*Electronic Supplementary Information (ESI)*

*for:*

# One-pot thermally chemocontrolled double Diels–Alder strategies. A route to [4+2] functionalisation/[4+2] derivatization of $C_{60}$

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## 1. X-ray crystallography

Data were collected on an Oxford-Diffraction Supernova diffractometer, equipped with a CCD area detector utilizing Mo-Kα (λ = 0.71073 Å) or Cu-Kα (λ = 1.54184 Å) radiation. 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 structure was 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. CCDC 886629 and 886630 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. Selected crystal data for all compounds are given in Table S1.

## 2. X-ray crystallographic information (crystal data/structure refinement) for 12 and 16

**Table S1:** Selected crystallographic data for compounds **12** and **16**

| Compound | **12** | **16** |
|---|---|---|
| empirical formula | $C_{18}H_{20}O_8$ | $C_{17}H_{19}NO_6$ |
| formula weight | 364.34 | 333.33 |
| Crystal system | Triclinic | Monoclinic |
| *a*/Å | 5.2551(4) | 13.3575(6) |
| *b*/Å | 12.1219(7) | 15.2746(8) |
| *c*/Å | 14.271(2) | 7.8745(4) |
| *α*/° | 109.989(6) | 90.00 |
| *β*/° | 95.075(7) | 98.222(4) |
| *γ*/° | 94.816(5) | 90.00 |
| V/Å$^3$ | 844.7(2) | 1590.2(2) |
| Radiation type | MoKα | CuKα |
| Temperature/K | 100(2) | 100(2) |
| Space group | *P-1* | $P2_1/c$ |
| *Z* | 2 | 2 |
| $\mu$/mm$^{-1}$ | 0.114 | 0.890 |
| Total/ independent reflections | 2969/2441 | 2836/2229 |
| $R_{int}$ | 0.0222 | 0.0280 |
| $R_1{}^a$ / $wR(F^2)^b$ ($I > 2\sigma(I)$) | 0.0436/0.1197 | 0.0452/0.1177 |
| GOF | 1.053 | 0.946 |

$^aR_1=\Sigma\|\,|Fo| - |Fc|\,|/\Sigma|Fo|$. $^bwR(F^2)=[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2)^2]]^{1/2}$, $w=1/[\sigma^2(F_o^2) + (m\cdot p)^2 + n\cdot p]$, $p=[\max(F_o^2,0) + 2F_c^2]/3$, and m and n are constants.

## 3. Crystal packing and interactions in the crystal structure of 12

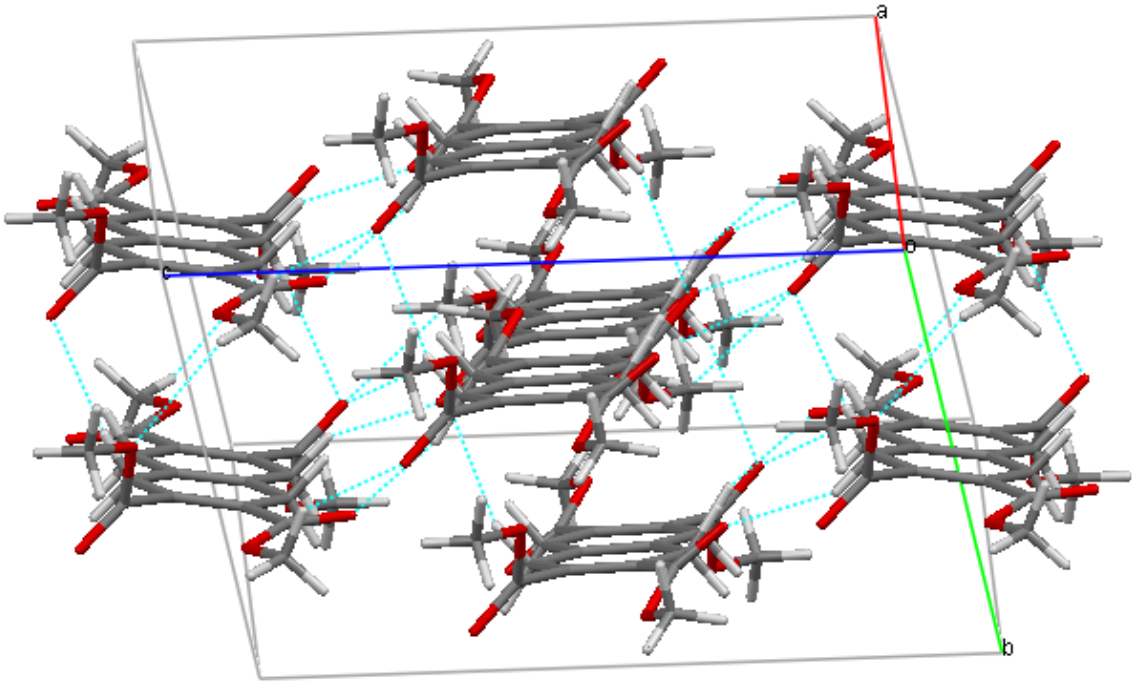



**Figure S1**

## 4. Crystal packing and interactions in the crystal structure of 16

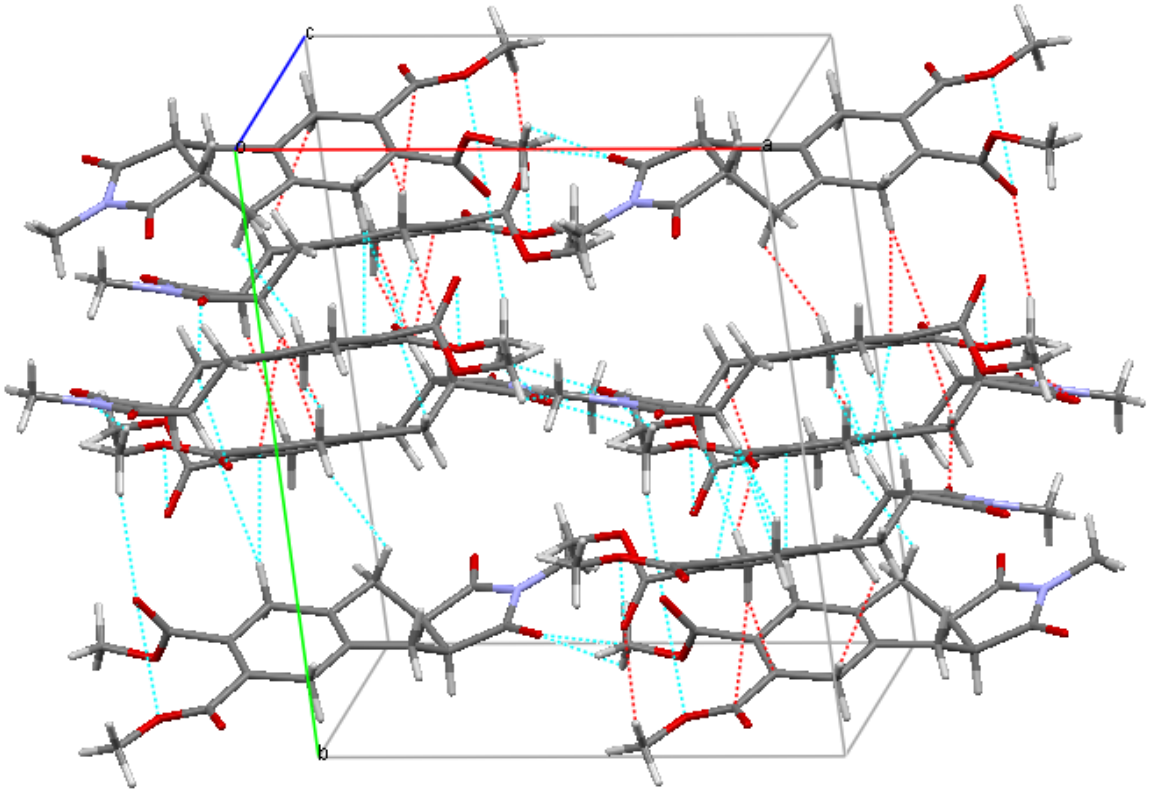
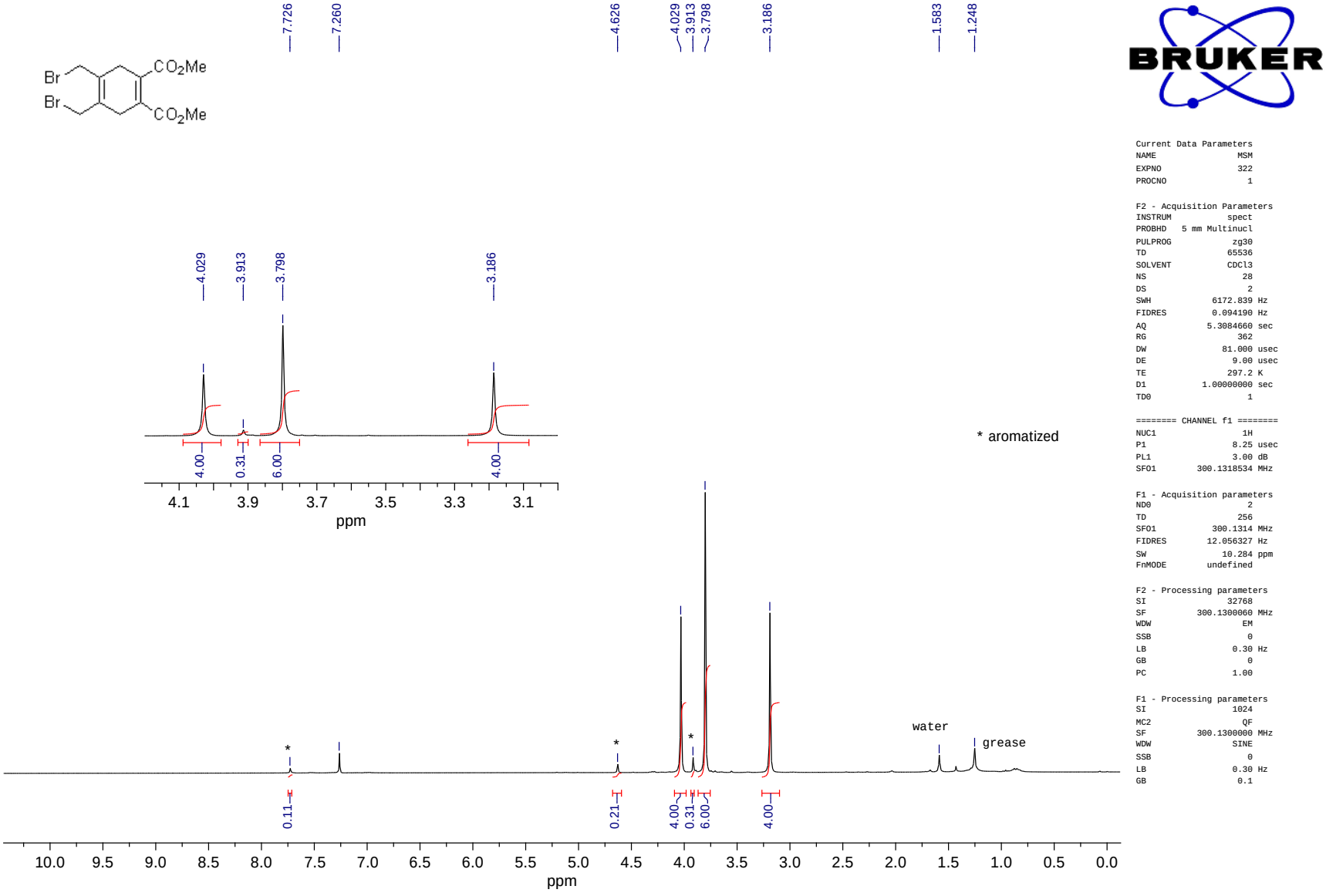


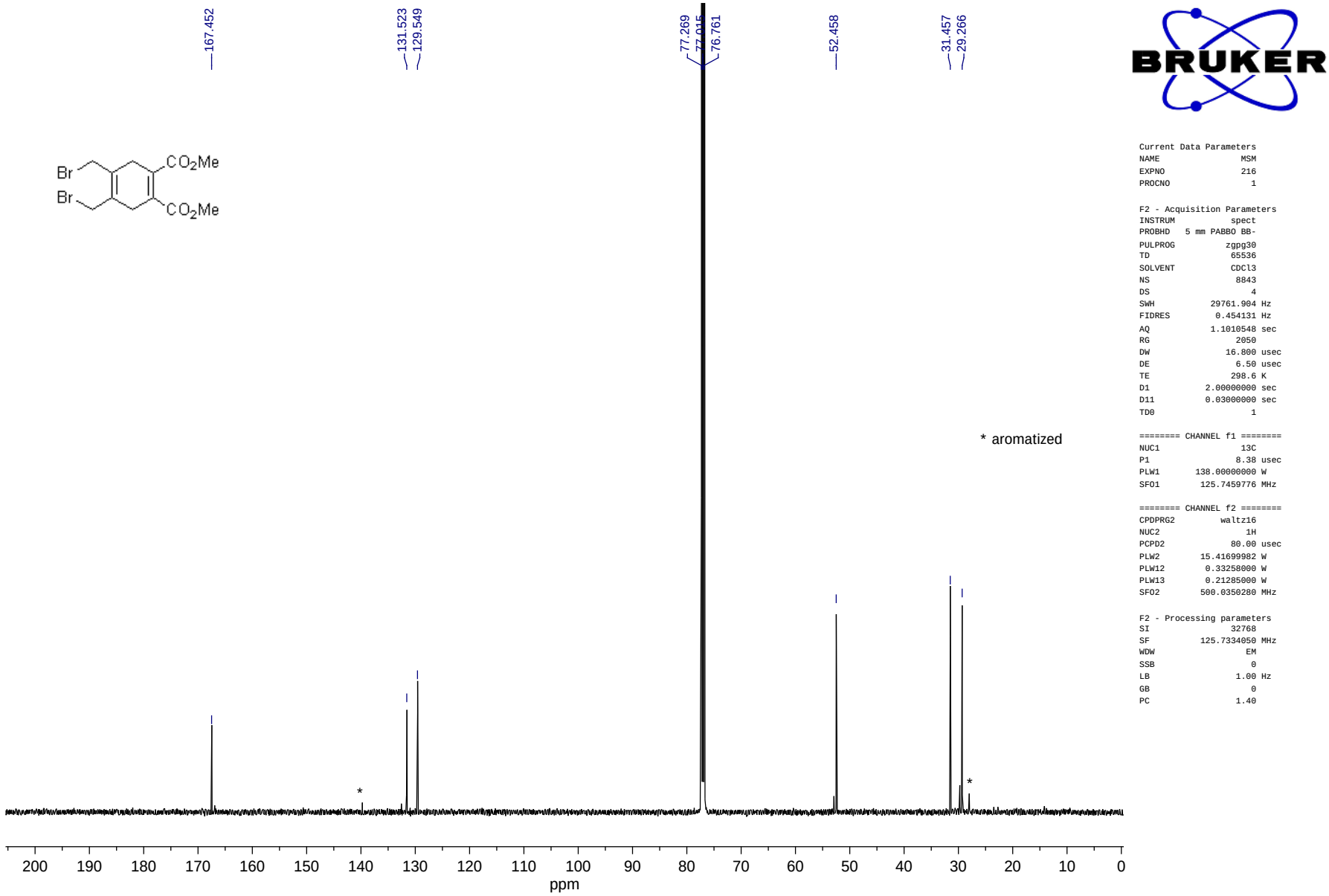

**Figure S2**

## 5. $^{1}$H NMR and $^{13}$C NMR spectra of compounds 9, 10, 12, 16 and 14

### $^{1}$H NMR spectrum of 9 (300 MHz, $CDCl_3$)



**$^{13}$C NMR spectrum of 9 (125 MHz, $CDCl_3$)**

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Current Data Parameters
NAME                  MSM
EXPNO                 216
PROCNO                  1

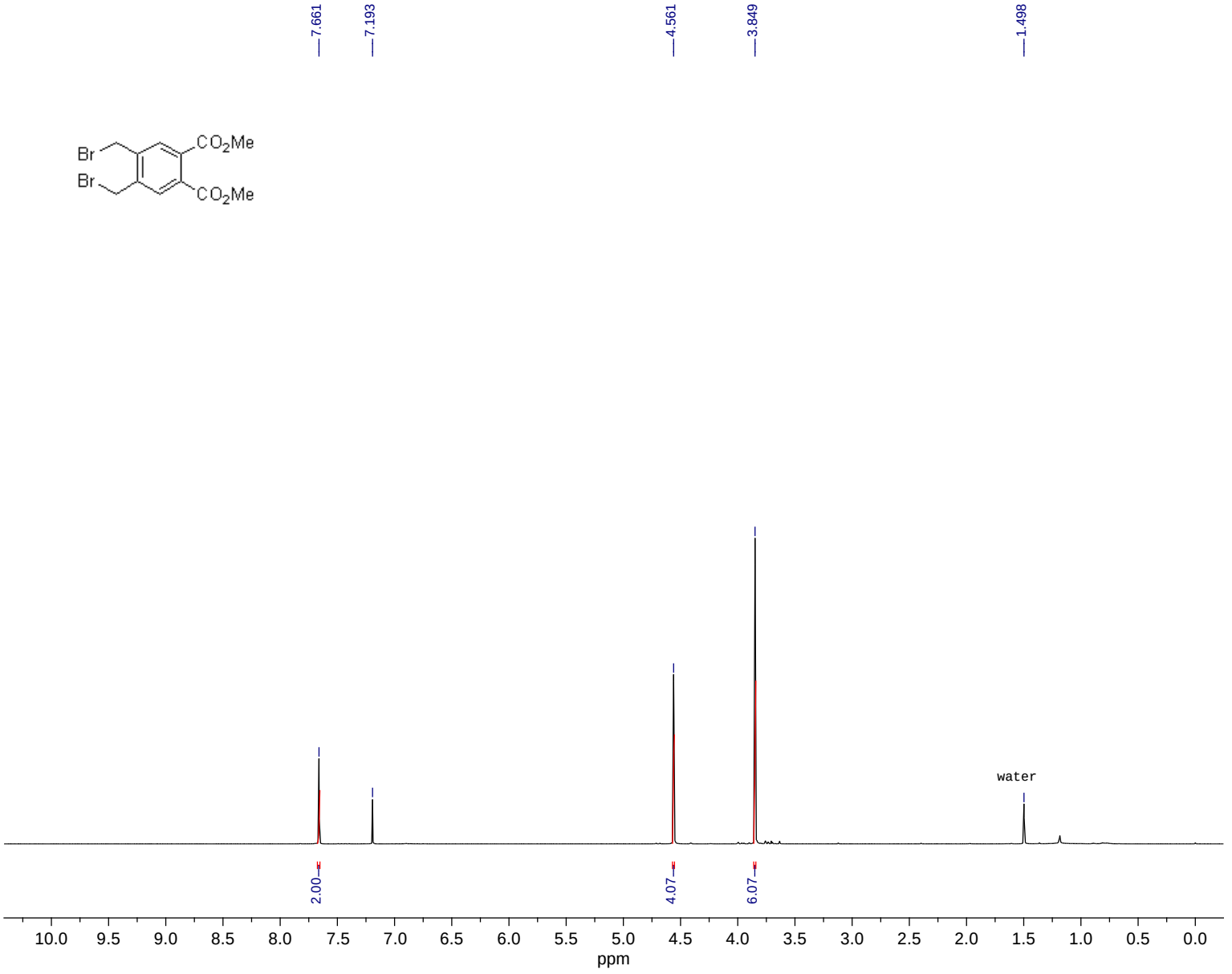
F2 - Acquisition Parameters
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    8843
DS                       4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010548 sec
RG                    2050
DW                  16.800 usec
DE                   6.50 usec
TE                  298.6 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.38 usec
PLW1          138.00000000 W
SFO1           125.7459776 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PLW2           15.41699982 W
PLW12           0.33258000 W
PLW13           0.21285000 W
SFO2           500.0350280 MHz

F2 - Processing parameters
SI                   32768
SF             125.7334050 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

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

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Current Data Parameters
NAME                  MSM
EXPNO                 213
PROCNO                  1

F2 - Acquisition Parameters
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                     144
DW                  48.400 usec
DE                   6.50 usec
TE                  297.5 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.75 usec
PLW1           15.41699982 W
SFO1           500.0361158 MHz

F2 - Processing parameters
SI                   65536
SF             500.0330736 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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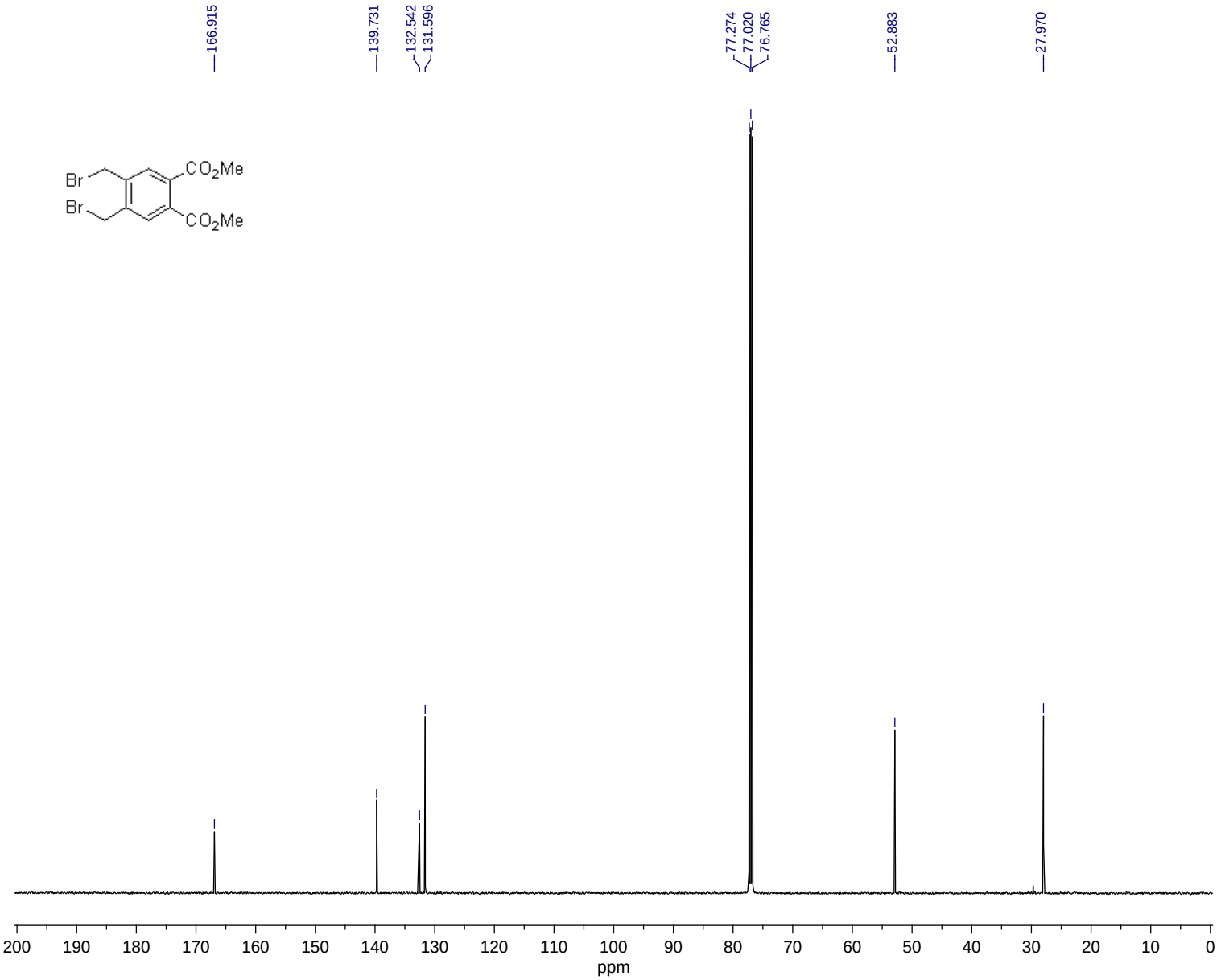
## $^{13}$C NMR spectrum of 10 (125 MHz, $CDCl_3$)

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Current Data Parameters
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EXPNO                 215
PROCNO                  1

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INSTRUM              spect
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PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    7168
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                  298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                   8.38 usec
PLW1         138.00000000 W
SFO1          125.7459776 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          15.41699982 W
PLW12          0.33258000 W
PLW13          0.21285000 W
SFO2          500.0350280 MHz

F2 - Processing parameters
SI                   32768
SF            125.7334050 MHz
WDW                     EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```
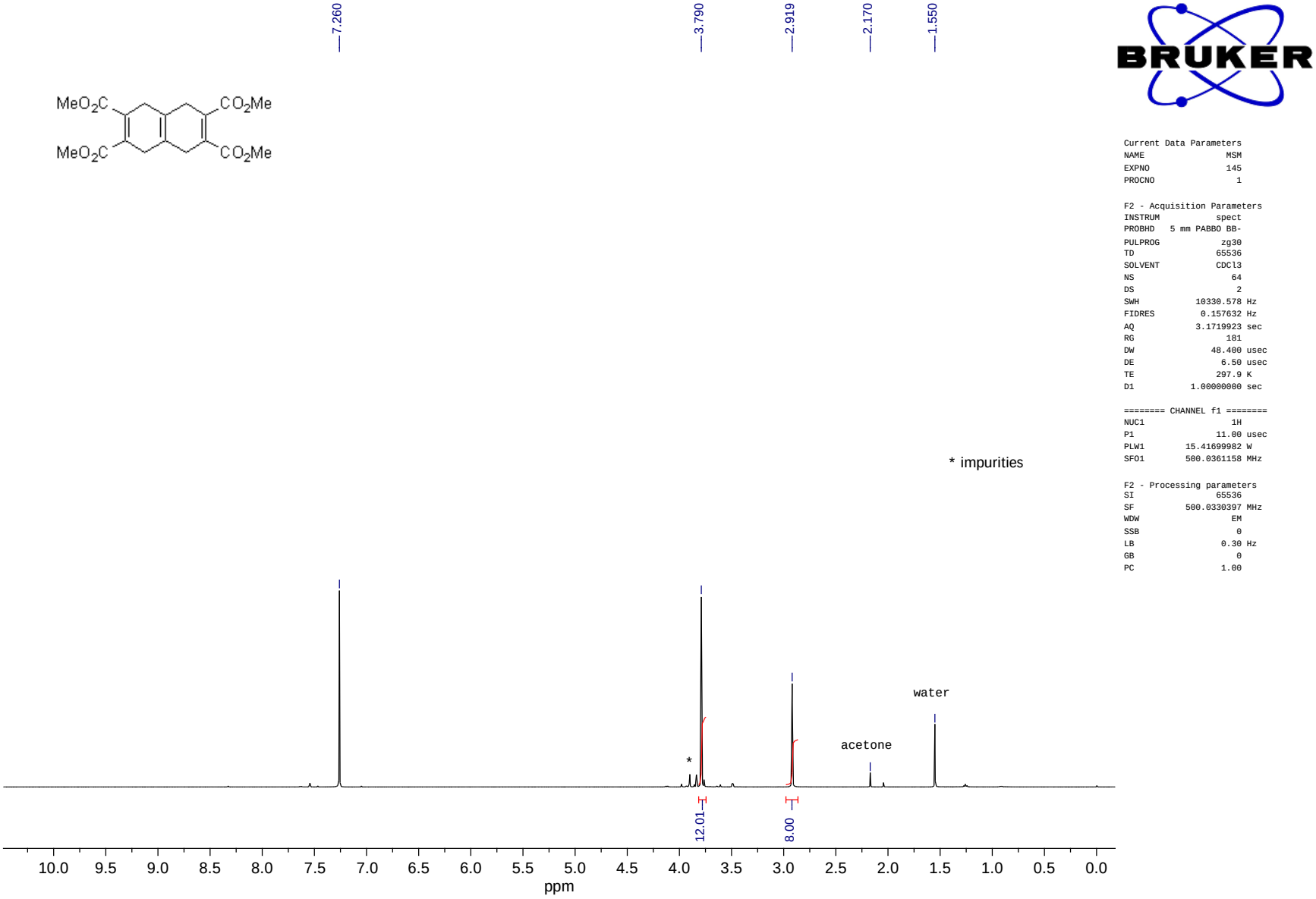

## $^1$H NMR spectrum of 12 (500 MHz, $CDCl_3$)

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Current Data Parameters
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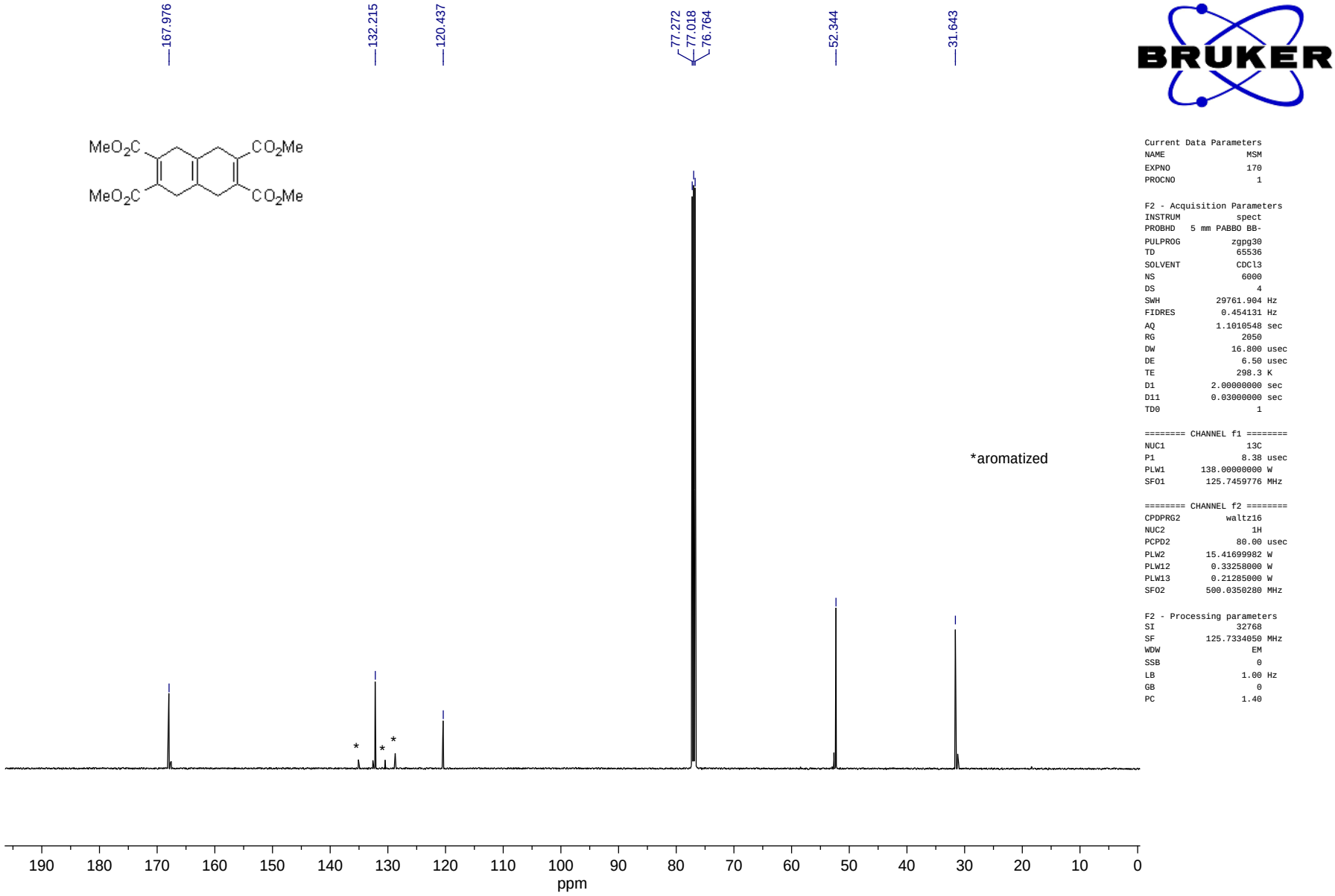
EXPNO                145
PROCNO                 1

F2 - Acquisition Parameters
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                   181
DW                48.400 usec
DE                 6.50 usec
TE                297.9 K
D1            1.00000000 sec

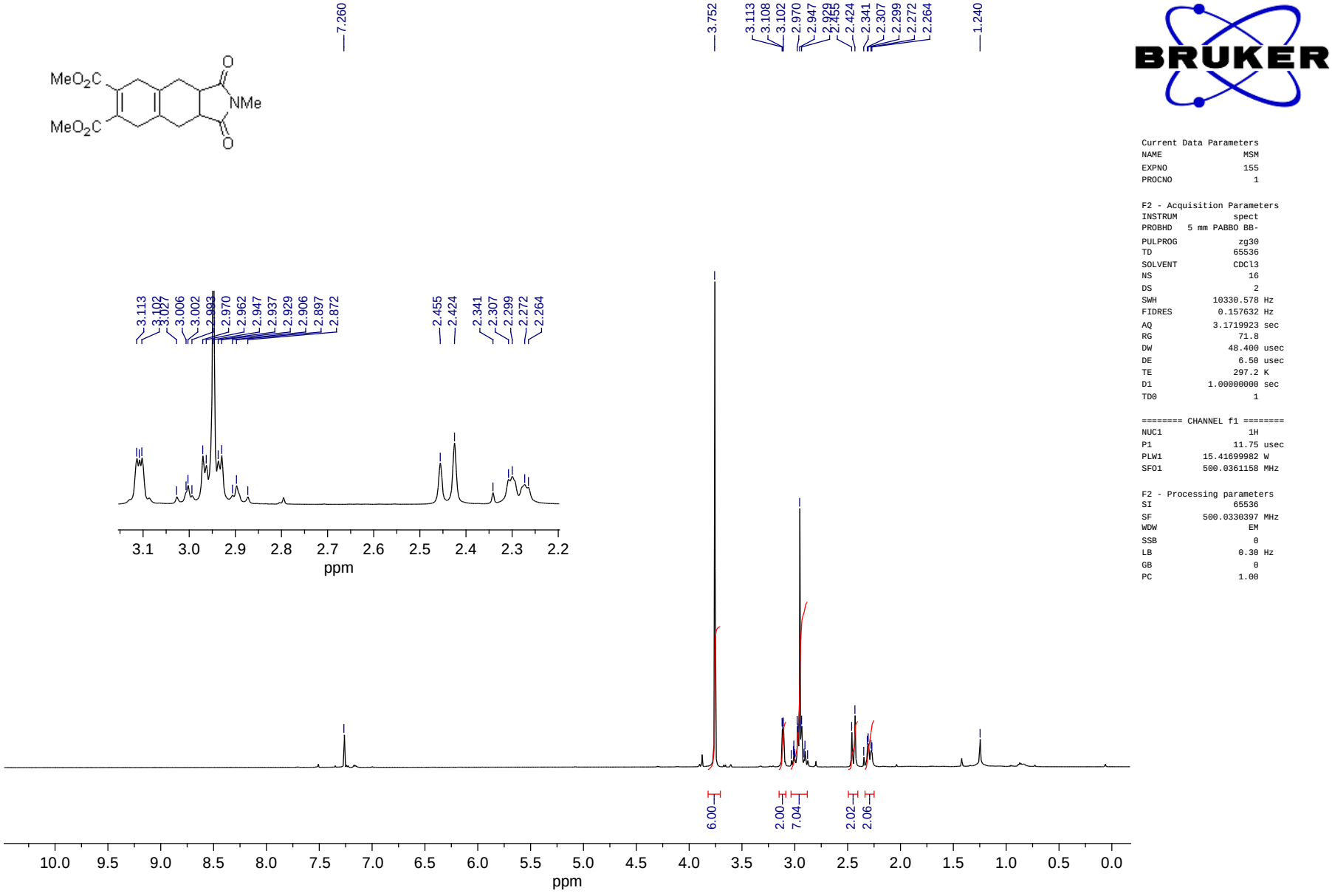
======== CHANNEL f1 ========
NUC1                 1H
P1                11.00 usec
PLW1         15.41699982 W
SFO1         500.0361158 MHz

F2 - Processing parameters
SI                 65536
SF           500.0330397 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

## $^{13}$C NMR spectrum of 12 (125 MHz, $CDCl_3$)



**$^1$H NMR spectrum of 16 (500 MHz, $CDCl_3$)**

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Current Data Parameters
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EXPNO                 155
PROCNO                  1

F2 - Acquisition Parameters
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                    71.8
DW                  48.400 usec
DE                   6.50 usec
TE                  297.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.75 usec
PLW1          15.41699982 W
SFO1          500.0361158 MHz

F2 - Processing parameters
SI                   65536
SF            500.0330397 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```
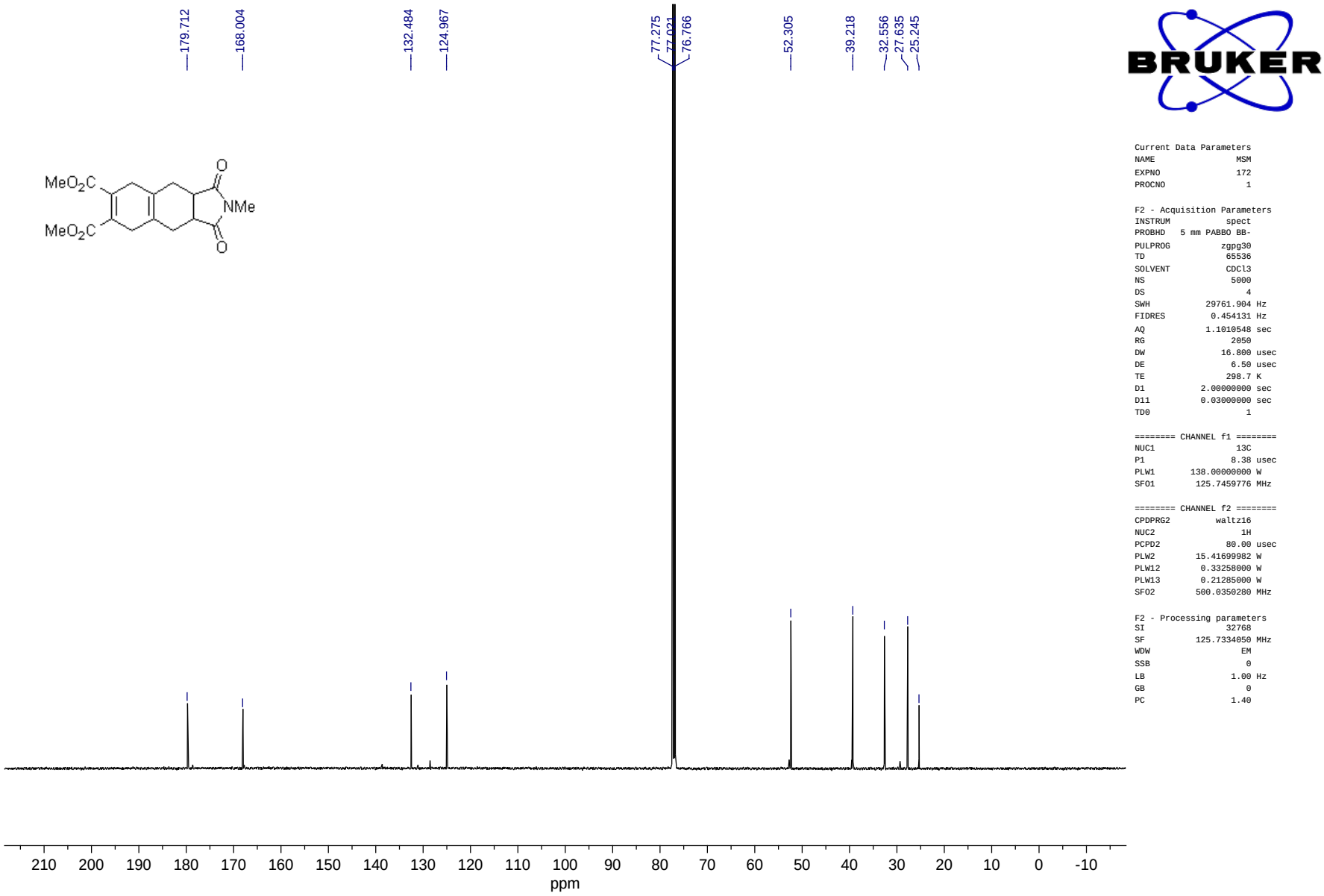

## $^{13}$C NMR spectrum of 16 (125 MHz, $CDCl_3$)

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Current Data Parameters
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EXPNO                 172
PROCNO                  1

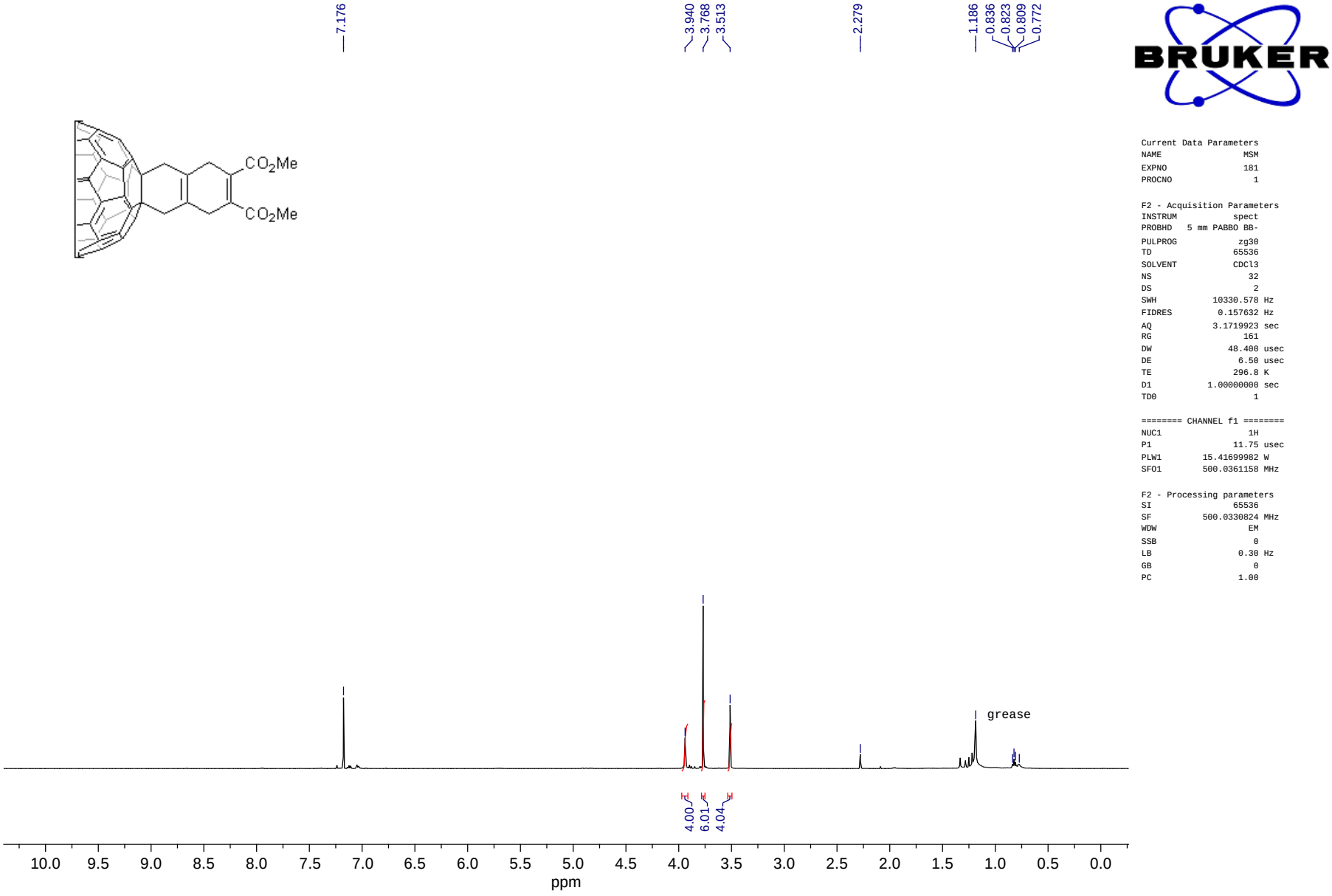
F2 - Acquisition Parameters
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    5000
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                    2050
DW                 16.800 usec
DE                  6.50 usec
TE                  298.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.38 usec
PLW1         138.00000000 W
SFO1          125.7459776 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          15.41699982 W
PLW12          0.33258000 W
PLW13          0.21285000 W
SFO2          500.0350280 MHz

F2 - Processing parameters
SI                   32768
SF             125.7334050 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

**$^1$H NMR spectrum of 14 (500 MHz, $CS_2$/$CDCl_3$, 1:1)**



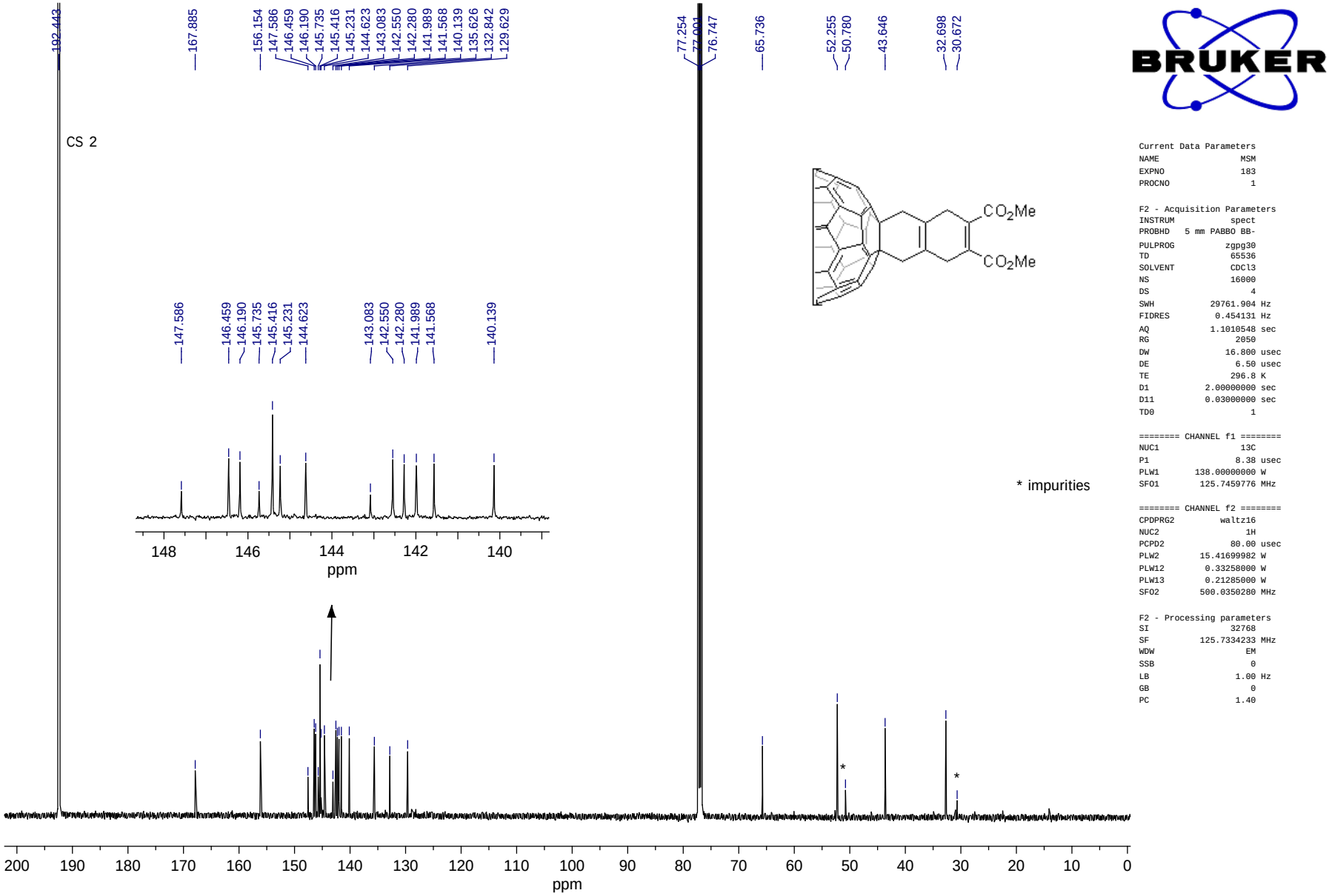

```
Current Data Parameters
NAME                  MSM
EXPNO                 181
PROCNO                  1

F2 - Acquisition Parameters
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                     161
DW                  48.400 usec
DE                   6.50 usec
TE                  296.8 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.75 usec
PLW1          15.41699982 W
SFO1          500.0361158 MHz

F2 - Processing parameters
SI                   65536
SF            500.0330824 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

**$^{13}$C NMR spectrum of 14 (125 MHz, $CS_2$/$CDCl_3$, 1:1)**

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Current Data Parameters
NAME                  MSM
EXPNO                 183
PROCNO                  1

F2 - Acquisition Parameters
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 16000
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                296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.38 usec
PLW1        138.00000000 W
SFO1         125.7459776 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         15.41699982 W
PLW12         0.33258000 W
PLW13         0.21285000 W
SFO2         500.0350280 MHz

F2 - Processing parameters
SI                 32768
SF           125.7334233 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```
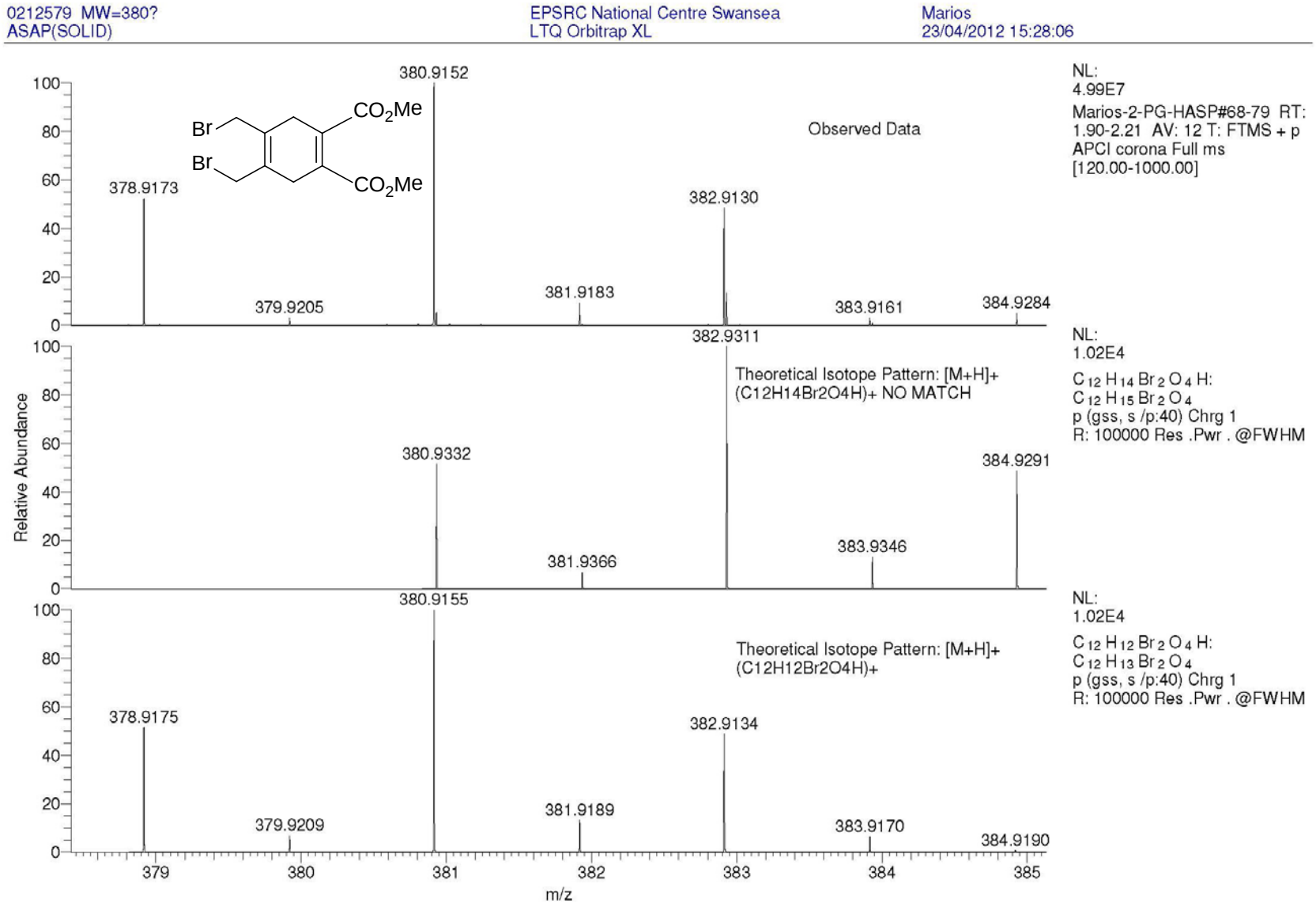
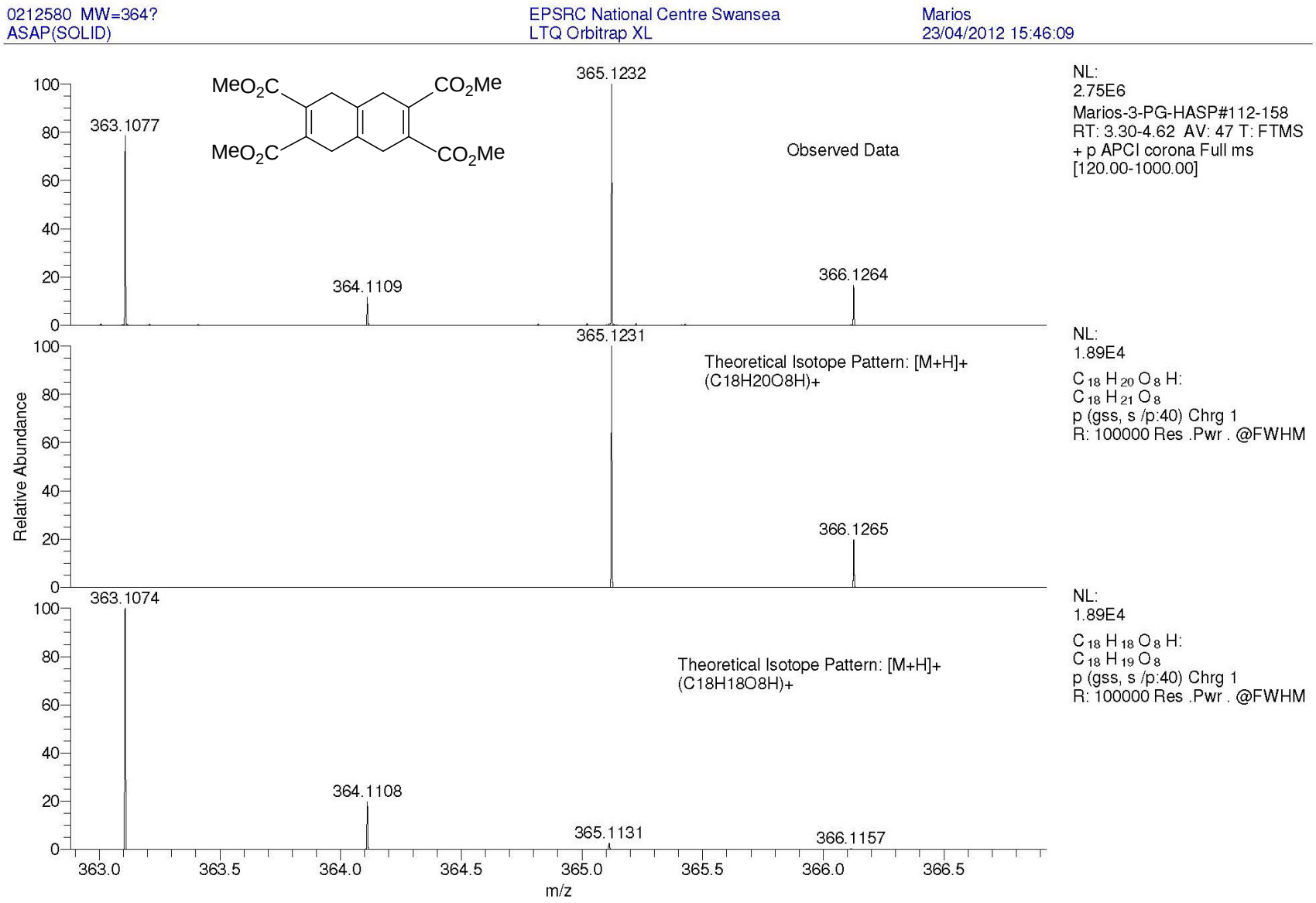

## 6. High resolution mass spectra (APCI+) of compounds 9, 12 and 16

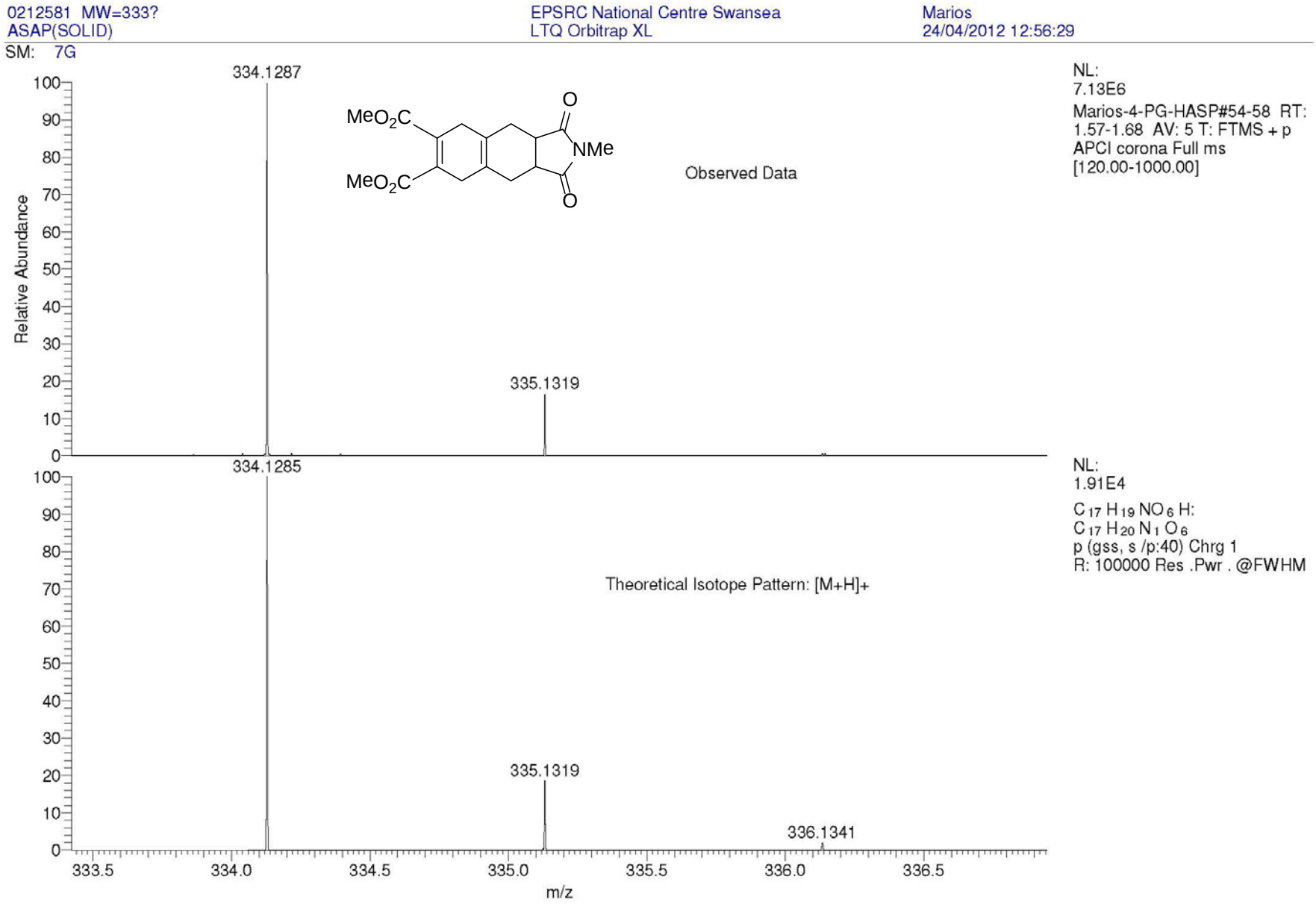
### Dimethyl 4,5-di(bromomethyl)-1,4-cyclohexadiene-1,2-dicarboxylate (9)



**Tetramethyl 1,4,5,8-tetrahydro-2,3,6,7-naphthalenetetracarboxylate (12)**

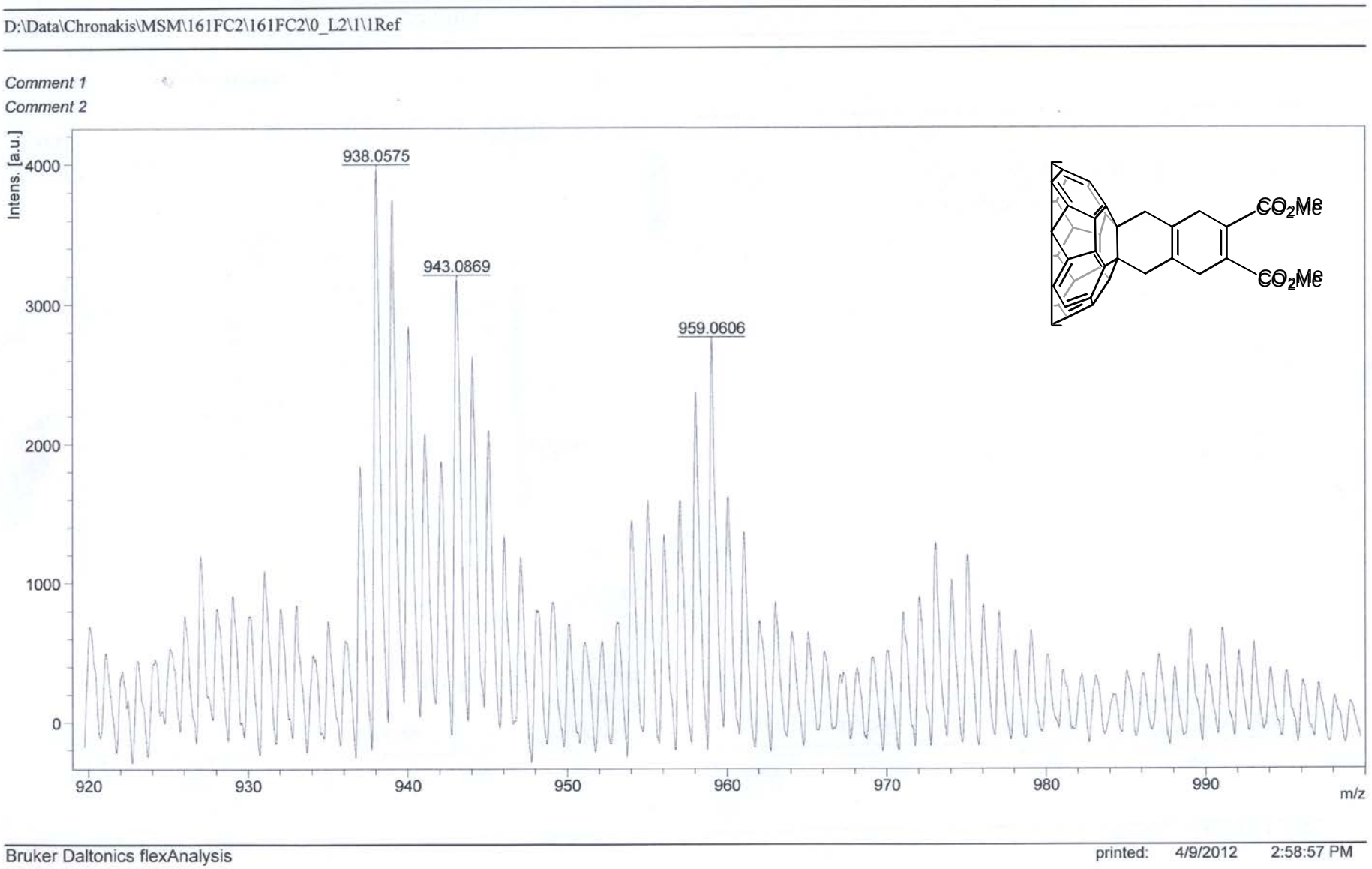


**Dimethyl 2-methyl-1,3-dioxo-2,3,3a,4,5,8,9,9a-octahydro-1*H*-benzo[*f*]isoindole-6,7-dicarboxylate (16)**

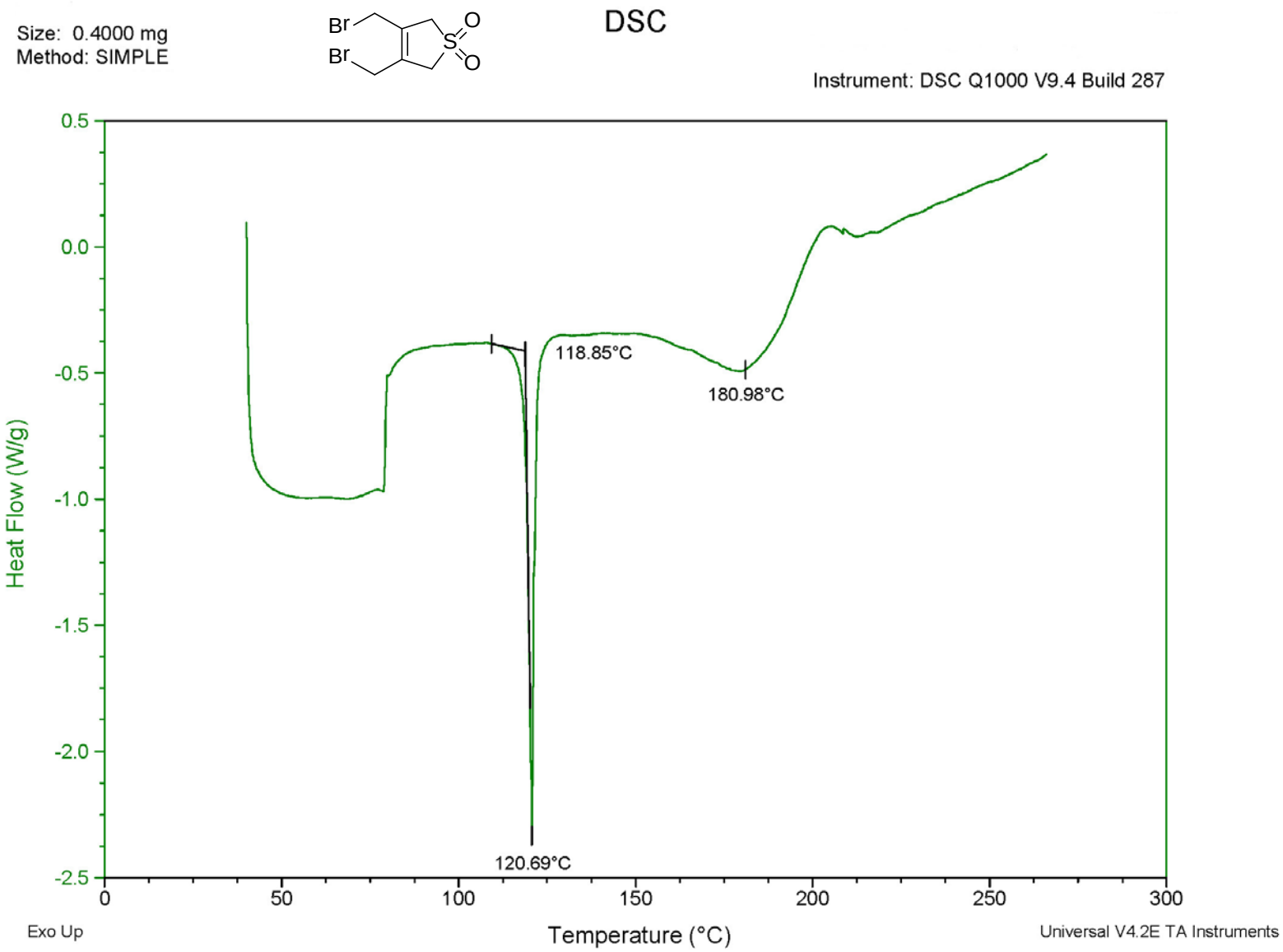


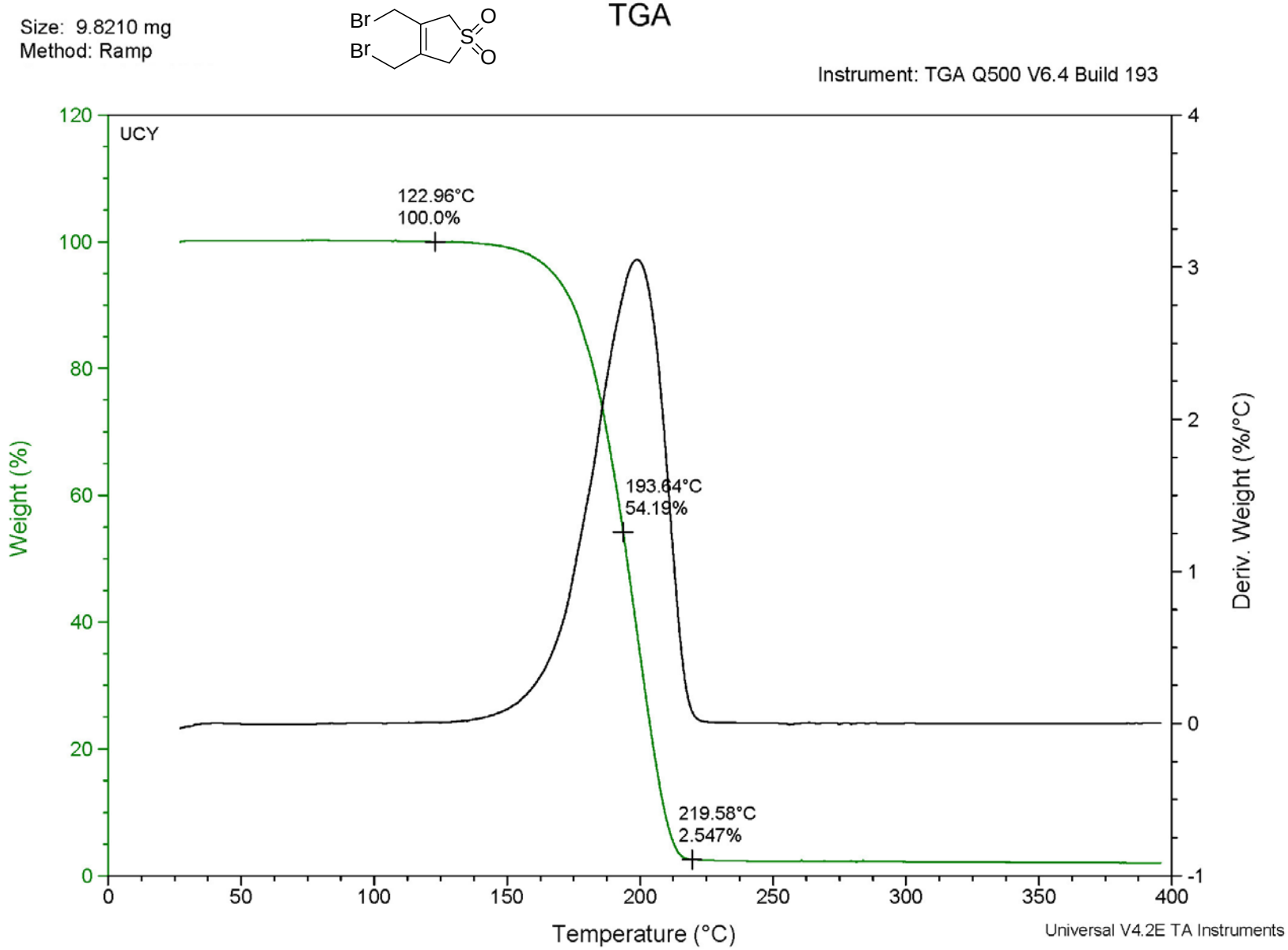
## 7. High resolution MALDI-TOF mass spectra of 14

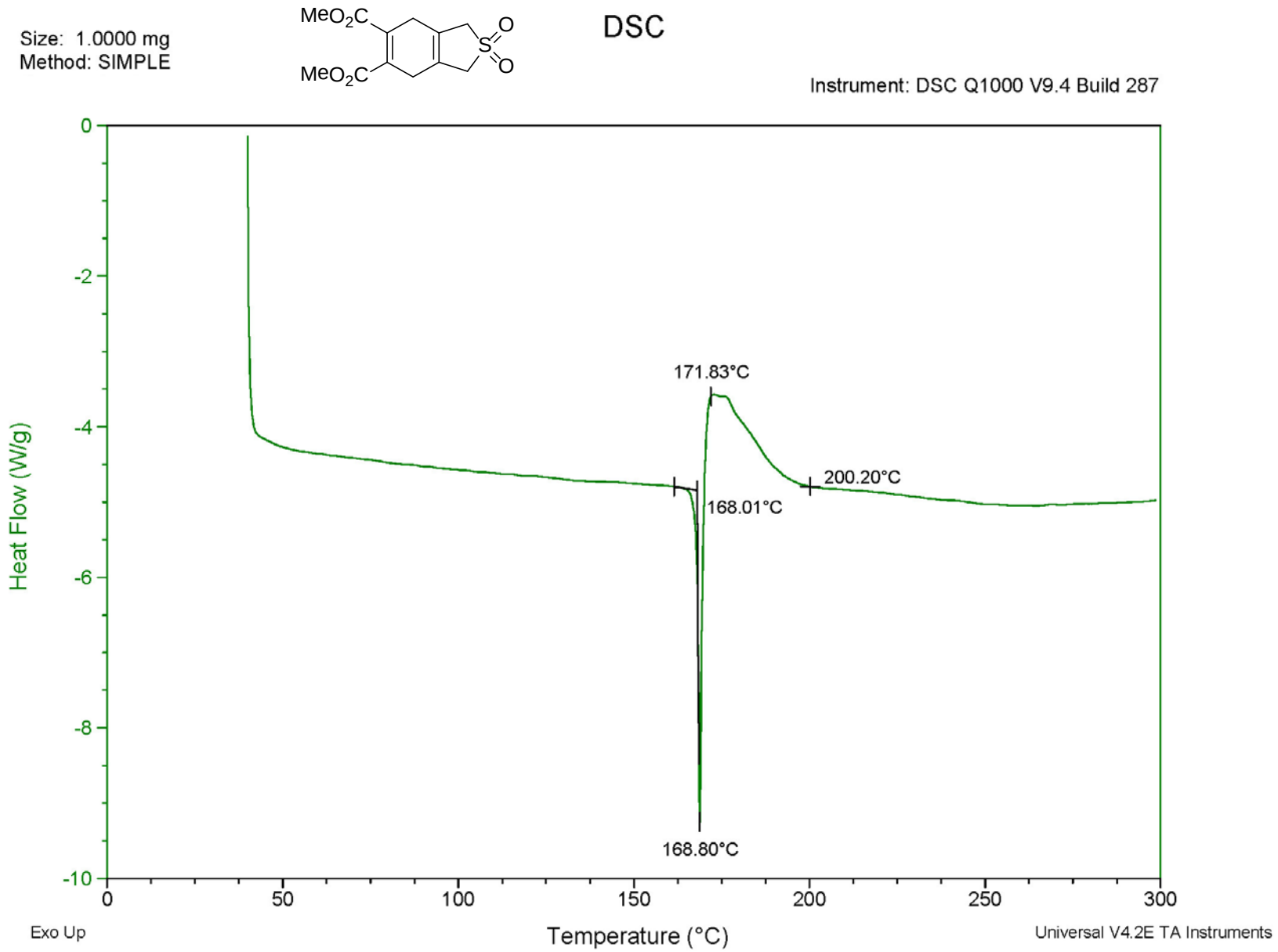
**Fullerene monoadduct 14 (negative mode, DCTB matrix)**

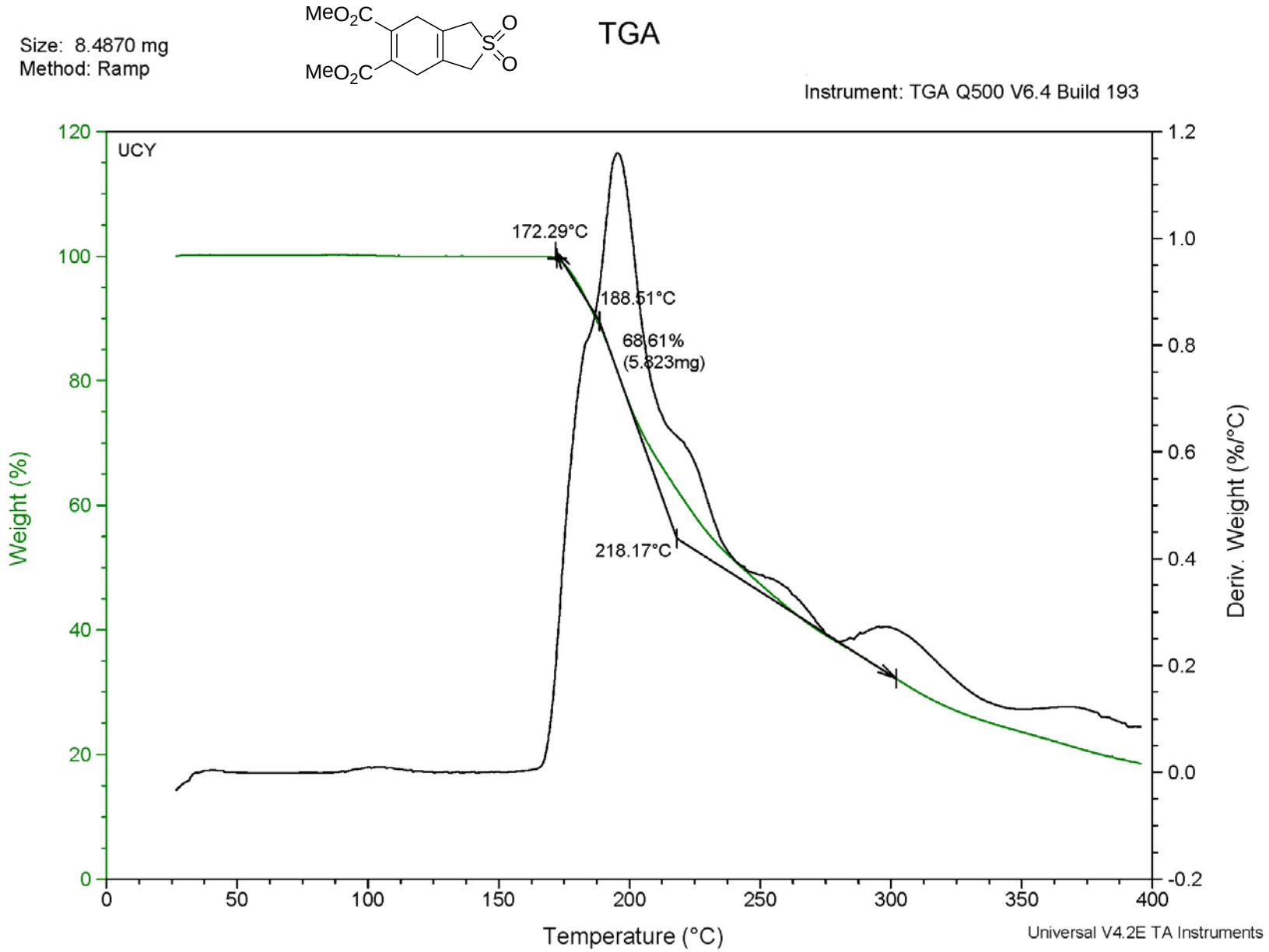


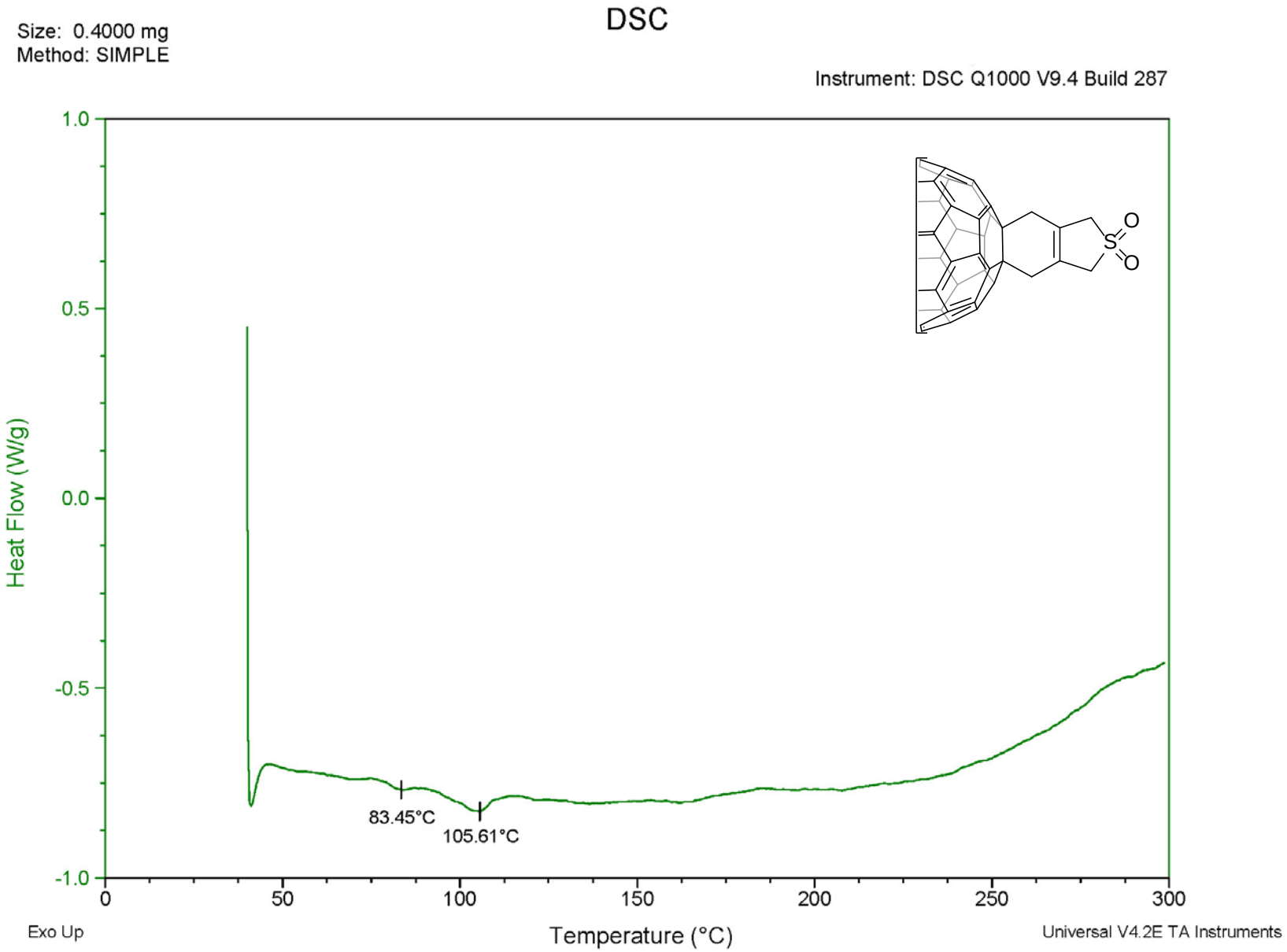
## 8. DSC and TGA data of 6, 11 and 17

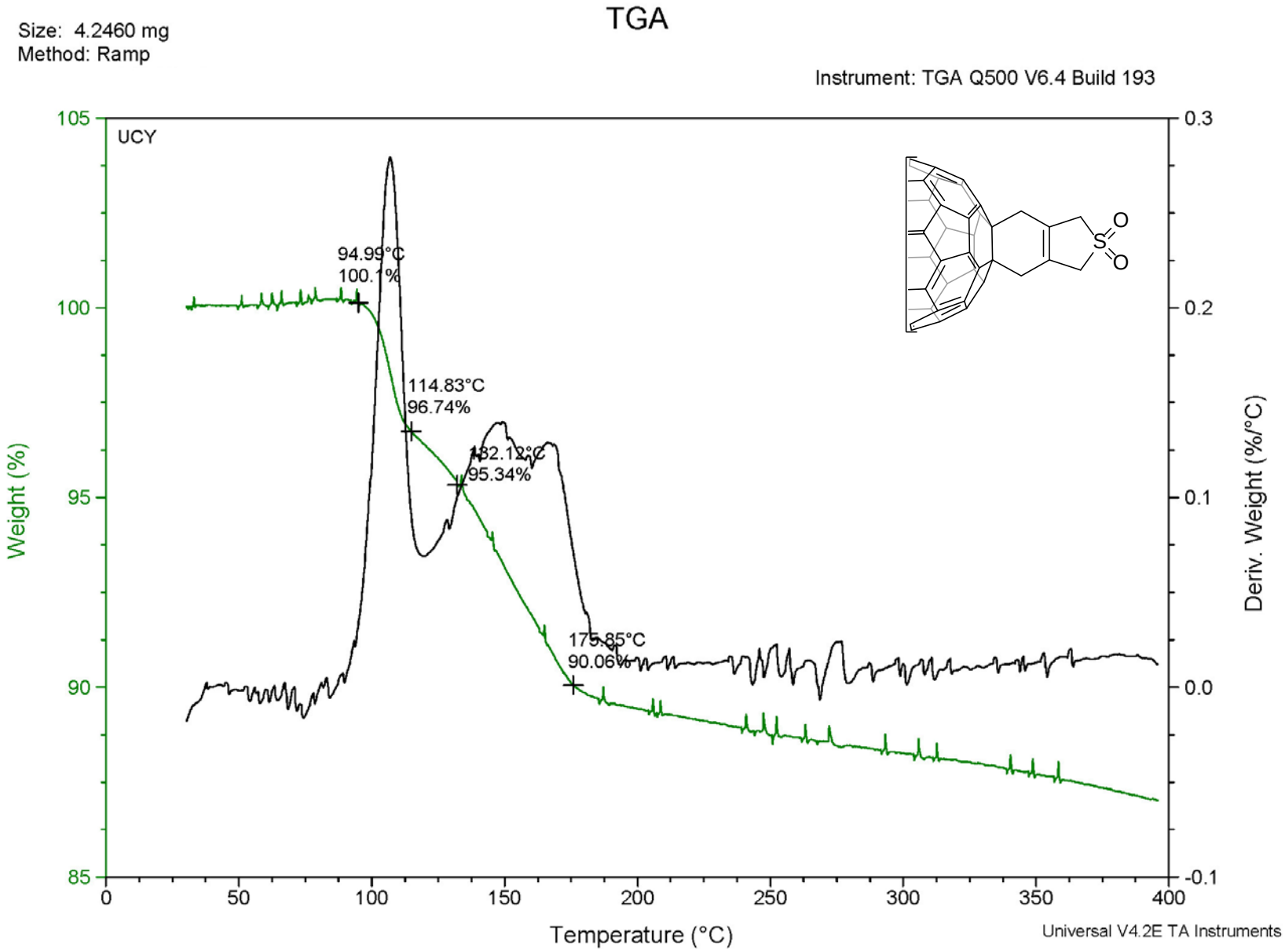












## 9. References

(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. Cryst.*, 1994, **27**, 435.

(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. Cryst.*, 1999, **32**, 837.

(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. Cryst.*, 2006, **39**, 453.