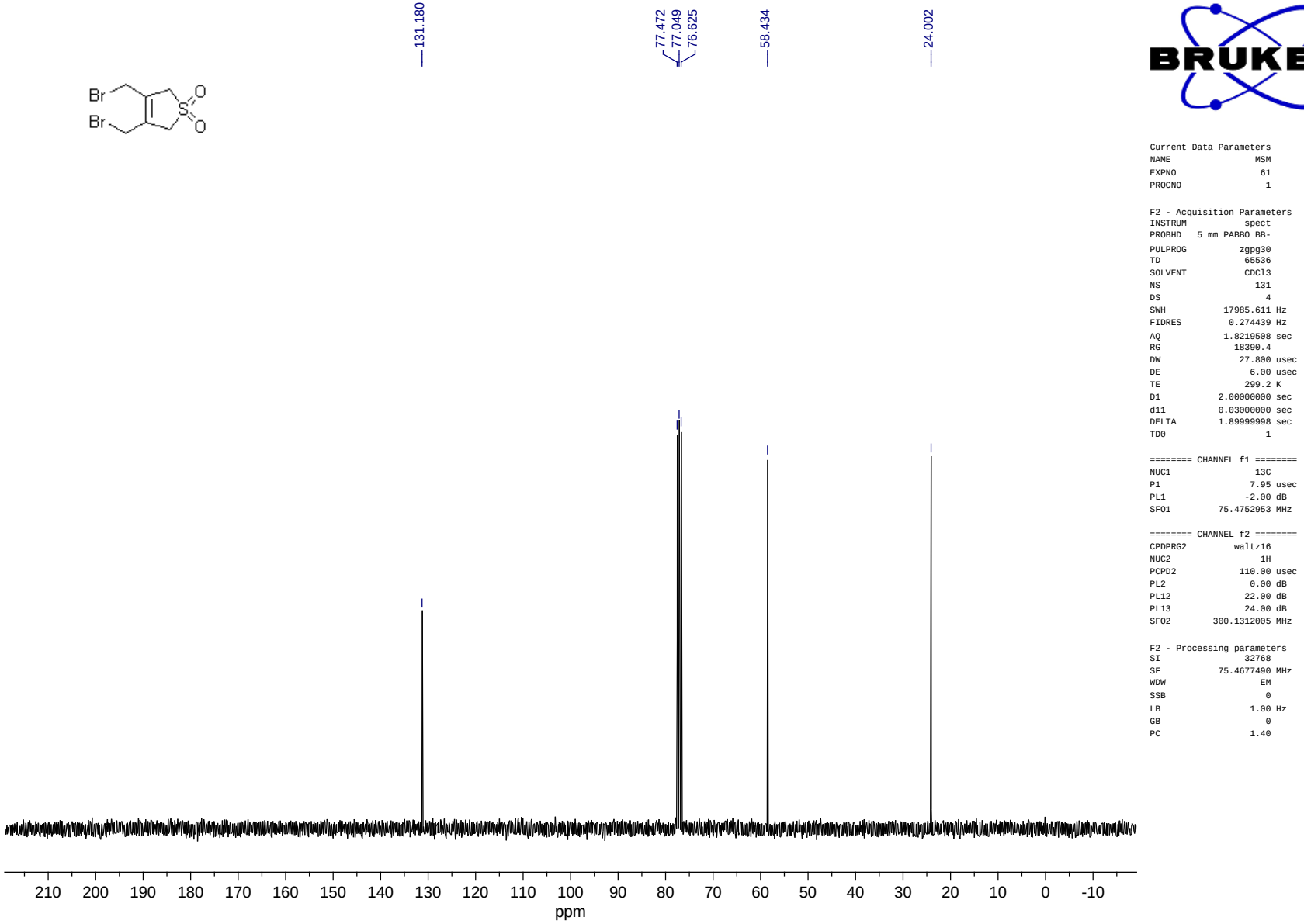
^{13}C NMR spectrum of 3 (75 MHz, $CDCl_3$)

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PROCNO                  1

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TD                   65536
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NS                     131
DS                       4
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FIDRES               0.274439 Hz
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======== CHANNEL f1 ========
NUC1                    13C
P1                    7.95 usec
PL1                  -2.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                110.00 usec
PL2                   0.00 dB
PL12                 22.00 dB
PL13                 24.00 dB
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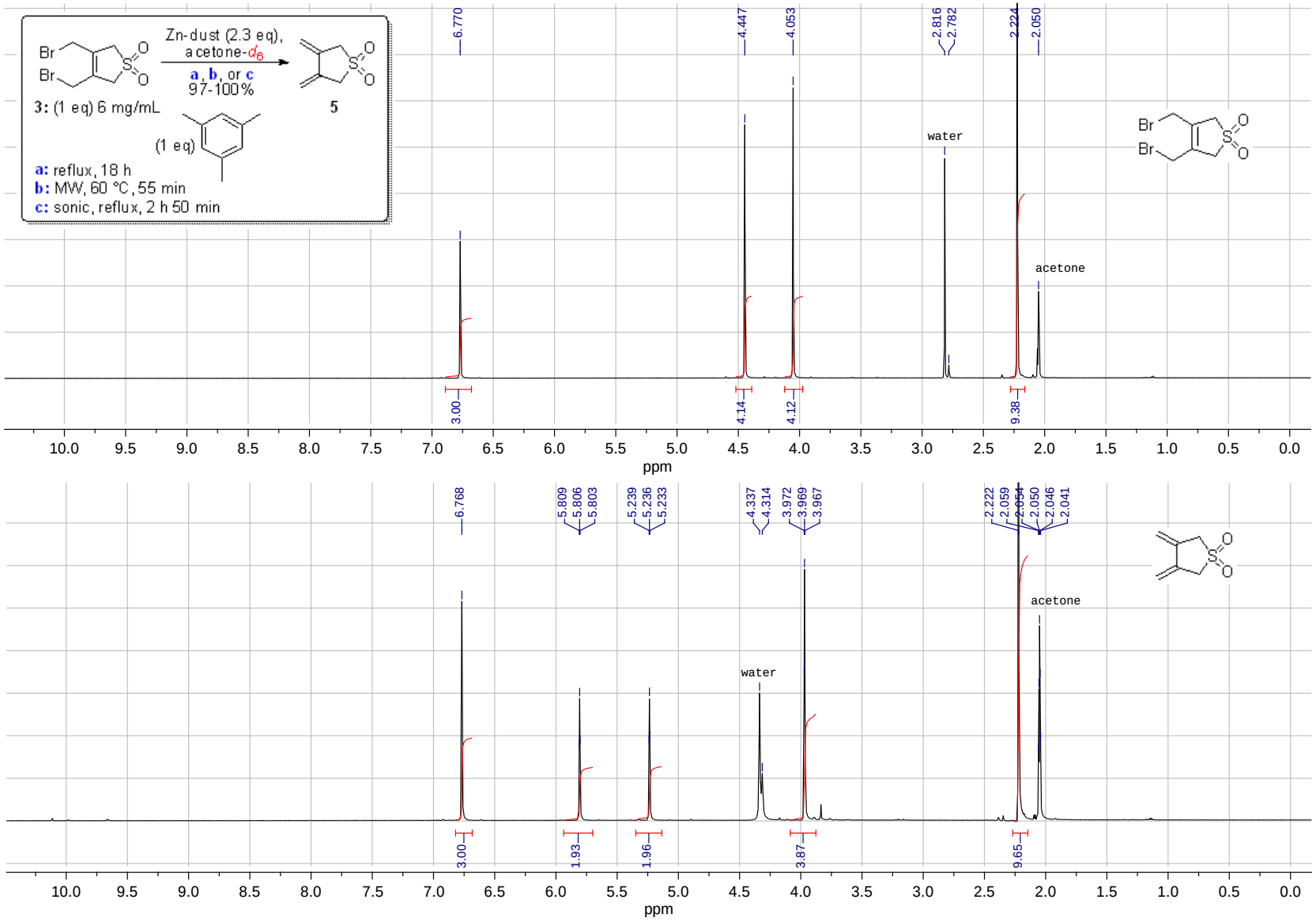
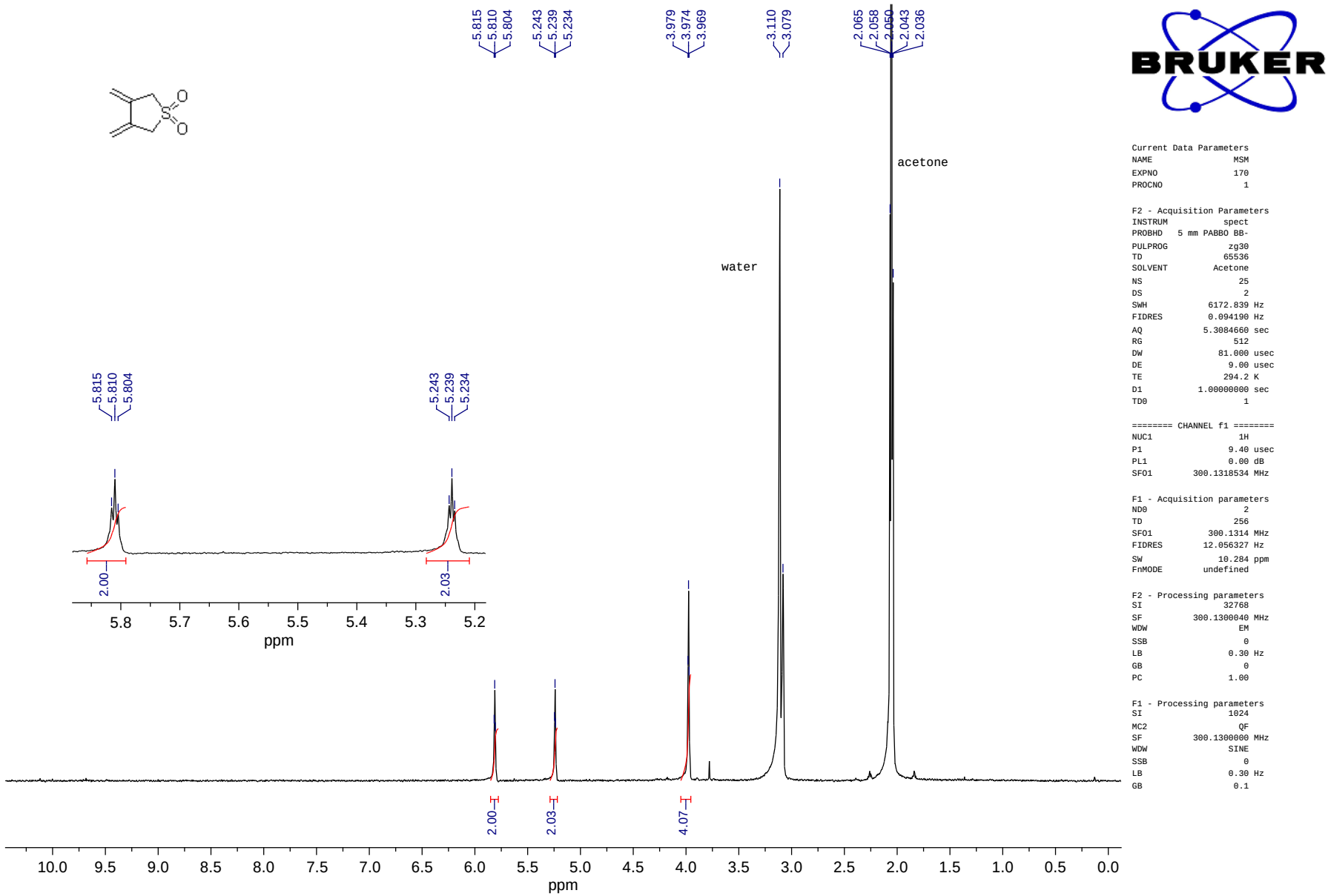
F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

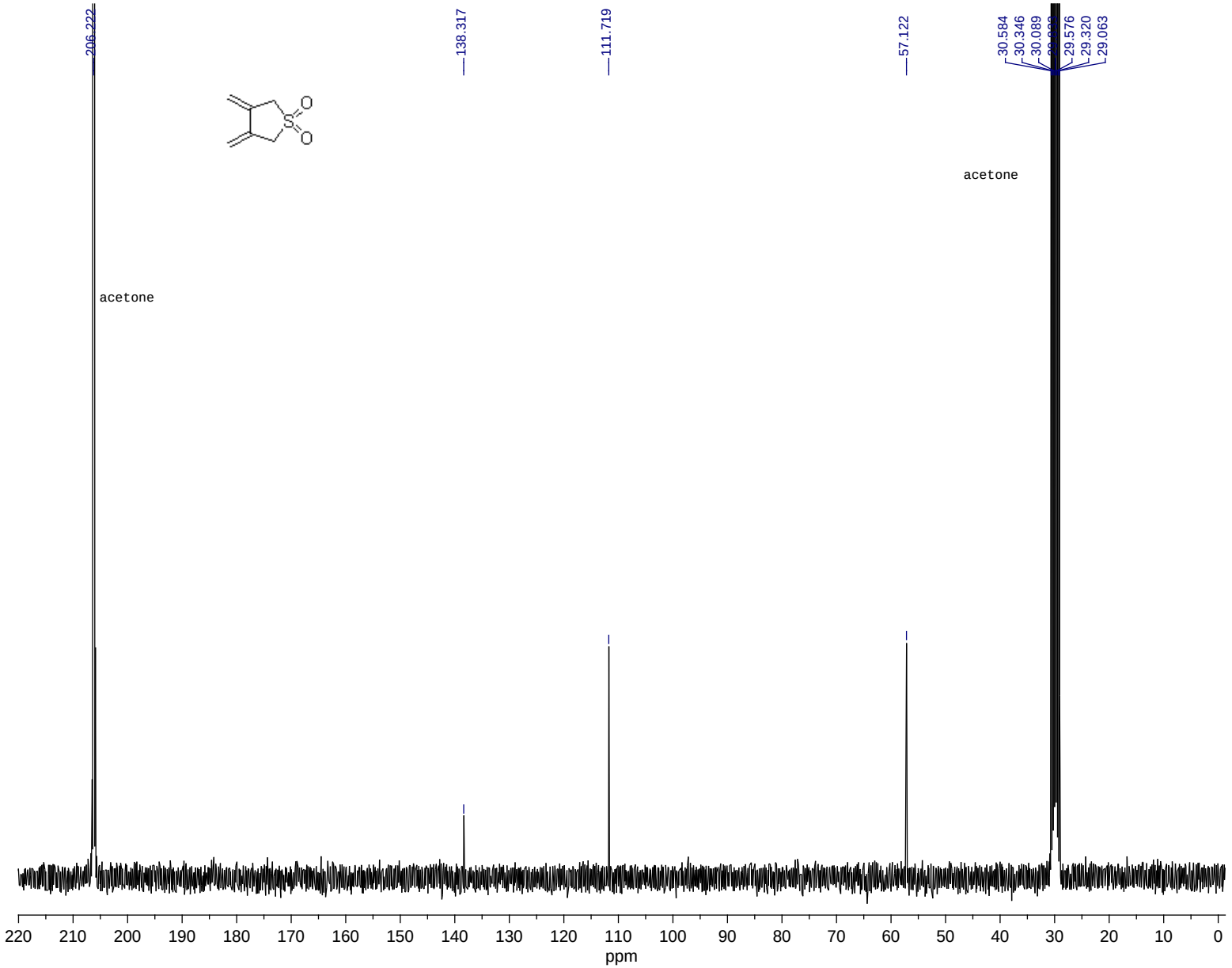
^{1}H NMR spectrum of the reaction of 3 (1 equiv) with Zn-dust (2.3 equiv) in the presence of mesitylene (1 equiv): beginning (top), upon completion (bottom) (500 MHz, acetone-d_6)



^{1}H NMR spectrum of 5 (300 MHz, acetone-d_6)



^{13}C NMR spectrum of 5 (75 MHz, acetone-d_6)

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PROCNO                 1

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TD                 65536
SOLVENT          Acetone
NS                  1087
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                5792.6
DW                27.800 usec
DE                 6.00 usec
TE                294.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.95 usec
PL1                 -2.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              110.00 usec
PL2                  0.00 dB
PL12                22.00 dB
PL13                24.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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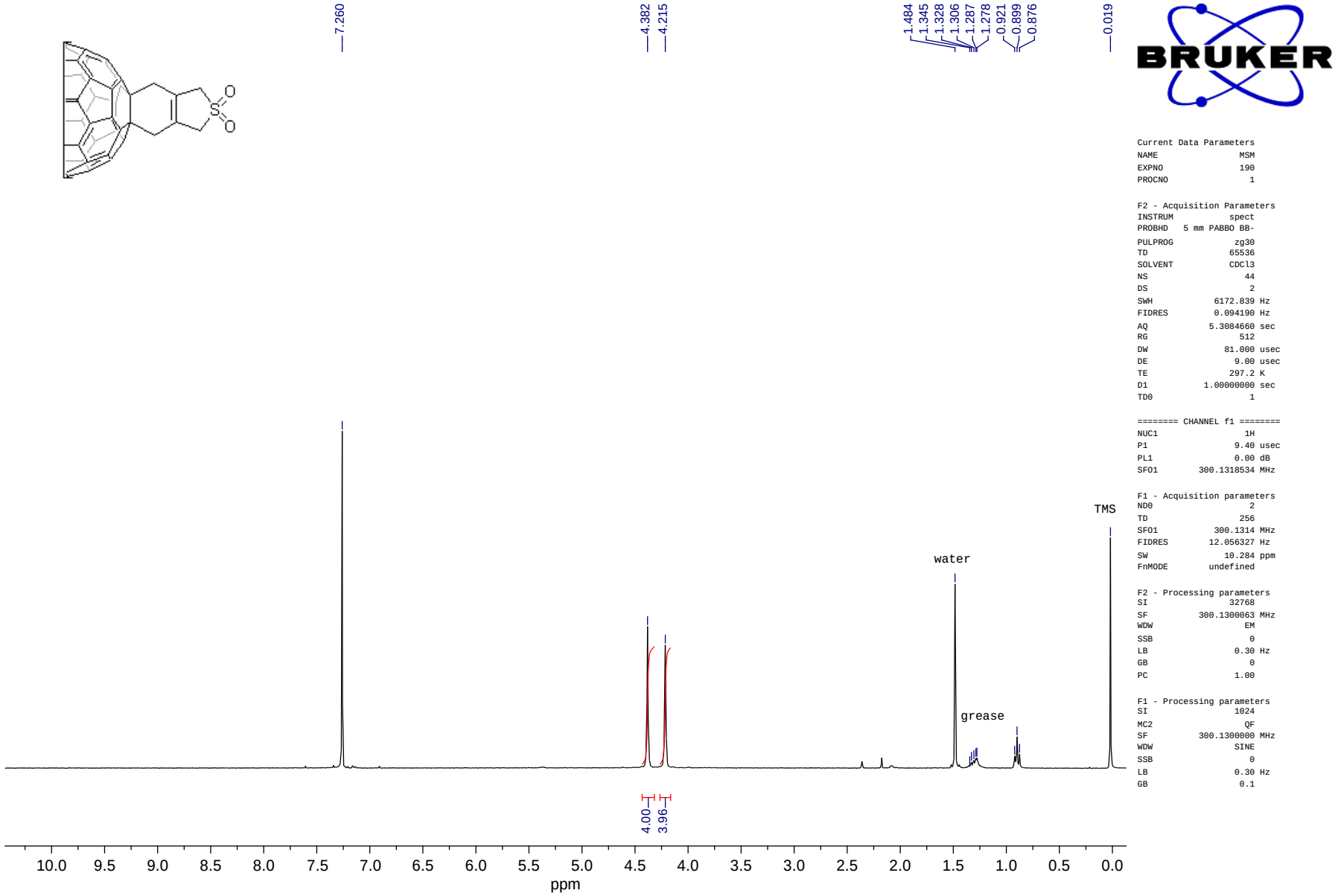
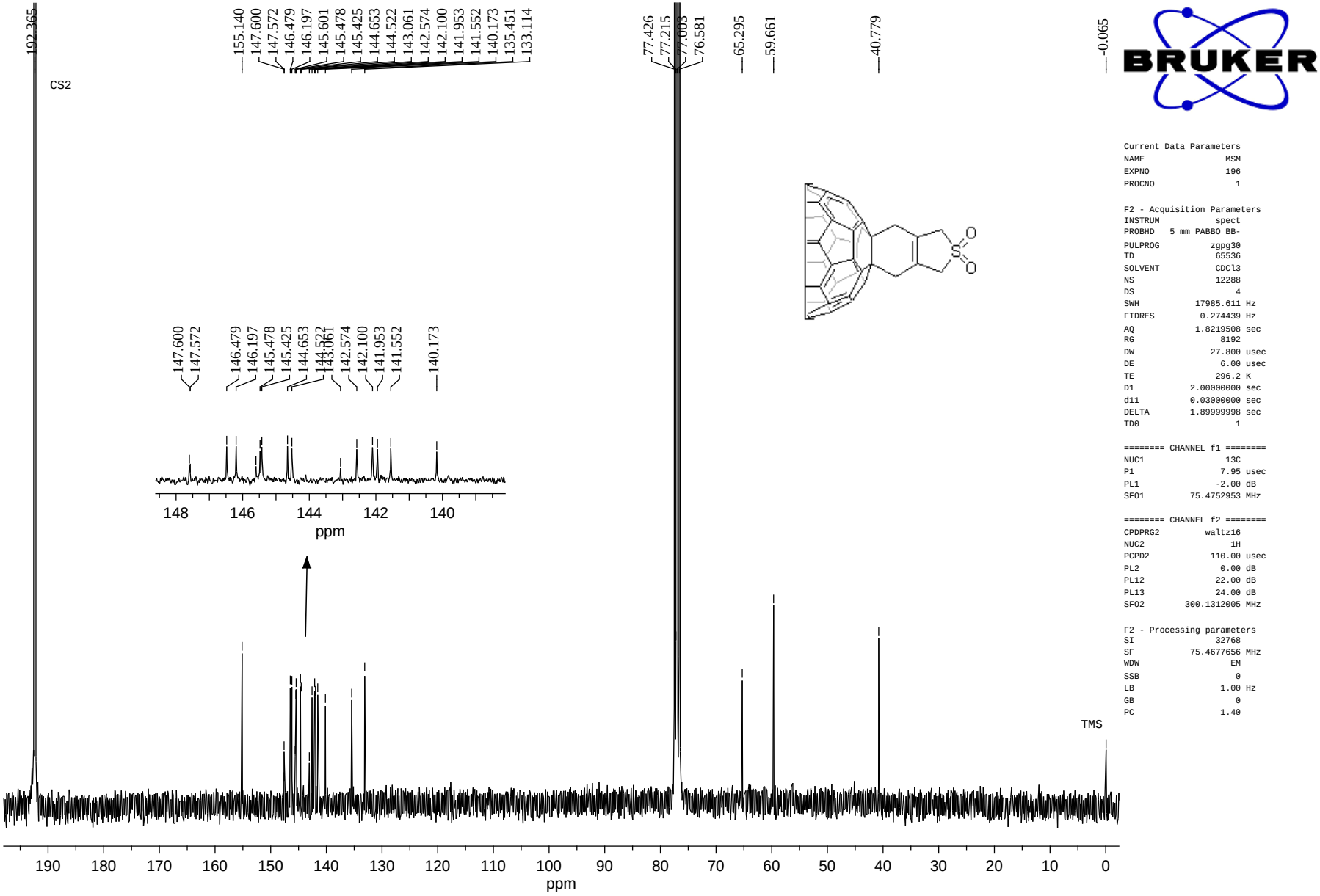
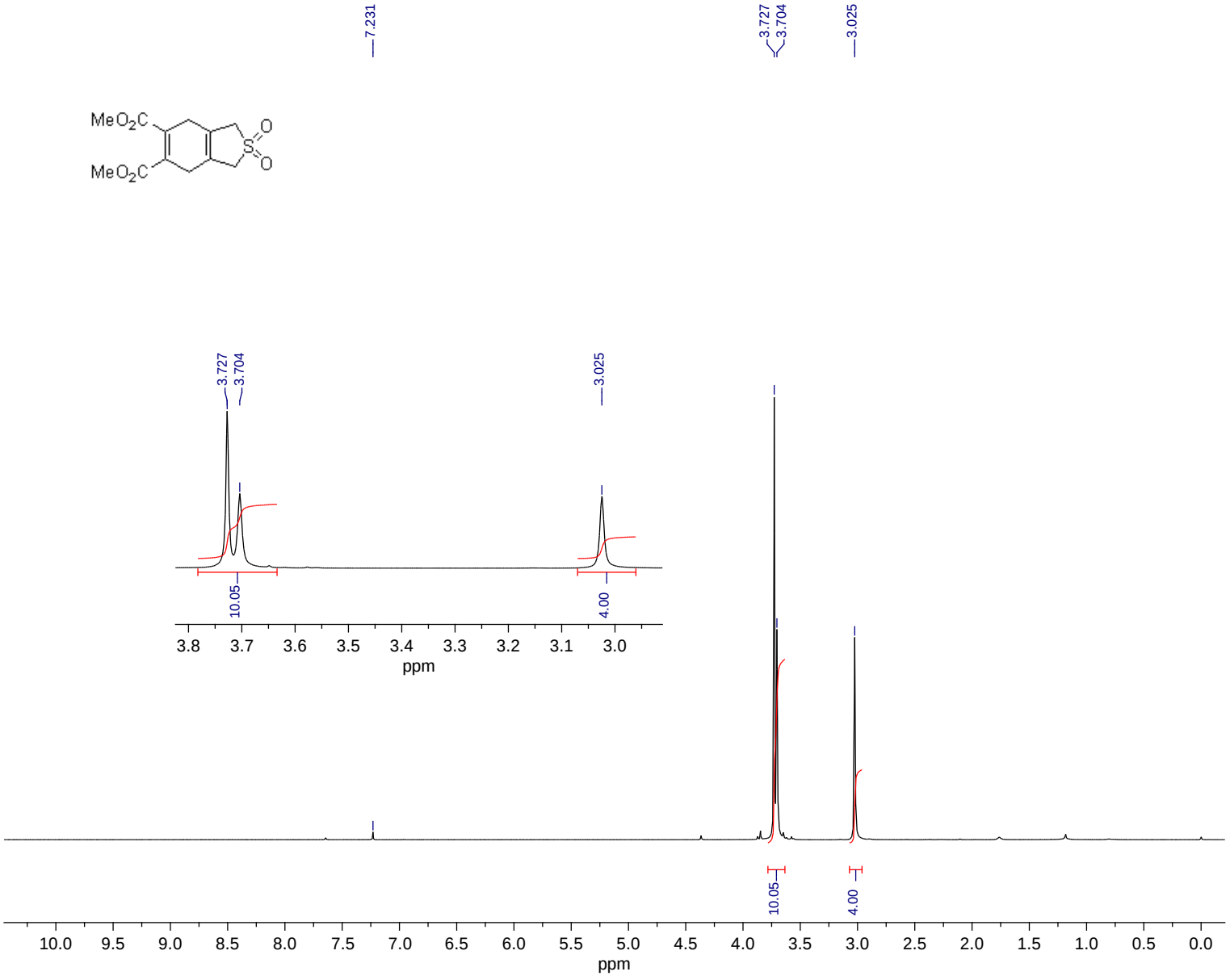
^{1}H NMR spectrum of 9 (300 MHz, CS_2/$CDCl_3$, 1:1)



^{13}C NMR spectrum of 9 (75 MHz, $CS_2/CDCl_3$, 1:1)



^{1}H NMR spectrum of 10 (500 MHz, $CDCl_3$)

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EXPNO                 139
PROCNO                  1

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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                      32
DW                 48.400 usec
DE                  6.50 usec
TE                 295.7 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.00 usec
PLW1          15.41699982 W
SFO1          500.0361158 MHz

F2 - Processing parameters
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SF            500.0330544 MHz
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SSB                      0
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PC                    1.00
```
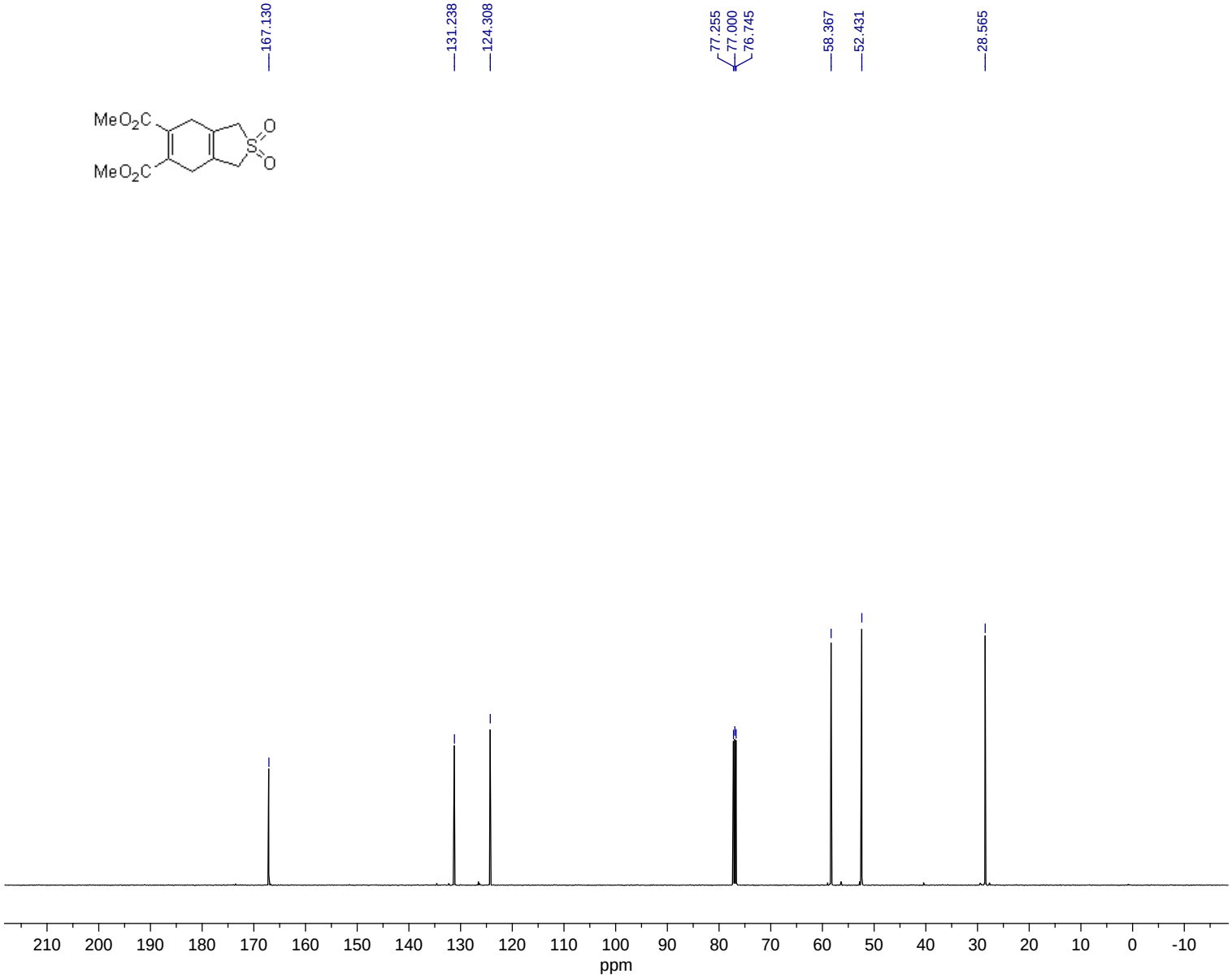

^{13}C NMR spectrum of 10 (125 MHz, $CDCl_3$)

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Current Data Parameters
NAME                  MSM
EXPNO                 140
PROCNO                  1

F2 - Acquisition Parameters
INSTRUM               spect
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PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2048
DS                       4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010548 sec
RG                    2050
DW                  16.800 usec
DE                   6.50 usec
TE                  296.5 K
D1               2.00000000 sec
D11              0.03000000 sec

======== CHANNEL f1 ========
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P1                    8.00 usec
PLW1          138.00000000 W
SFO1           125.7459776 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PLW2           13.00000000 W
PLW12           0.31738001 W
PLW13           0.20313001 W
SFO2           500.0350280 MHz

F2 - Processing parameters
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SF              125.7334220 MHz
WDW                     EM
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LB                    1.00 Hz
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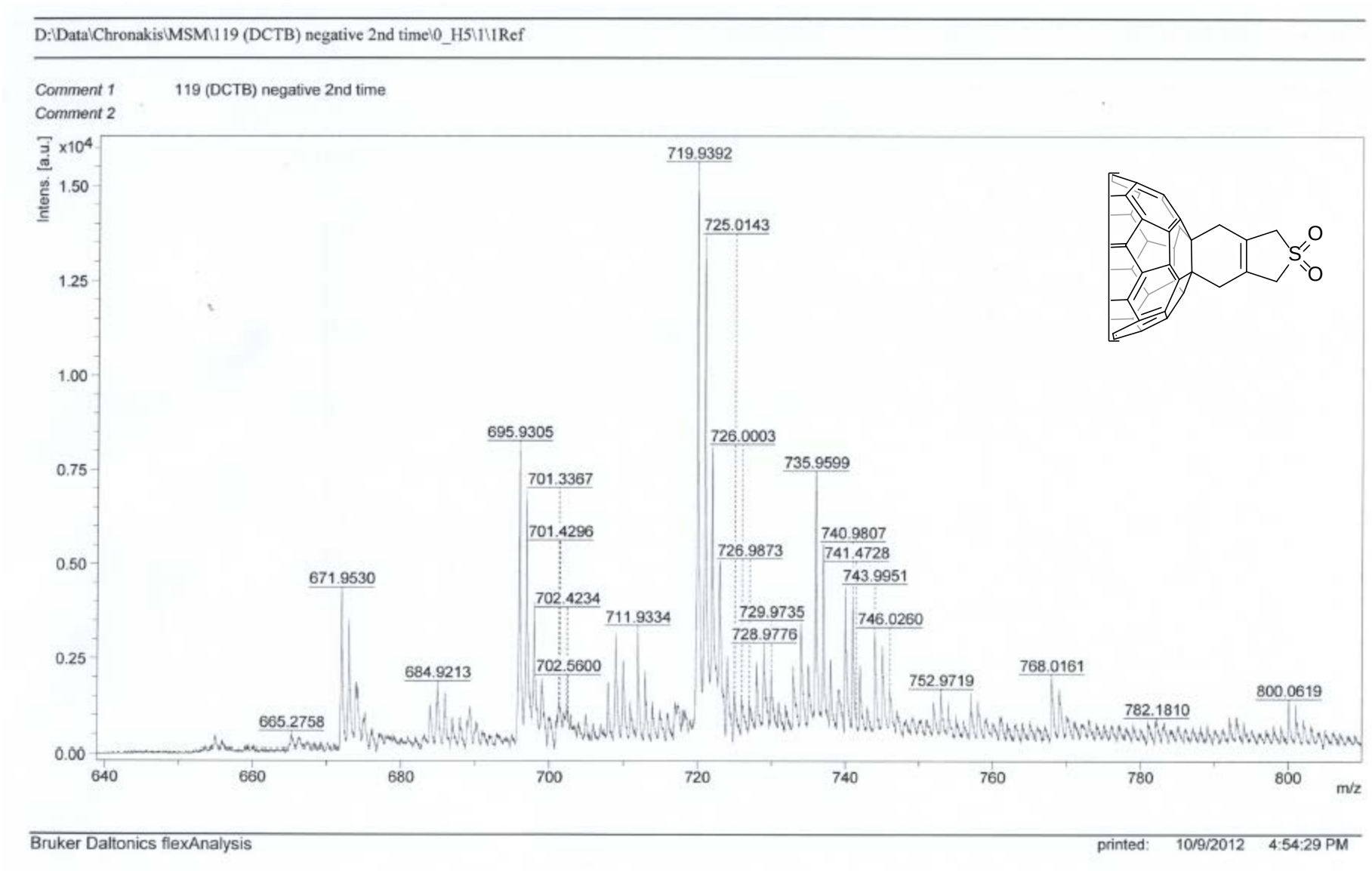
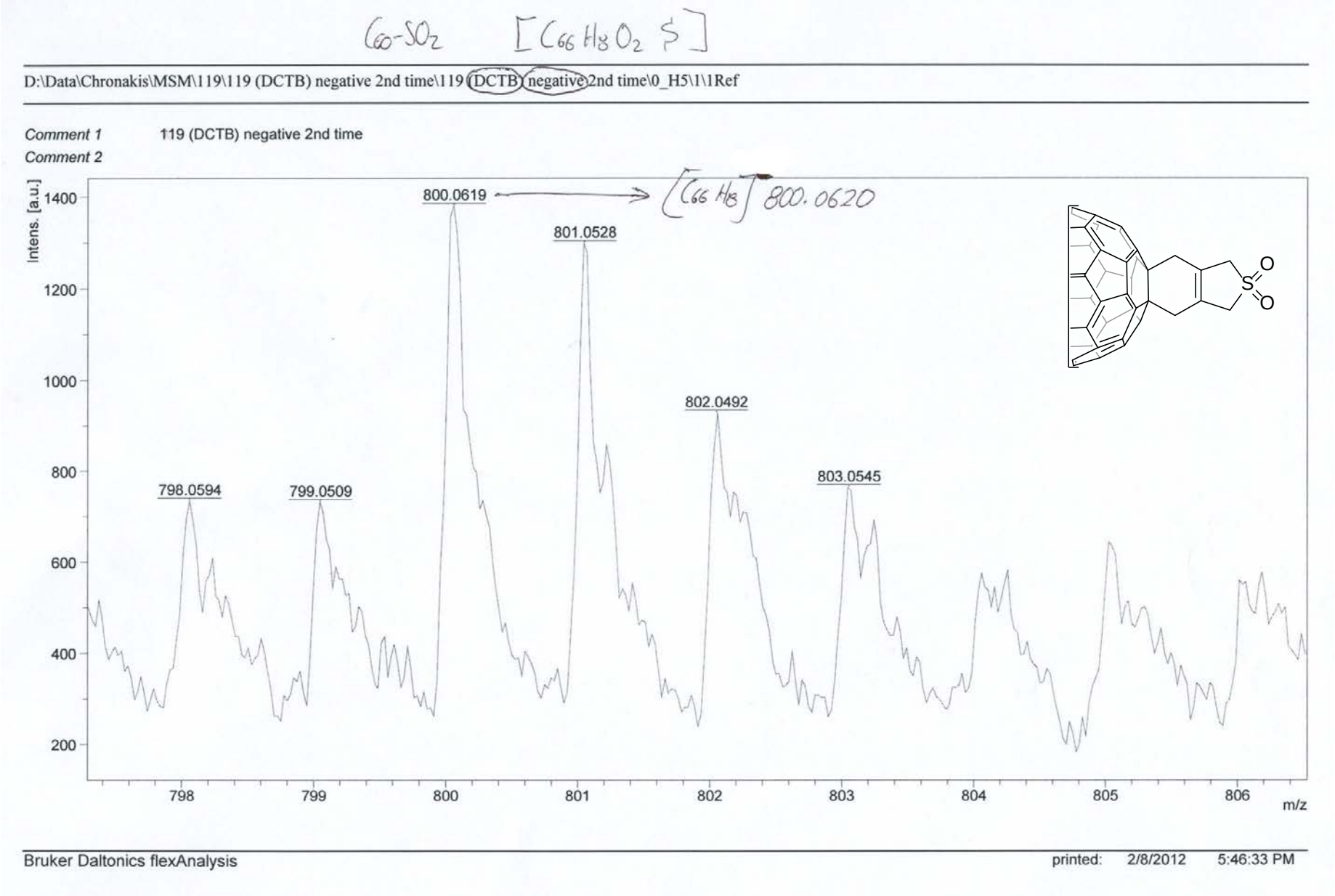
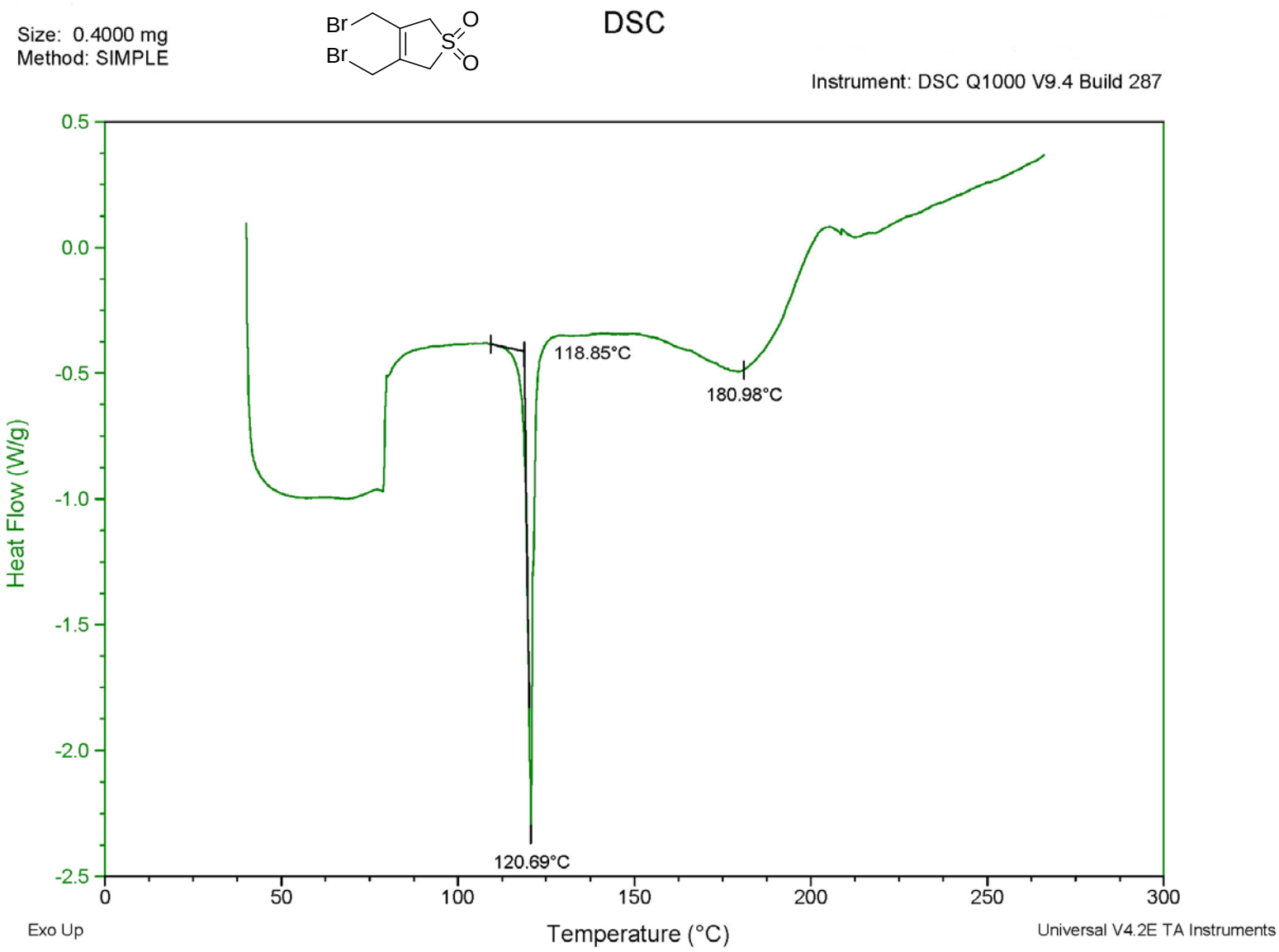
3. High resolution MALDI-TOF mass spectra of 9 (negative mode, DCTB)

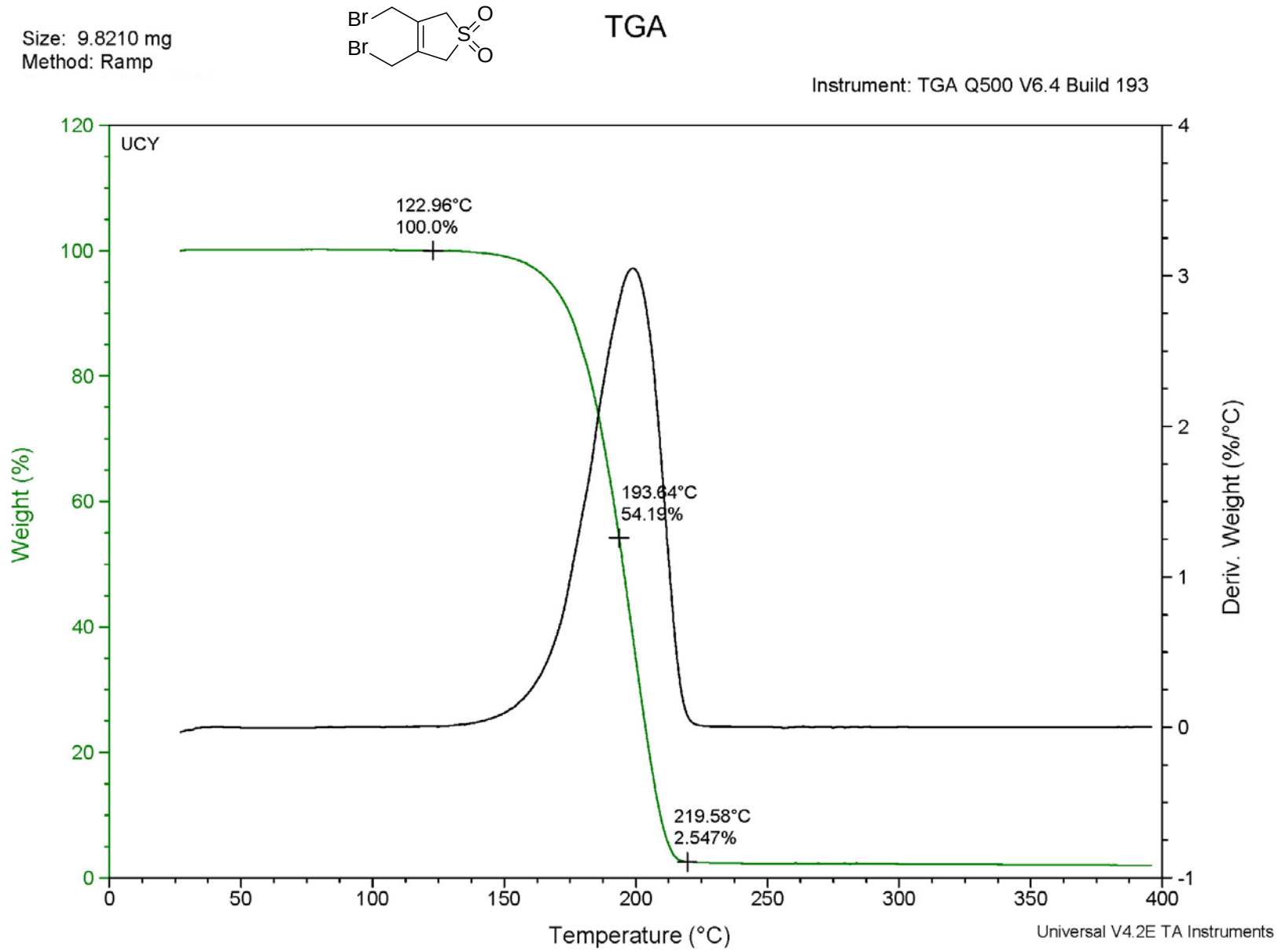


High resolution MALDI-TOF mass spectra of 9 (negative mode, DCTB)



4. DSC and TGA data for 3





5. X-ray crystallographic information (crystal data/structure refinement) for 10 and 3

Table S1: Selected crystallographic data for compounds **10** and **3**

Compound	**10**	**3**
Chemical formula	$C_{12}H_{14}O_6S$	$C_6H_8Br_2O_2S$
Formula Mass	286.29	304.00
Crystal system	Monoclinic	Triclinic
a/Å	8.170(2)	9.330(5)
b/Å	7.029(2)	9.624(5)
c/Å	22.066(4)	12.480(5)
α/°	90.00	70.661(5)
β/°	97.99(2)	73.733(5)
γ/°	90.00	63.117(5)
Unit cell volume/Å^3	1254.9(5)	931.7(8)
Temperature/K	100(2)	100(2)
Space group	$P2_1/n$	$P\bar{1}$
No. of formula units per unit cell, *Z*	4	4
Radiation type	Mo-Kα	Mo-Kα
Absorption coefficient, μ/mm^{-1}	0.279	8.874
No. of reflections measured	6494	5407
No. of independent reflections	2213	3278
R_{int}	0.0914	0.0482
Final R_1[a] values ($I > 2\sigma(I)$)	0.0802	0.0380
Final $wR(F^2)$[b] values ($I > 2\sigma(I)$)	0.1921	0.0714
Final R_1[a] values (all data)	0.1190	0.0508
Final $wR(F^2)$[b] values (all data)	0.2191	0.0785
Goodness of fit on F^2	0.994	0.966

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR = [\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[wFo^2)^2]]^{1/2}$, $w = 1/[\sigma^2(Fo^2) + (m\cdot p)^2 + n\cdot p]$, $p = [\max(Fo^2,0) + 2Fc^2,0]/3$, and *m* and *n* are constants.

6. Crystal packing and interactions in the crystal structure of 3

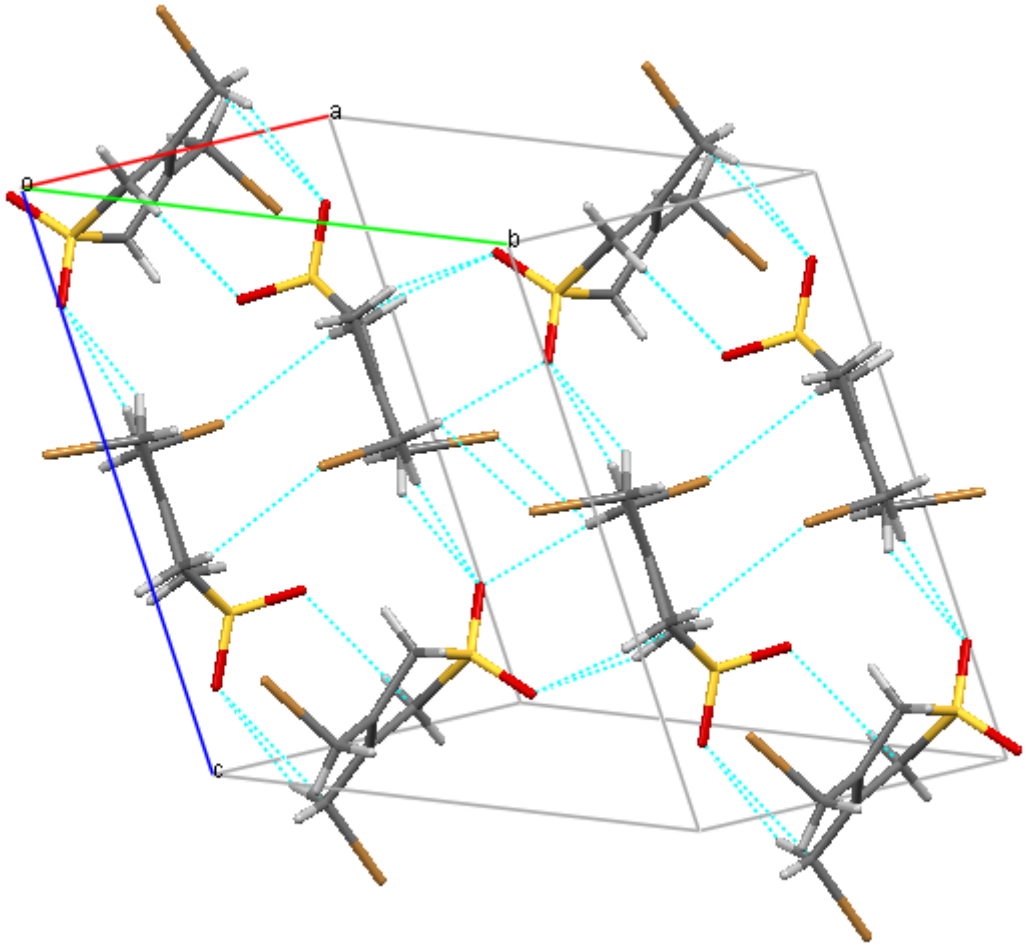


Figure S1

7. Crystal packing and interactions in the crystal structure of 10

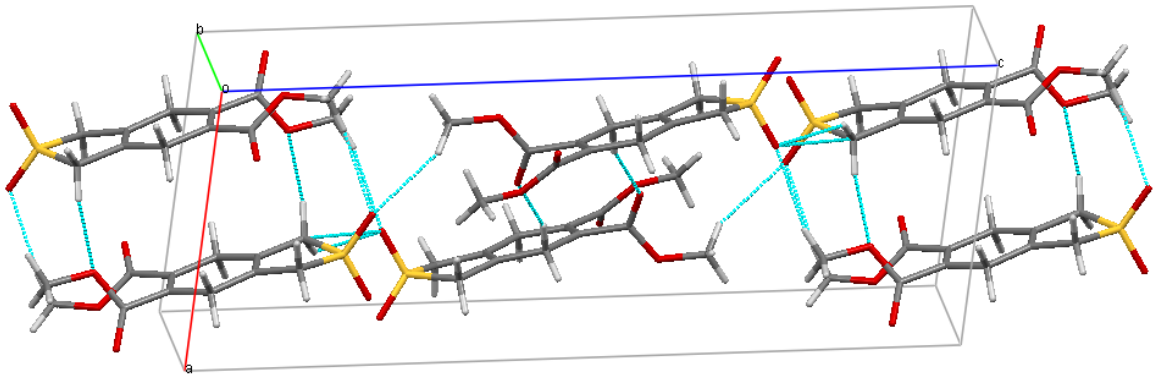


Figure S2

8. References

(1) Oxford Diffraction (2008). CrysAlis CCD and CrysAlis RED, version 1.171.32.15, Oxford Diffraction Ltd, Abingdon, Oxford, England.

(2) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, "SIR92 - a program for automatic solution of crystal structures by direct methods," *J. Appl. Crystallogr.*, vol.27, p. 435, 1994.

(3) G. M. Sheldrick, "SHELXL97-A program for the refinement of crystal structure", University of Göttingen, Germany.

(4) L. J. Farrugia, "WinGX suite for single crystal small molecule crystallography", *J. Appl. Crystallogr.*, vol. 32, pp. 837-838, 1999.

(5) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van De Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453.