

Electronic Supplementary Information (ESI)

for:

**One-pot thermally chemocontrolled double Diels–Alder
strategies. A route to [4+2] functionalisation/[4+2] derivatization
of C₆₀**

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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-K α ($\lambda = 0.71073$ Å) or Cu-K α ($\lambda = 1.54184$ 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 SIR92² and refined on F² using full-matrix least squares using SHELXL97.³ Software packages used: CrysAlis CCD¹ for data collection, CrysAlis RED¹ for cell refinement and data reduction, WINGX for geometric calculations⁴ and MERCURY⁵ 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
<i>a</i> /Å	5.2551(4)	13.3575(6)
<i>b</i> /Å	12.1219(7)	15.2746(8)
<i>c</i> /Å	14.271(2)	7.8745(4)
<i>α</i> /°	109.989(6)	90.00
<i>β</i> /°	95.075(7)	98.222(4)
<i>γ</i> /°	94.816(5)	90.00
<i>V</i> /Å ³	844.7(2)	1590.2(2)
Radiation type	MoKα	CuKα
Temperature/K	100(2)	100(2)
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	2
<i>μ</i> /mm ⁻¹	0.114	0.890
Total/ independent reflections	2969/2441	2836/2229
<i>R</i> _{int}	0.0222	0.0280
<i>R</i> ₁ ^a / <i>wR</i> (<i>F</i> ²) ^b (<i>I</i> > 2σ(<i>I</i>))	0.0436/0.1197	0.0452/0.1177
GOF	1.053	0.946

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

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

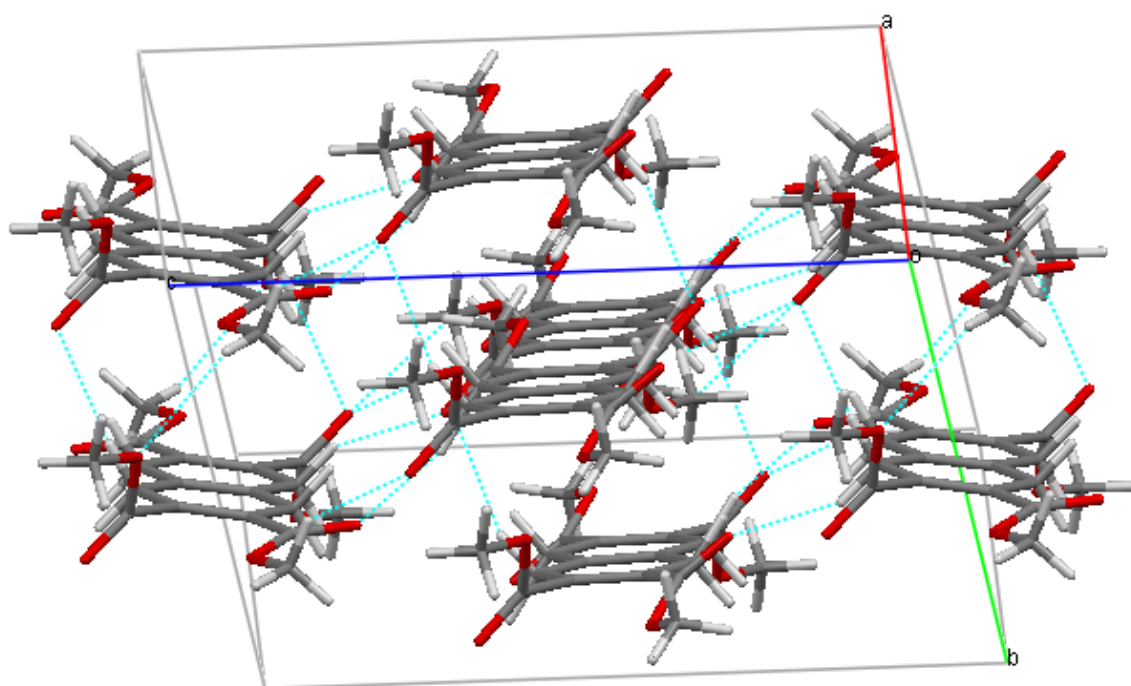


Figure S1

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

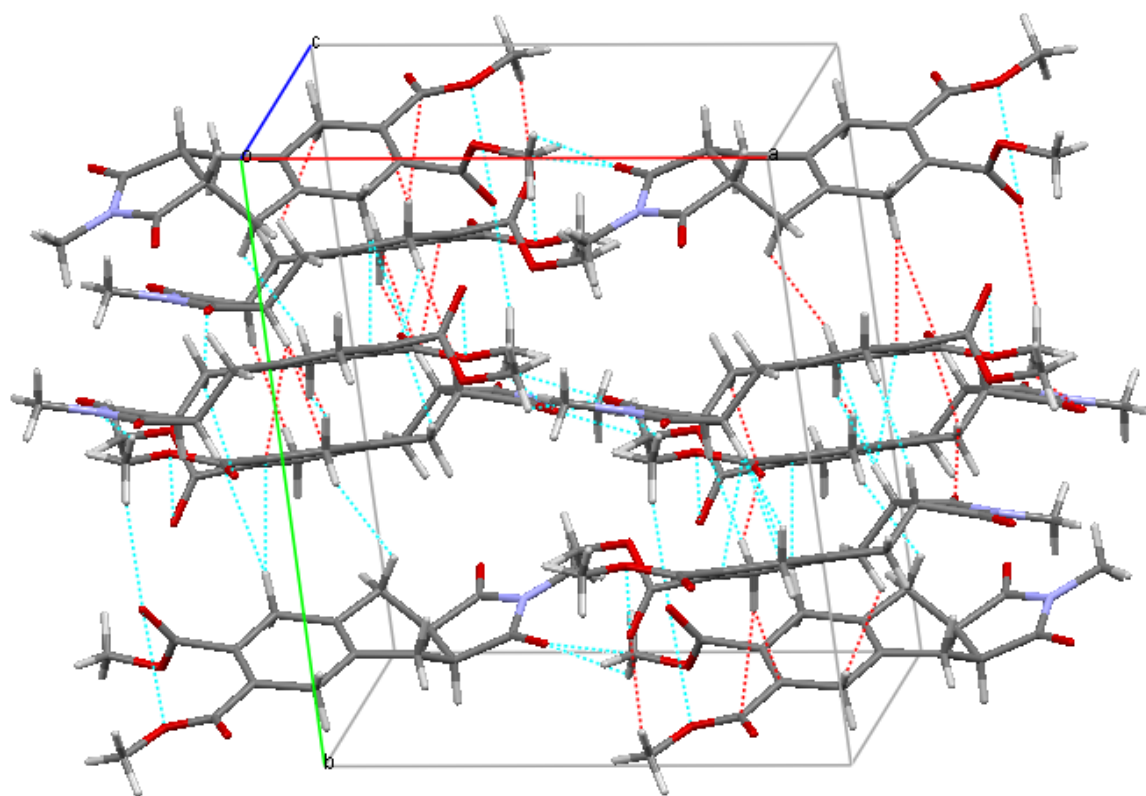
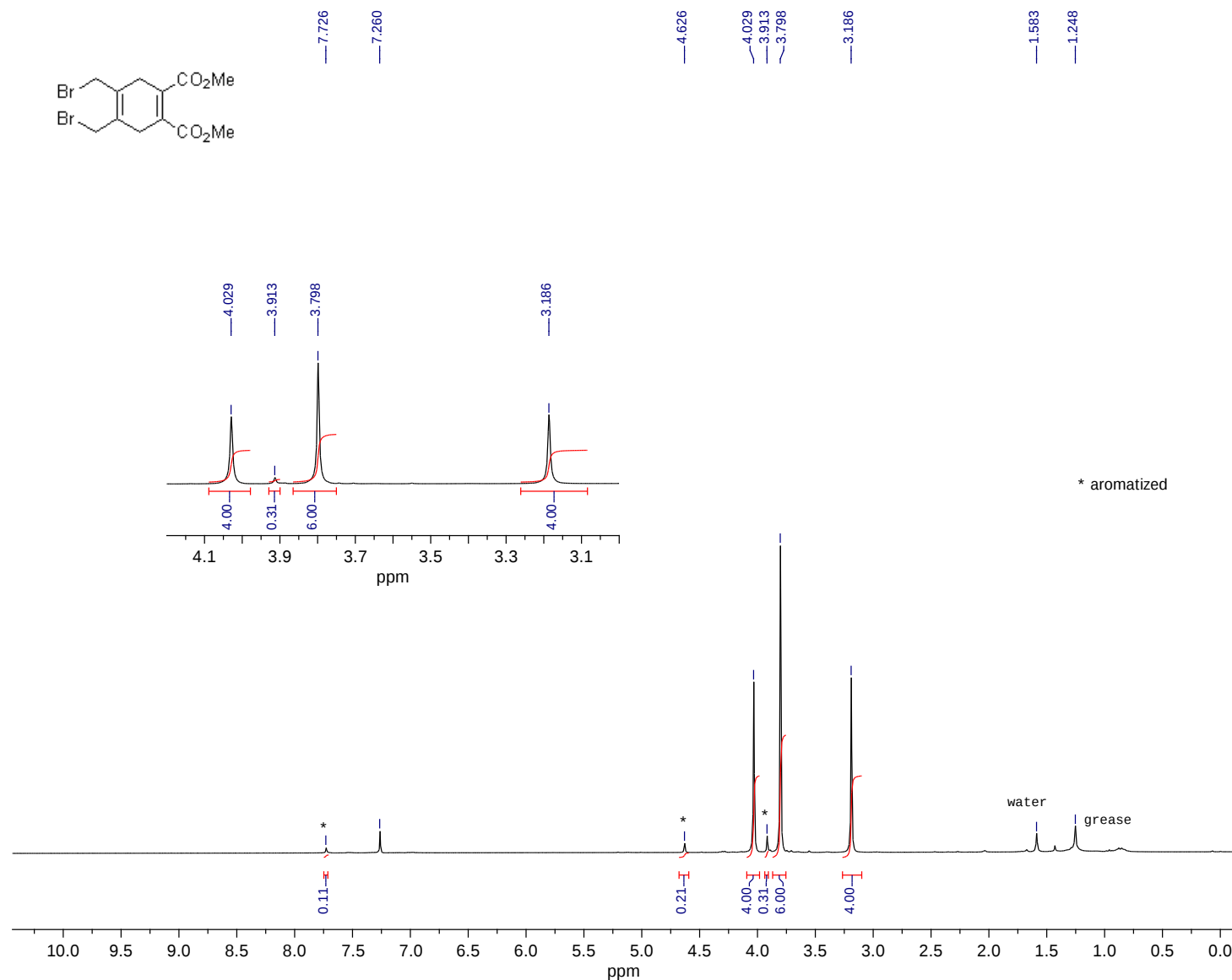


Figure S2

5. ¹H NMR and ¹³C NMR spectra of compounds 9, 10, 12, 16 and 14

¹H NMR spectrum of 9 (300 MHz, CDCl₃)



Current Data Parameters
NAME MSM
EXPNO 322
PROCNO 1

F2 - Acquisition Parameters
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 28
DS 2
SWH 6172.839 Hz
FIDRES 0.094198 Hz
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RG 362
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DE 9.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1

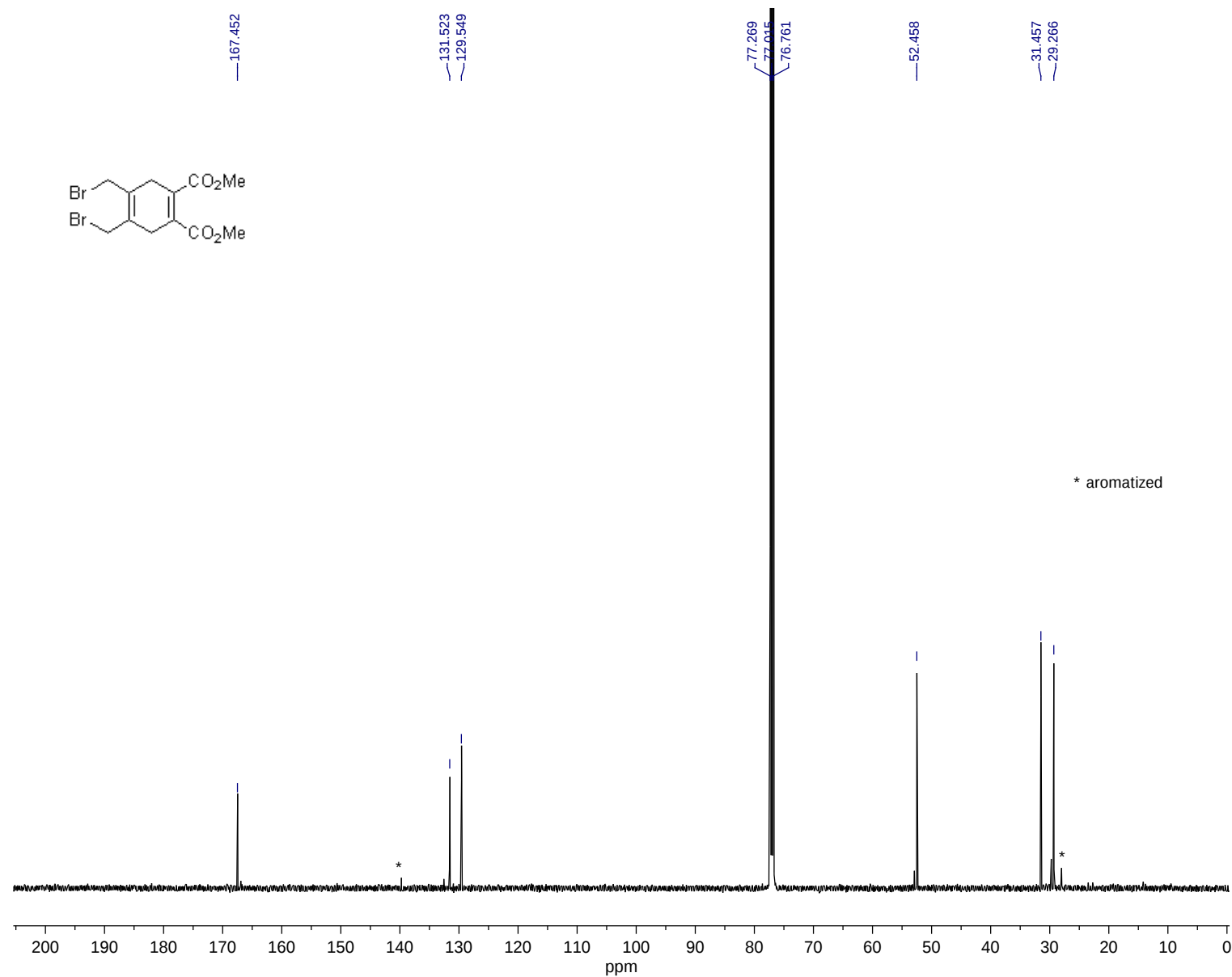
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PL1 3.00 dB
SF01 300.1318534 MHz

F1 - Acquisition parameters
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SF01 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined

F2 - Processing parameters
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SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
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GB 0.1

¹³C NMR spectrum of 9 (125 MHz, CDCl₃)



Current Data Parameters
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PROCNO 1

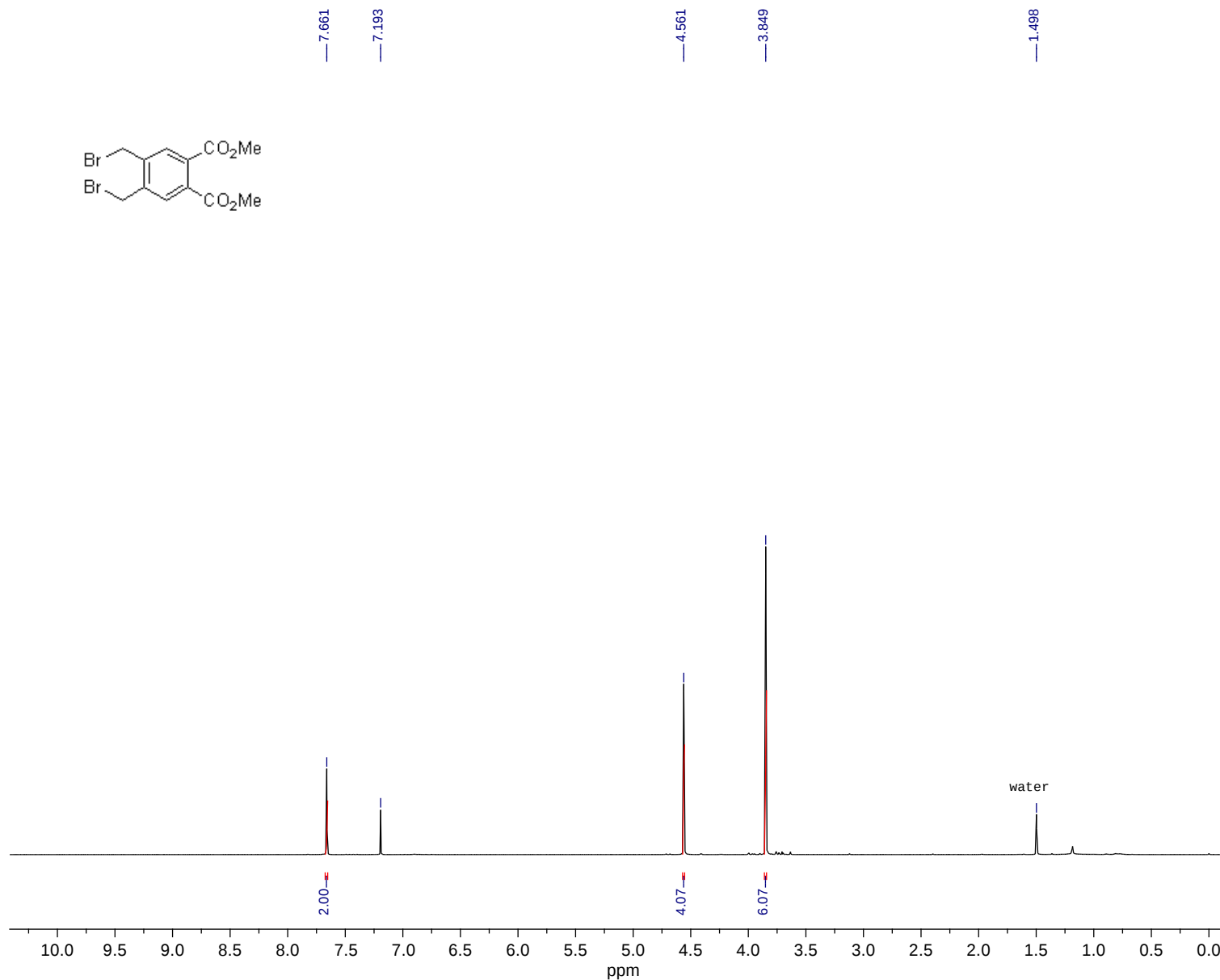
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TD 65536
SOLVENT CDCl3
NS 8843
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.38 usec
PLW1 138.00000000 W
SF01 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
SF02 500.0350280 MHz

F2 - Processing parameters
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹H NMR spectrum of 10 (500 MHz, CDCl₃)



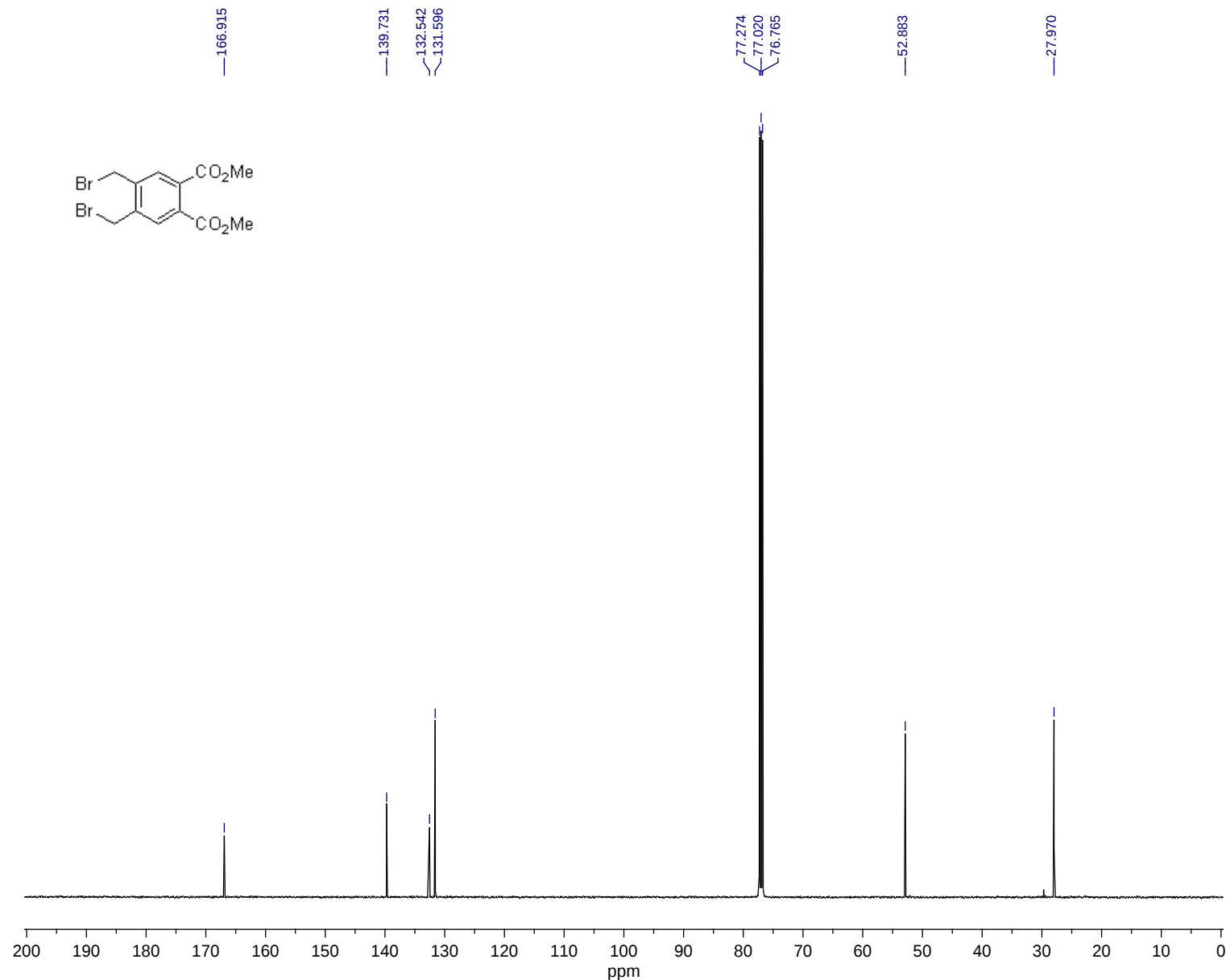
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 144
DW 48.400 usec
DE 6.50 usec
TE 297.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W
SF01 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

¹³C NMR spectrum of 10 (125 MHz, CDCl₃)



Current Data Parameters

NAME	MSM
EXPNO	215
PROCNO	1

F2 - Acquisition Parameters

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	1.1010540 sec
RG	2050
DW	16.800 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
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===== CHANNEL f1 =====

NUC1	13C
P1	8.38 usec
PLW1	138.00000000 W
SF01	125.7459776 MHz

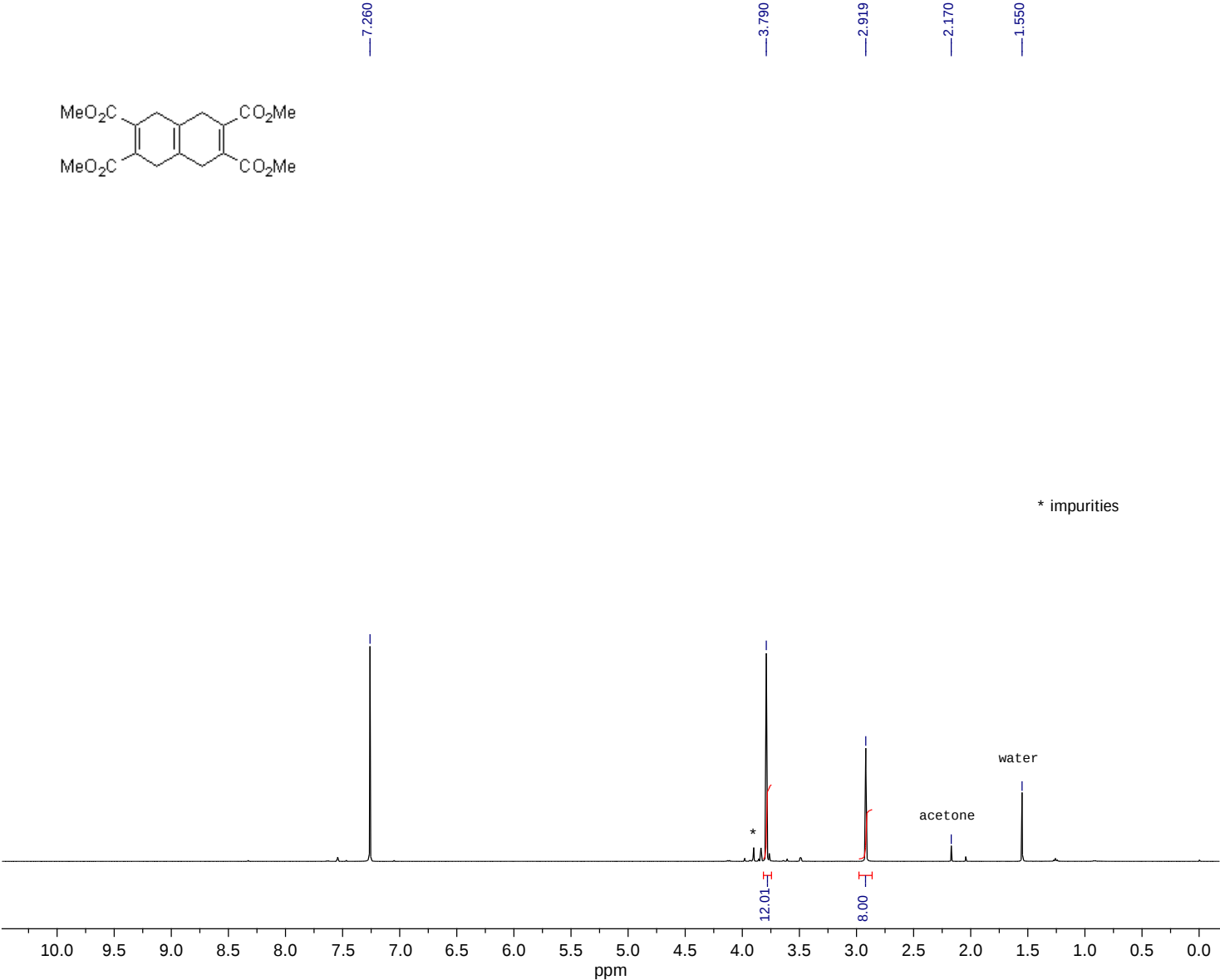
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CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PLW2	15.41699982 W
PLW12	0.33258000 W
PLW13	0.21285000 W
SF02	500.0350280 MHz

F2 - Processing parameters

SI	32768
SF	125.7334050 MHz
WDW	EM
SSB	0
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GB	0
PC	1.40

¹H NMR spectrum of 12 (500 MHz, CDCl₃)



Current Data Parameters
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PROCNO 1

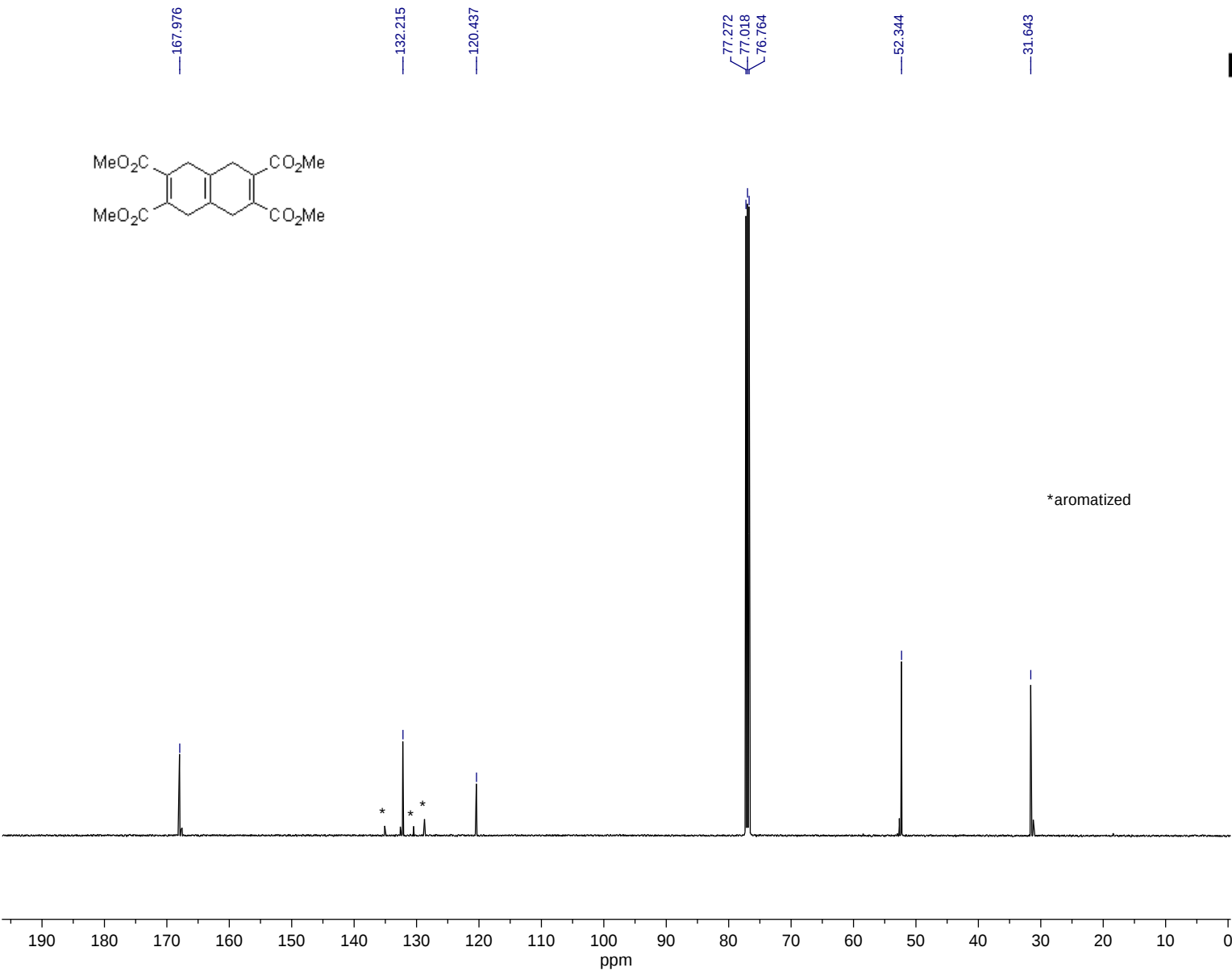
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INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SMH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 181
DW 48.400 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 11.00 usec
PLW1 15.41699982 W
SF01 500.0361158 MHz

F2 - Processing parameters
SI 65536
SF 500.0339397 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

* impurities

¹³C NMR spectrum of 12 (125 MHz, CDCl₃)



Current Data Parameters

NAME	MSM
EXPNO	170
PROCNO	1

F2 - Acquisition Parameters

INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	6000
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	298.3 K
D1	2.0000000 sec
D11	0.0300000 sec
TD0	1

===== CHANNEL f1 =====

NUC1	13C
P1	8.38 usec
PLW1	138.0000000 W
SFO1	125.7459776 MHz

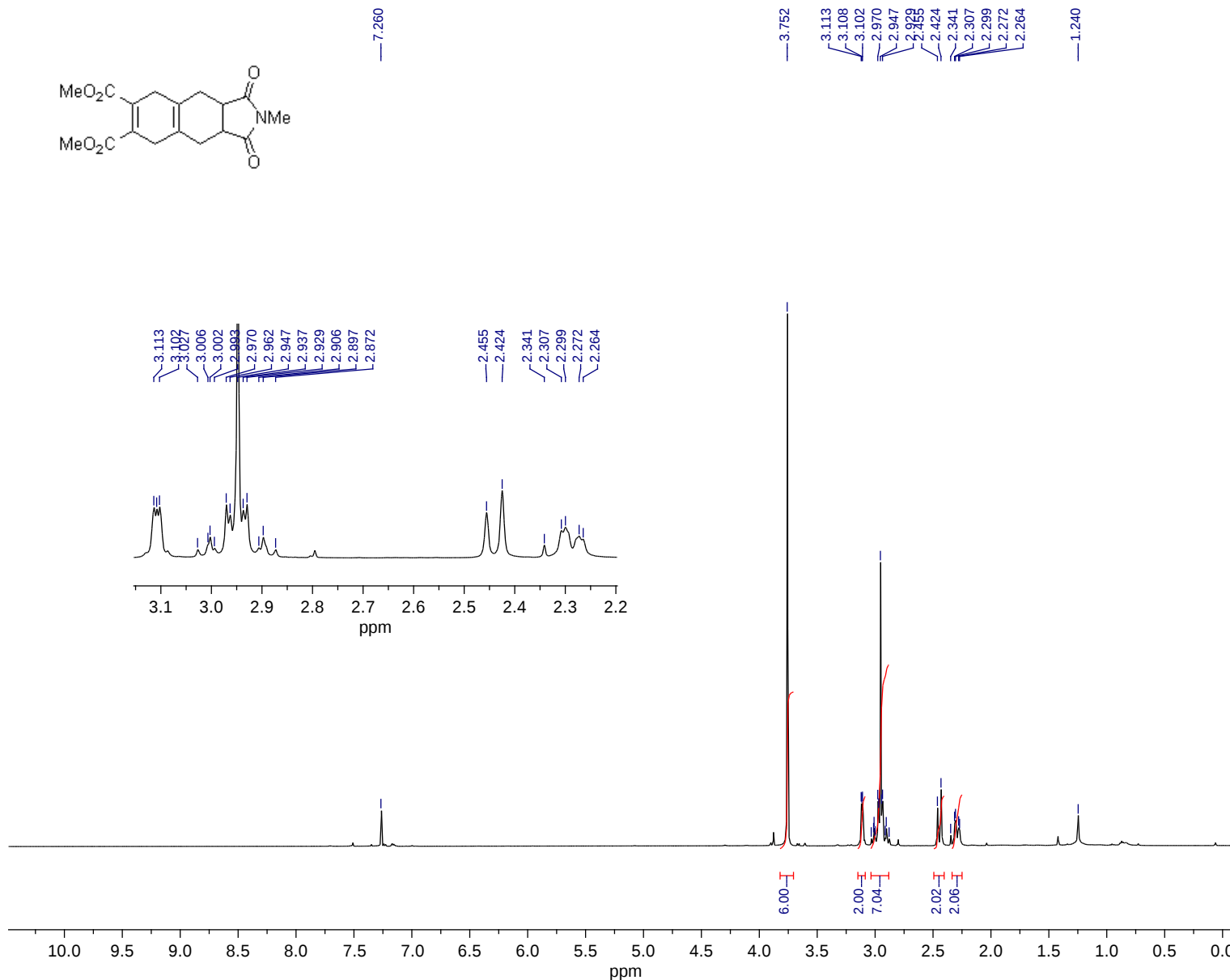
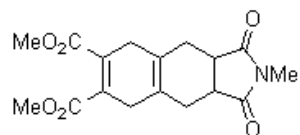
===== CHANNEL f2 =====

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PLW2	15.41699082 W
PLW12	0.33250000 W
PLW13	0.21285000 W
SFO2	500.0350280 MHz

F2 - Processing parameters

SI	32768
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WDW	EM
SSB	0
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GB	0
PC	1.40

¹H NMR spectrum of 16 (500 MHz, CDCl₃)



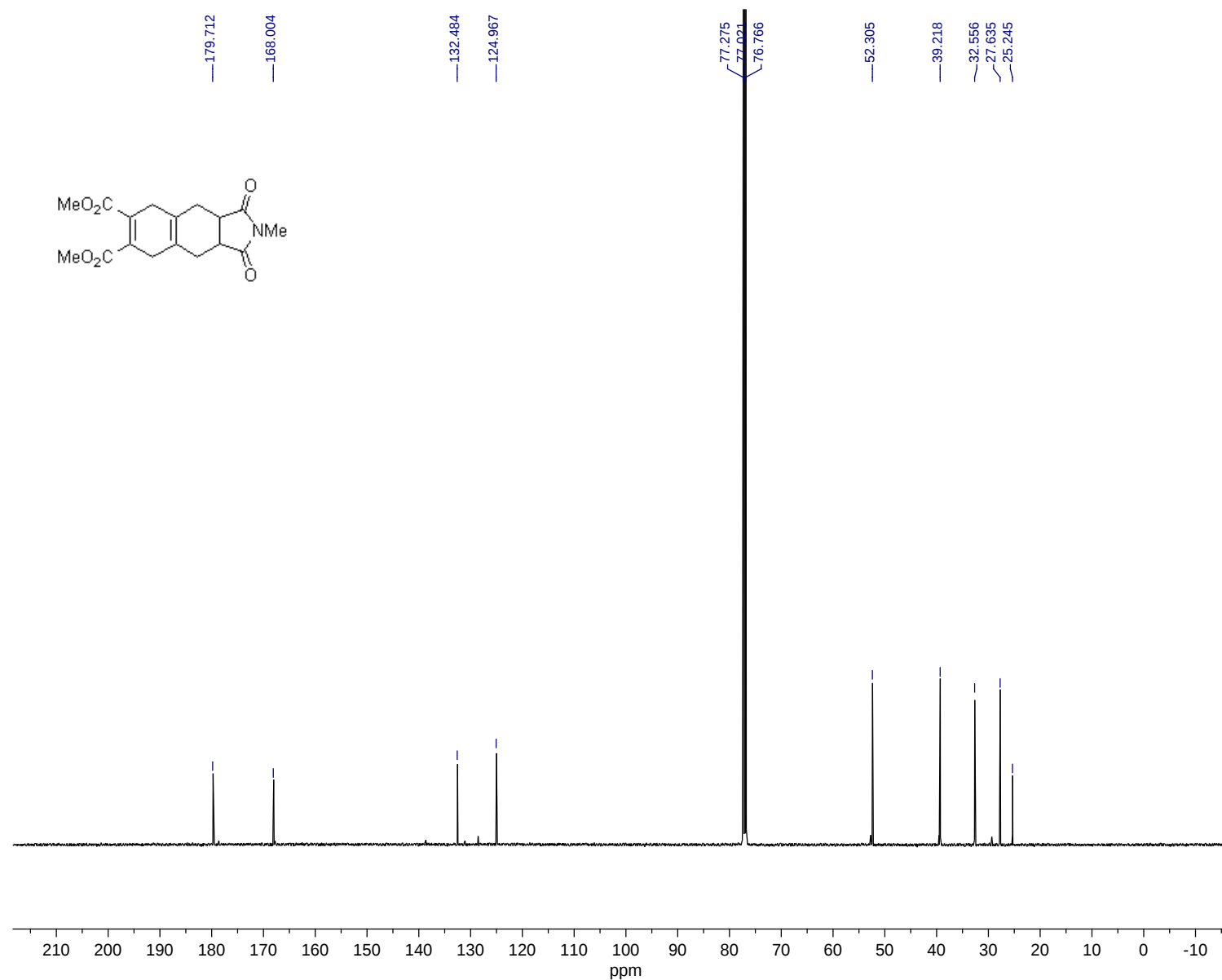
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PROCNO 1

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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
T00 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W
SF01 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

¹³C NMR spectrum of 16 (125 MHz, CDCl₃)



Current Data Parameters
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EXPNO 172
PROCNO 1

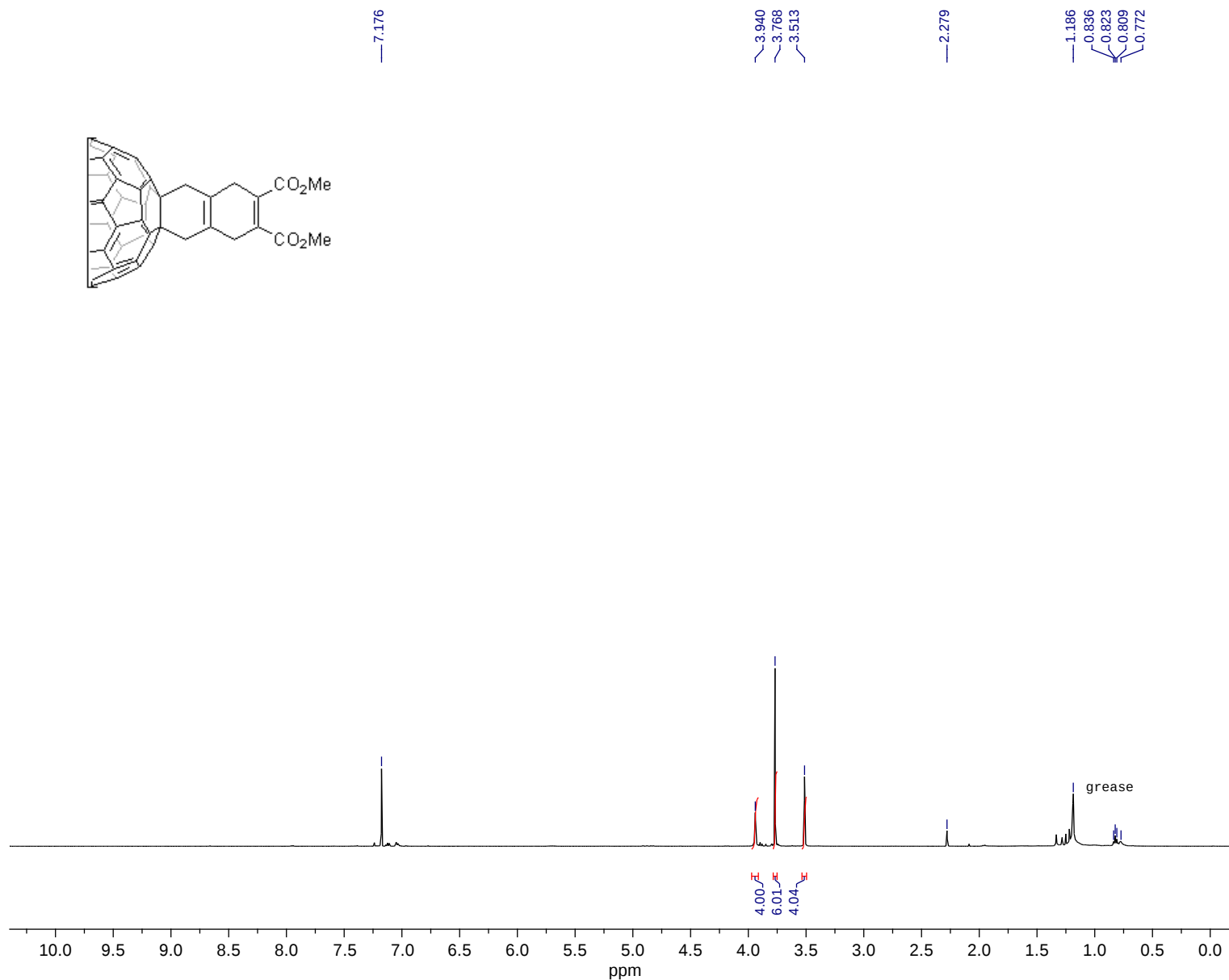
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TD 65536
SOLVENT CDCl3
NS 5000
DS 4
SWH 29761.984 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.38 usec
PLW1 138.00000000 W
SF01 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
SF02 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

¹H NMR spectrum of 14 (500 MHz, CS₂/CDCl₃, 1:1)



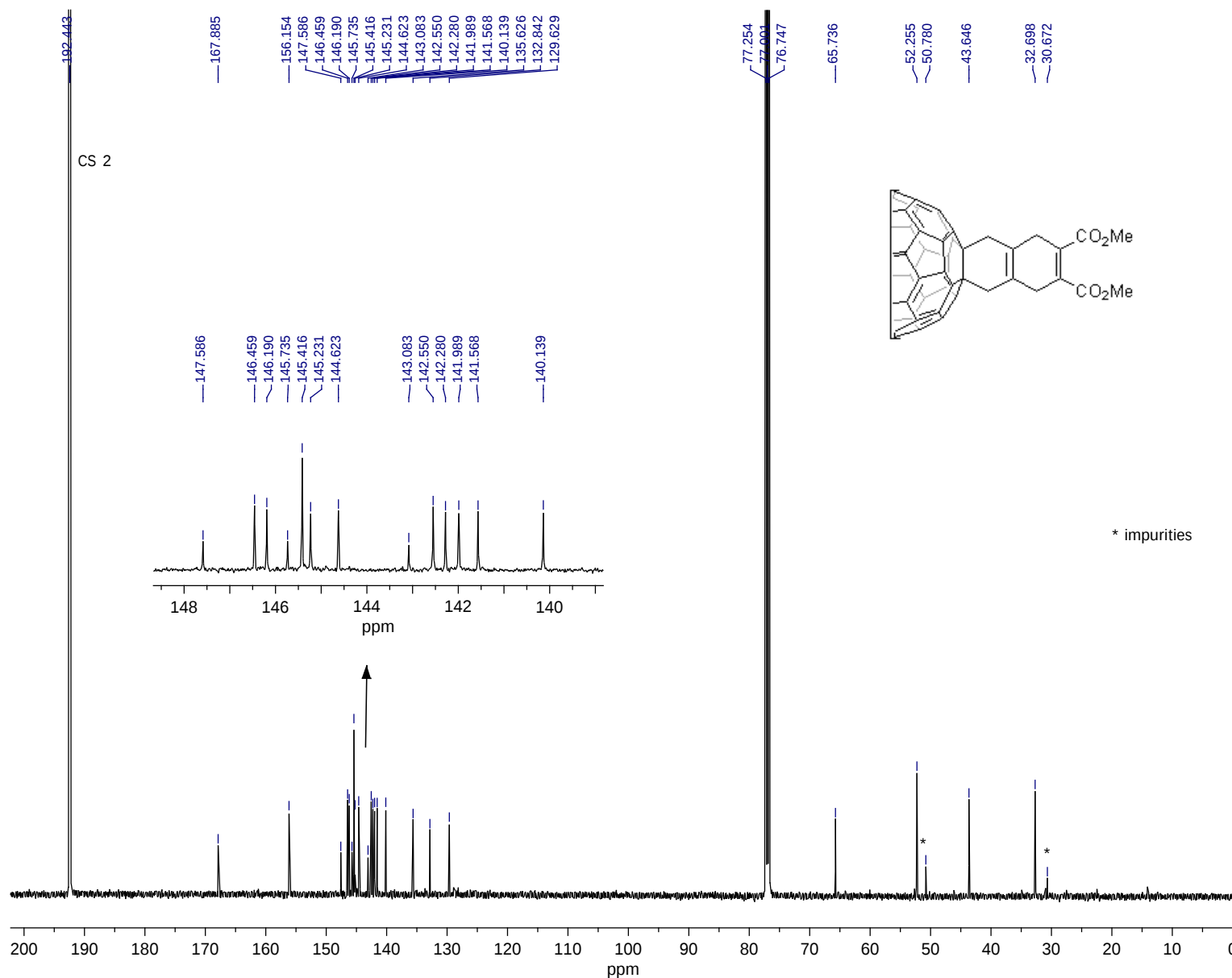
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EXPNO 181
PROCNO 1

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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
T00 1

===== CHANNEL f1 =====
NUC1 1H
P1 11.75 usec
PLW1 15.41699982 W
SF01 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

¹³C NMR spectrum of 14 (125 MHz, CS₂/CDCl₃, 1:1)



Current Data Parameters
NAME MSM
EXPNO 183
PROCNO 1

F2 - Acquisition Parameters
INSTRUM spect
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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 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.38 usec
PLW1 138.0000000 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
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SSB 0
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GB 0
PC 1.40

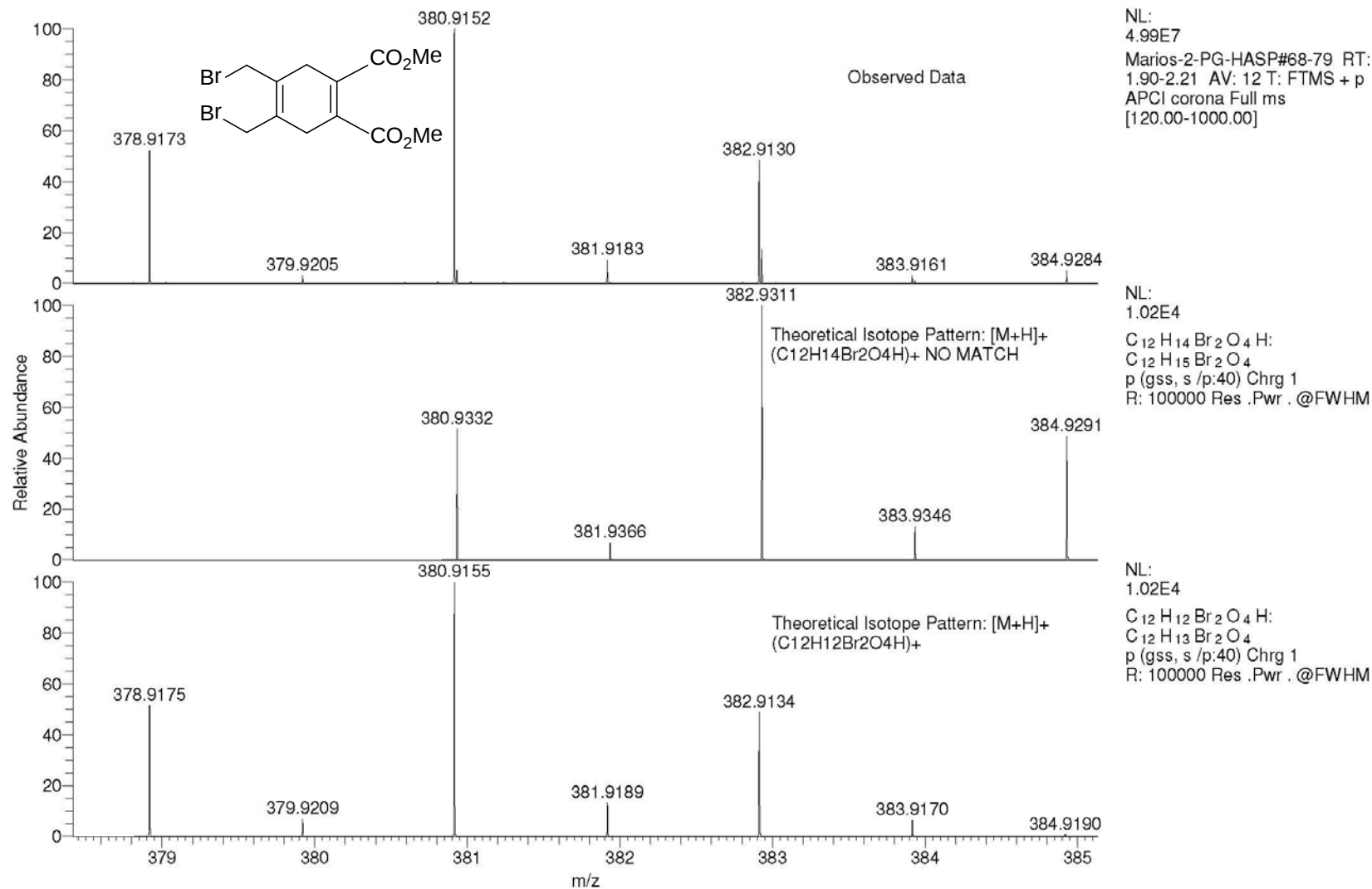
6. High resolution mass spectra (APCI+) of compounds 9, 12 and 16

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

0212579 MW=380?
ASAP(SOLID)

EPSRC National Centre Swansea
LTQ Orbitrap XL

Marios
23/04/2012 15:28:06

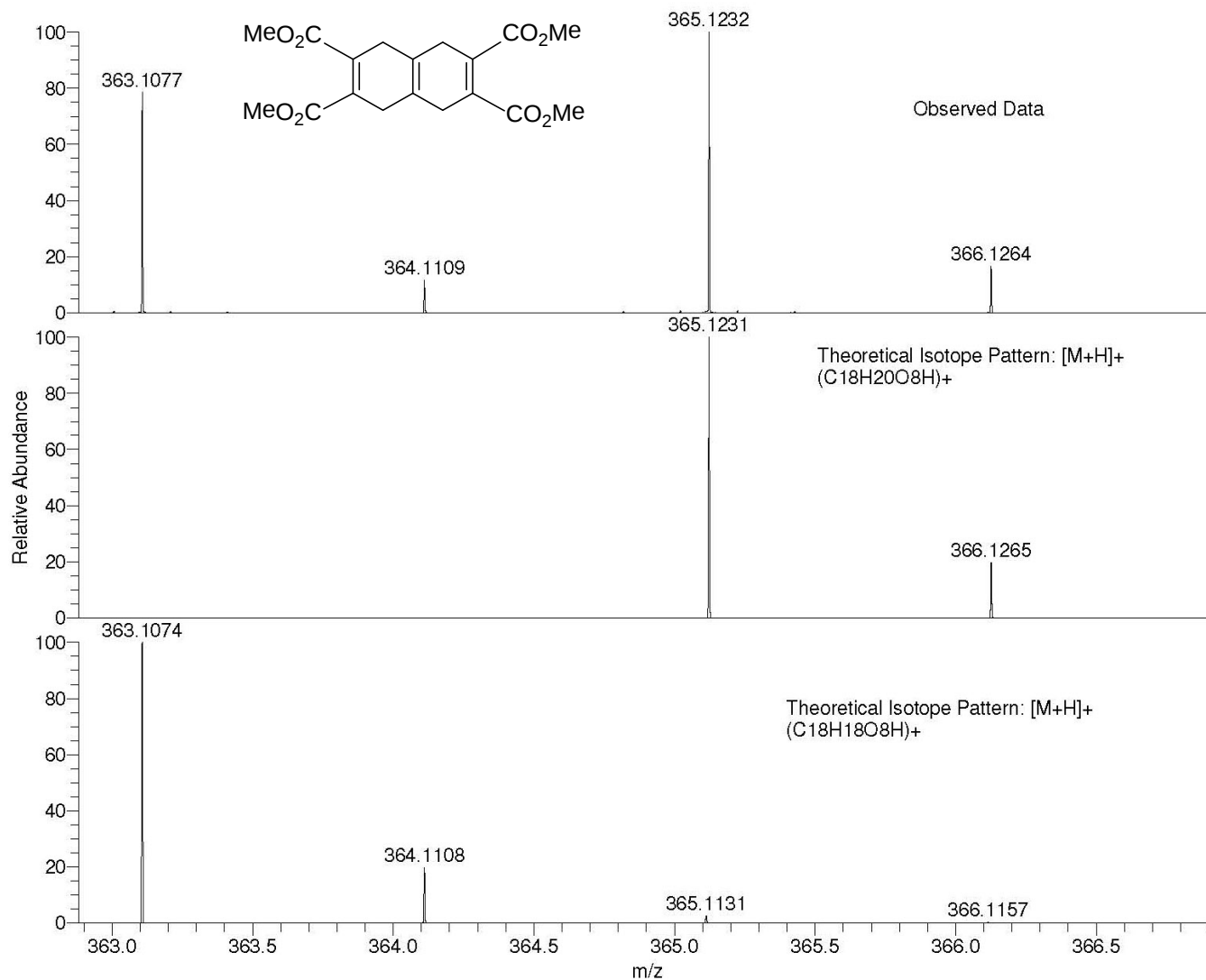


Tetramethyl 1,4,5,8-tetrahydro-2,3,6,7-naphthalenetetracarboxylate (12)

0212580 MW=364?
ASAP(SOLID)

EPSRC National Centre Swansea
LTQ Orbitrap XL

Marios
23/04/2012 15:46:09



NL:
2.75E6
Marios-3-PG-HASP#112-158
RT: 3.30-4.62 AV: 47 T: FTMS
+ p APCI corona Full ms
[120.00-1000.00]

NL:
1.89E4
 $C_{18}H_{20}O_8H$:
 $C_{18}H_{21}O_8$
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM

NL:
1.89E4
 $C_{18}H_{18}O_8H$:
 $C_{18}H_{19}O_8$
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM

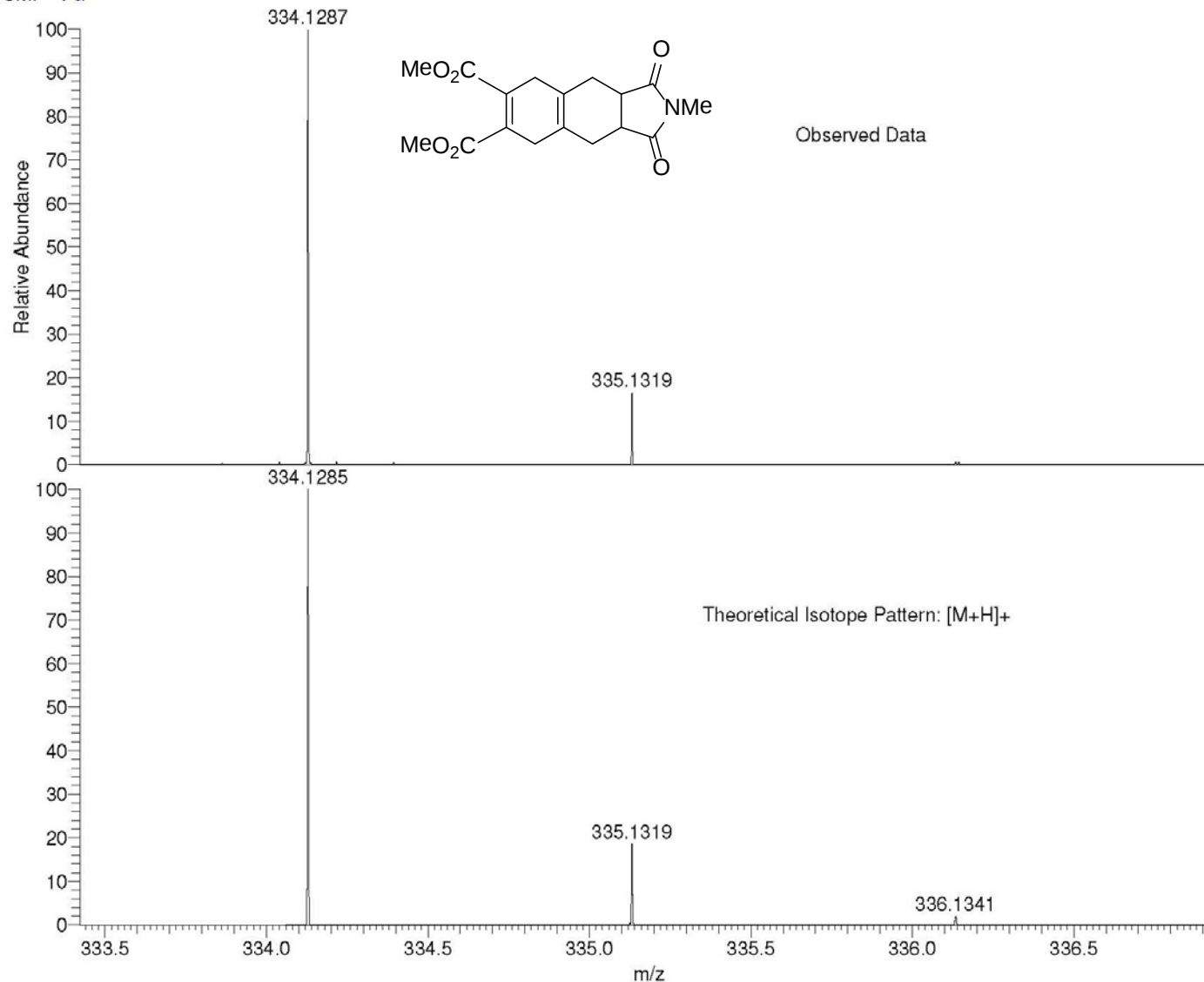
Dimethyl 2-methyl-1,3-dioxo-2,3,3a,4,5,8,9,9a-octahydro-1H-benzo[f]isoindole-6,7-dicarboxylate (16)

0212581 MW=333?
ASAP(SOLID)

EPSRC National Centre Swansea
LTQ Orbitrap XL

Marios
24/04/2012 12:56:29

SM: 7G



NL:
7.13E6
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1.57-1.68 AV: 5 T: FTMS + p
APCI corona Full ms
[120.00-1000.00]

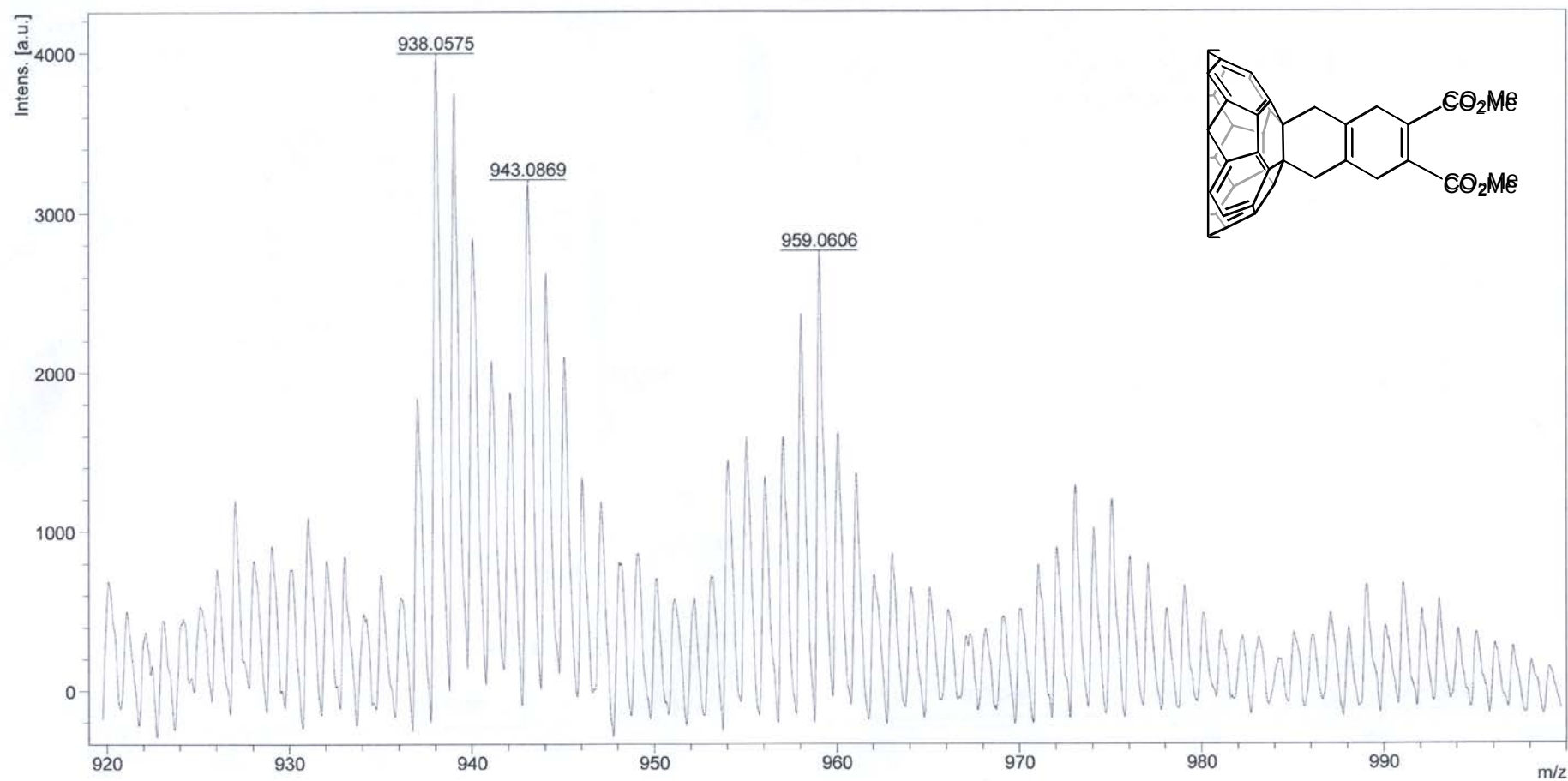
NL:
1.91E4
C₁₇H₁₉NO₆H:
C₁₇H₂₀N₁O₆
p (gss, s /p:40) Chrg 1
R: 100000 Res .Pwr . @FWHM

7. **High resolution MALDI-TOF mass spectra of 14**
Fullerene monoadduct 14 (negative mode, DCTB matrix)

D:\Data\Chronakis\MSM\161FC2\161FC2\0_L2\1\1Ref

Comment 1

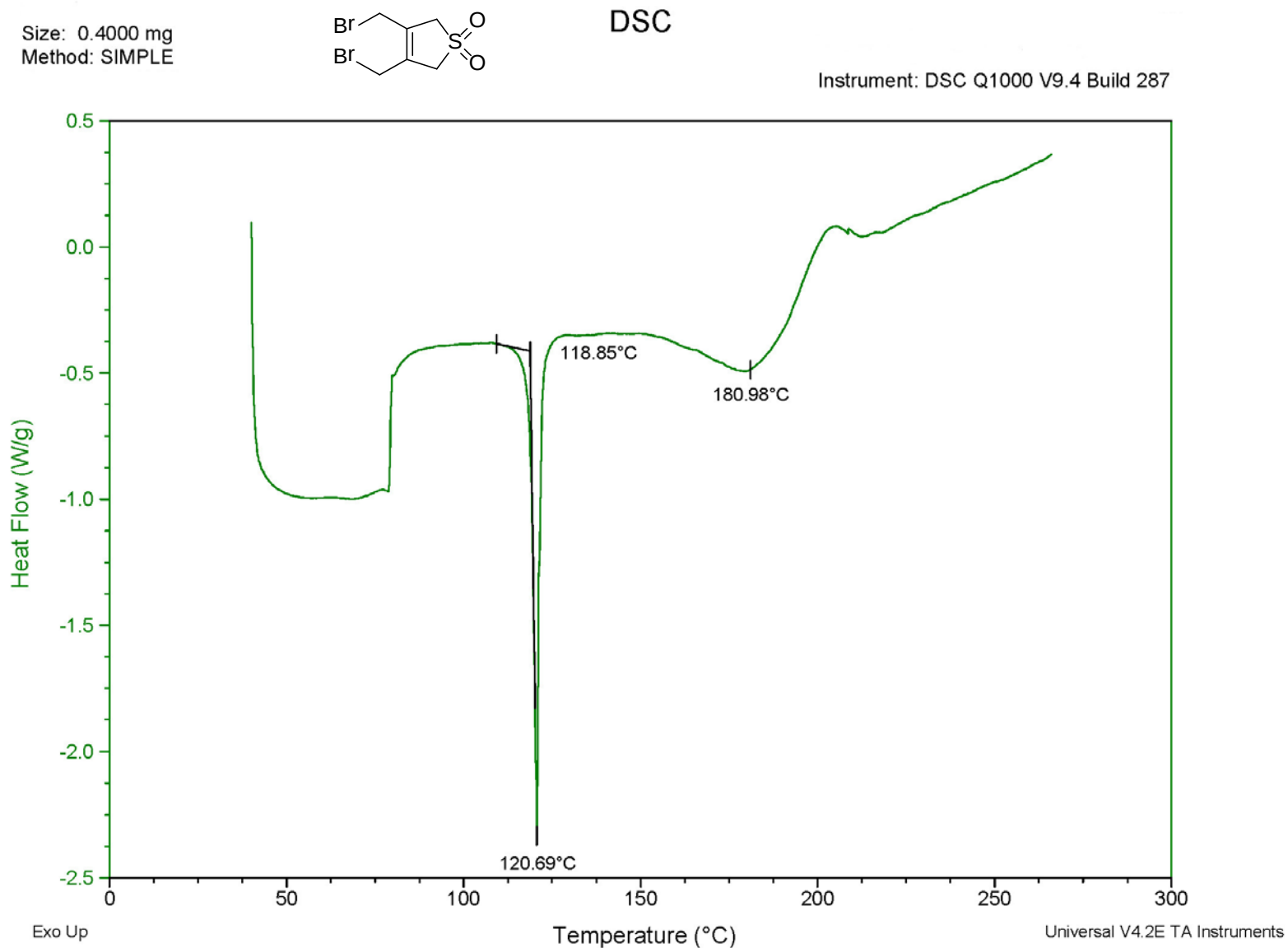
Comment 2



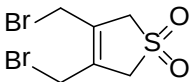
Bruker Daltonics flexAnalysis

printed: 4/9/2012 2:58:57 PM

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

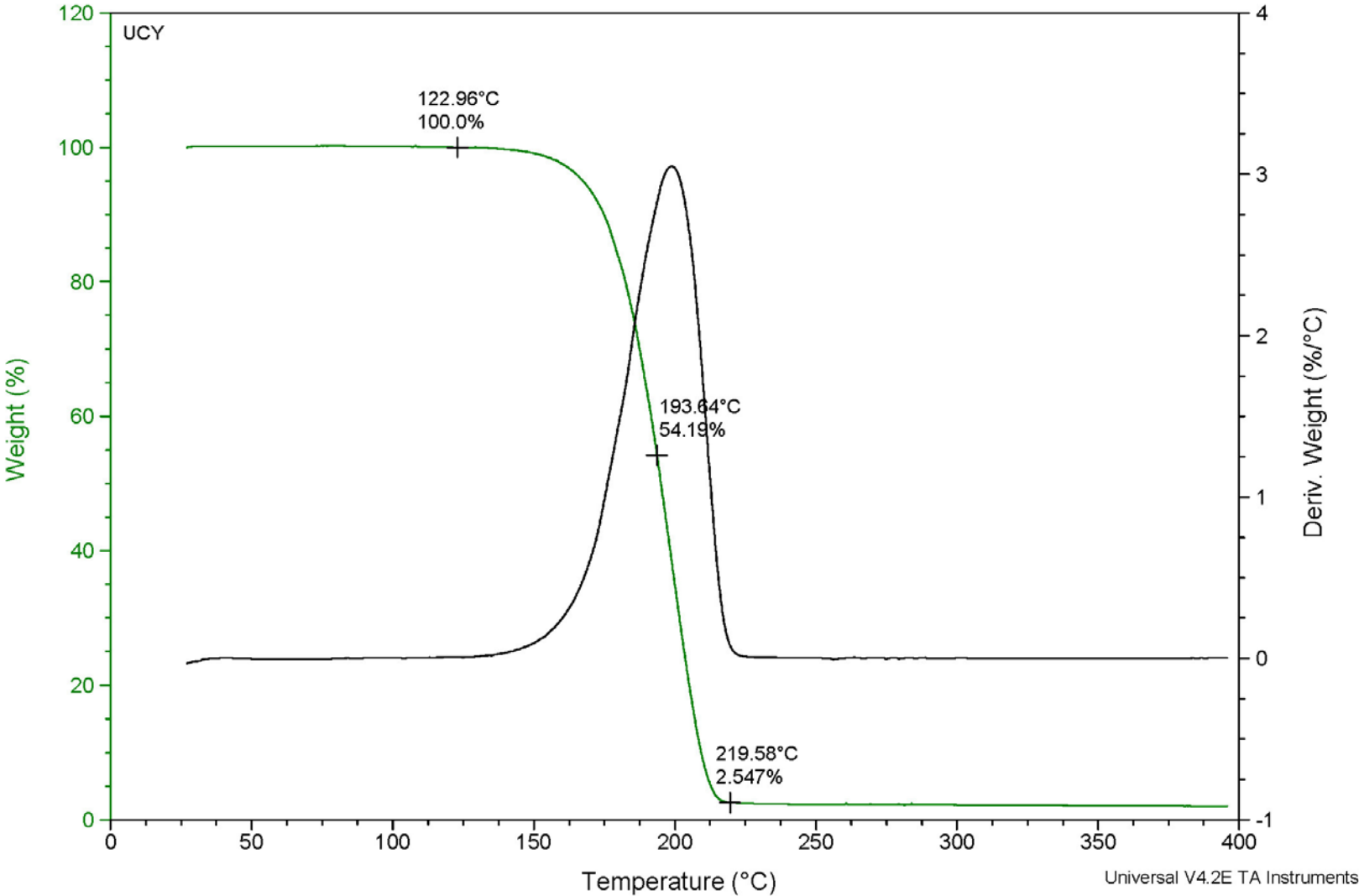


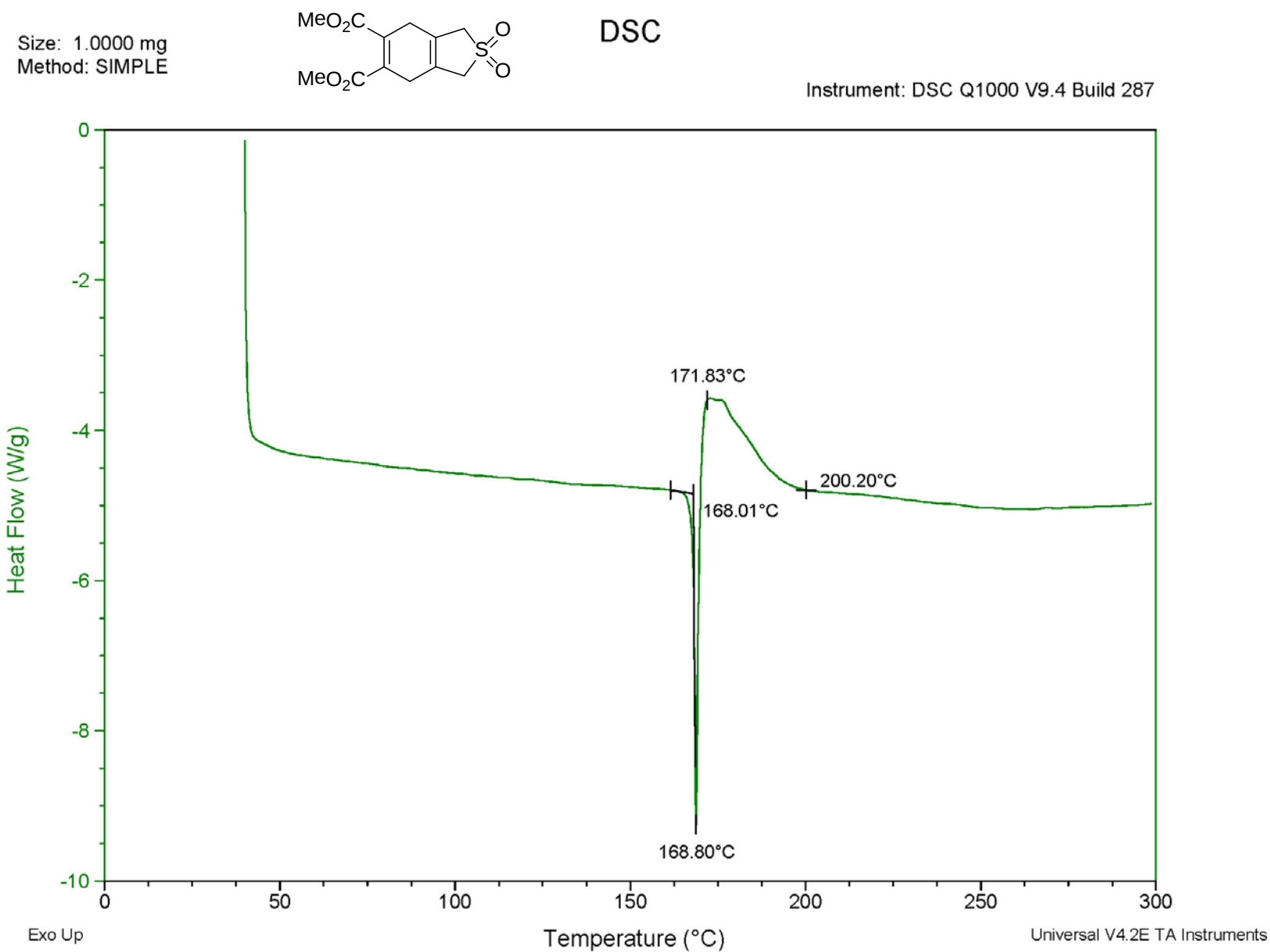
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Method: Ramp

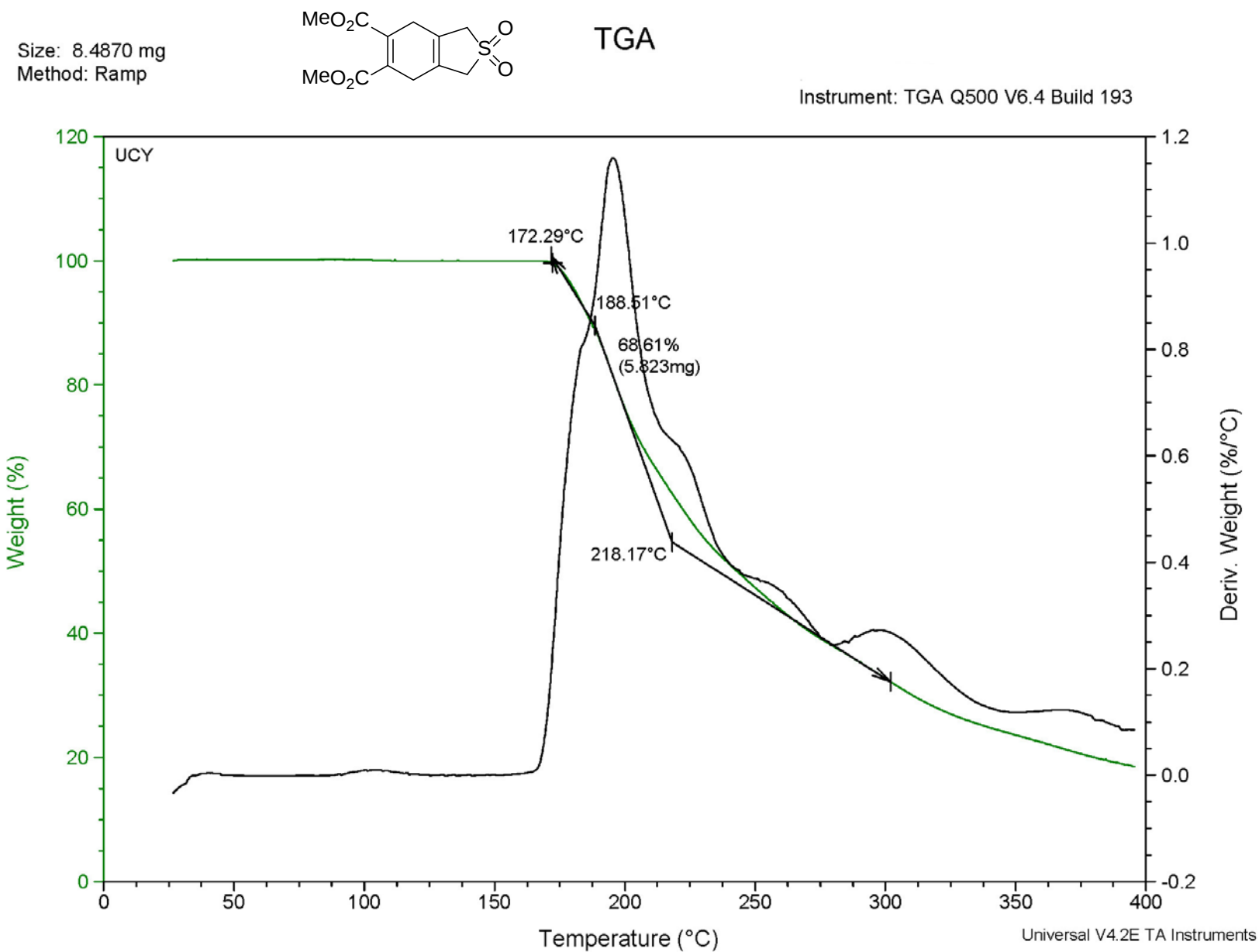


TGA

Instrument: TGA Q500 V6.4 Build 193



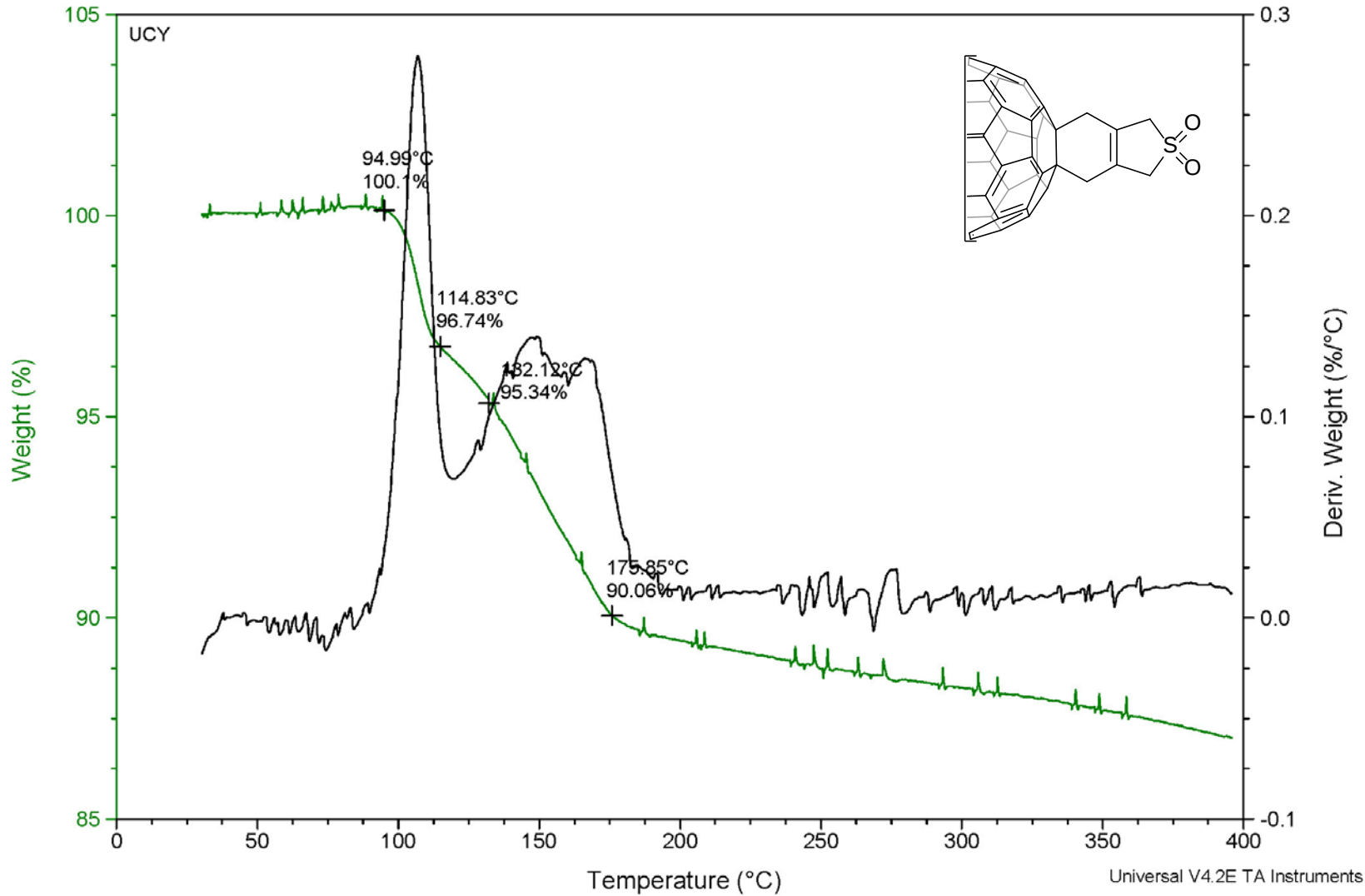




Size: 4.2460 mg
Method: Ramp

TGA

Instrument: TGA Q500 V6.4 Build 193



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.