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Supporting Information

Rapid and catalyst free synthesis of new bis(benzo[g]chromene) and bis(pyrano[3,2-c]chromene) derivatives and optimization of reaction conditions using response surface methodology

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Experimental

General

The various amines, 1,1-bis(methylthio)-2-nitroethene, terephthalaldehyde, Isophthalaldehyde, 2-hdroxy-1,4-naphthoquinone, 4-hydroxycumarin, and solvents were purchased from Sigma-Aldrich chemical company and were used as received without further purification. Melting points were determined with an electrothermal 9100 apparatus. Infrared (IR) spectra were recorded on a Bruker Tensor 27 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DRX-300 Avance instrument (300 MHz for ^1H and 75.4 and 62.8 MHz for ^{13}C) with DMSO as solvent. Chemical shifts are expressed in parts per million (ppm), and coupling constant (J) are reported in hertz (Hz). Mass spectra were recorded with an Agilent 5975C VL MSD with Triple-Axis Detector operating at an ionization potential of 70 eV.

General procedure for the synthesis of product 6 and 7

A mixture of amine (2 mmol), 1,1-bis(methylthio)-2-nitroethene (2 mmol, 0.330 g) and 10 mL EtOH/H_2O (85:15) in a 50 mL flask was stirred for 6 hours at 89 ˚C. After completion of the reaction (monitored by TLC, ethyl acetate/n-hexane, 1:1), phthaldialdehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (2 mmol, 0.348 g) or 4-hydroxycumarin (2 mmol, 0.324 g) were added to the reaction mixture, and it was stirred at 89 ˚C for the time given in Table 5. Then, the reaction mixture was filtered to give the crude product. The solid was washed with EtOH to give pure product **6** or **7** in good to high yield.

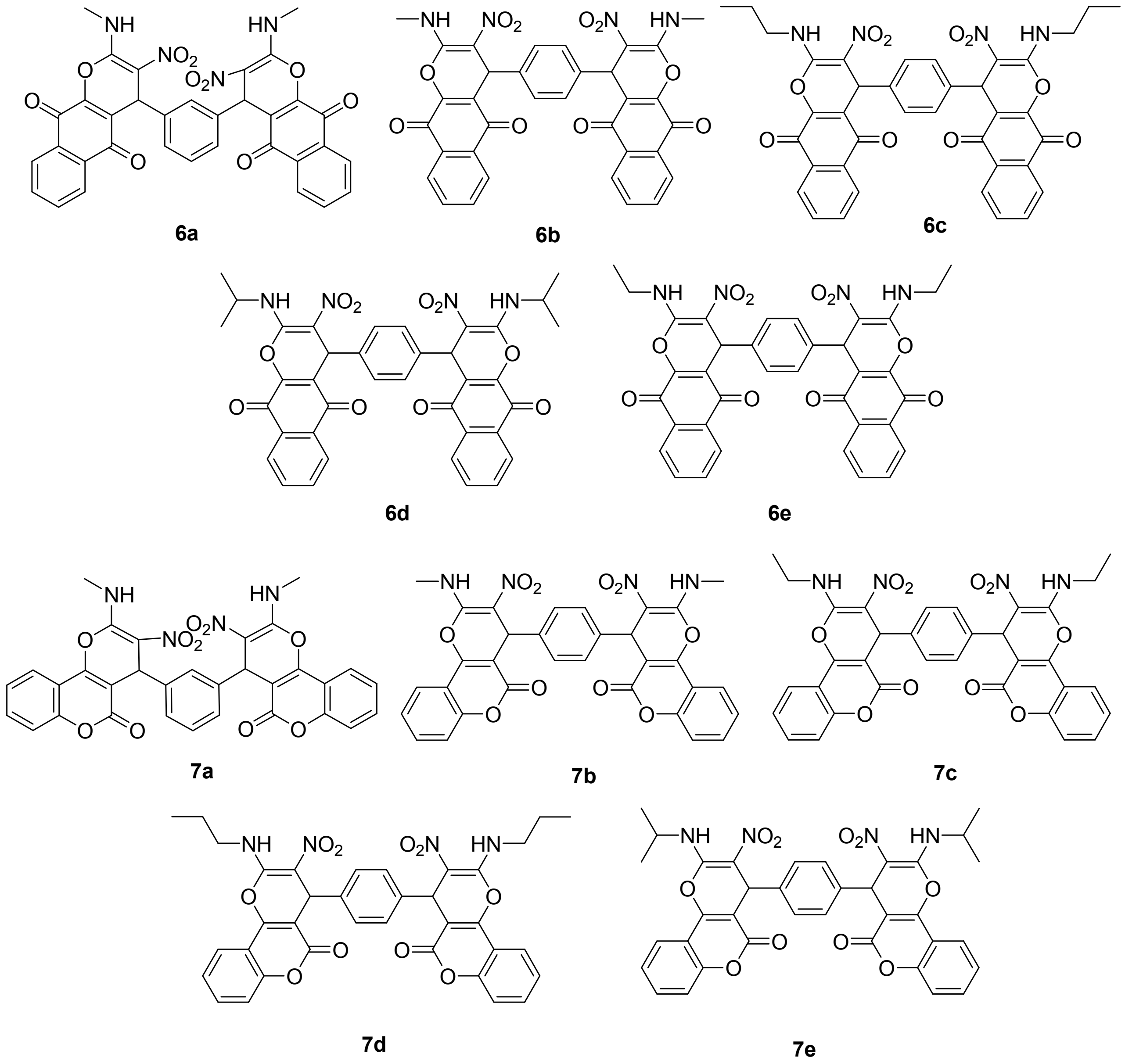
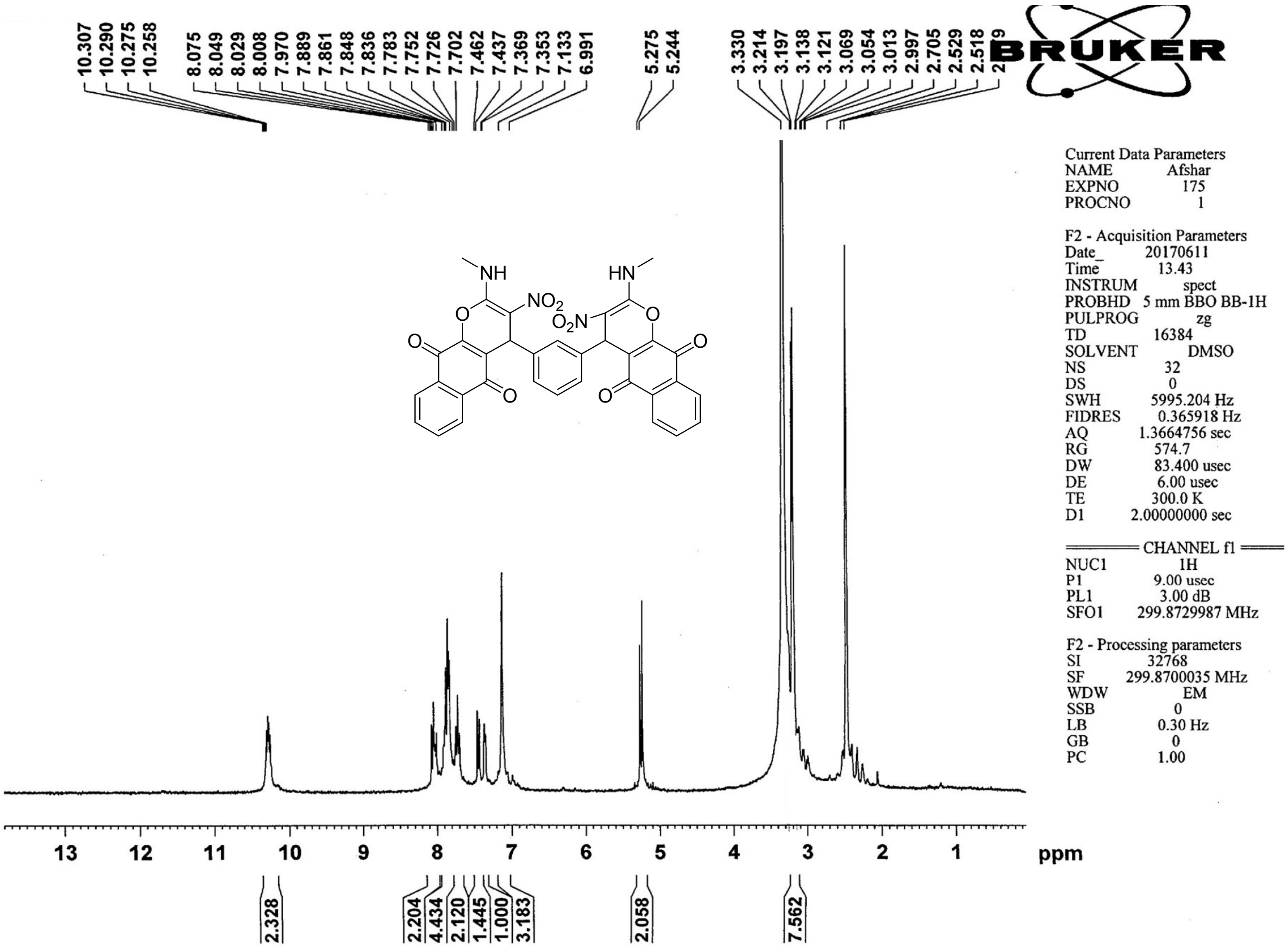


Figure 1. Structure of all products **6a-e** and **7a-e.**



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TD 16384
SOLVENT DMSO
NS 32
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FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 574.7
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec

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P1 9.00 usec
PL1 3.00 dB
SFO1 299.8729987 MHz

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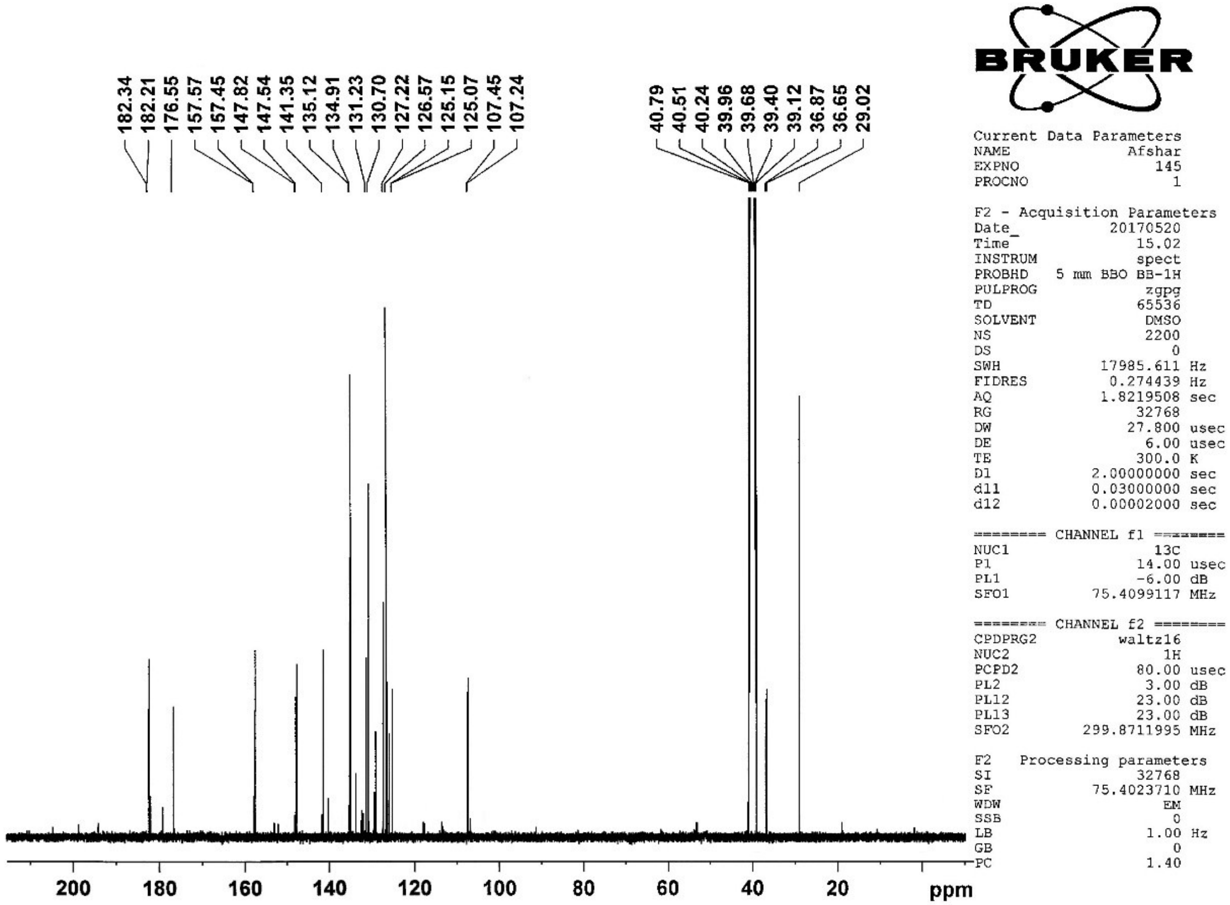
^{1}H NMR of 6a



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SOLVENT                DMSO
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FIDRES             0.274439 Hz
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TE                    300.0 K
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PL1                   -6.00 dB
SFO1             75.4099117 MHz

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PL13                  23.00 dB
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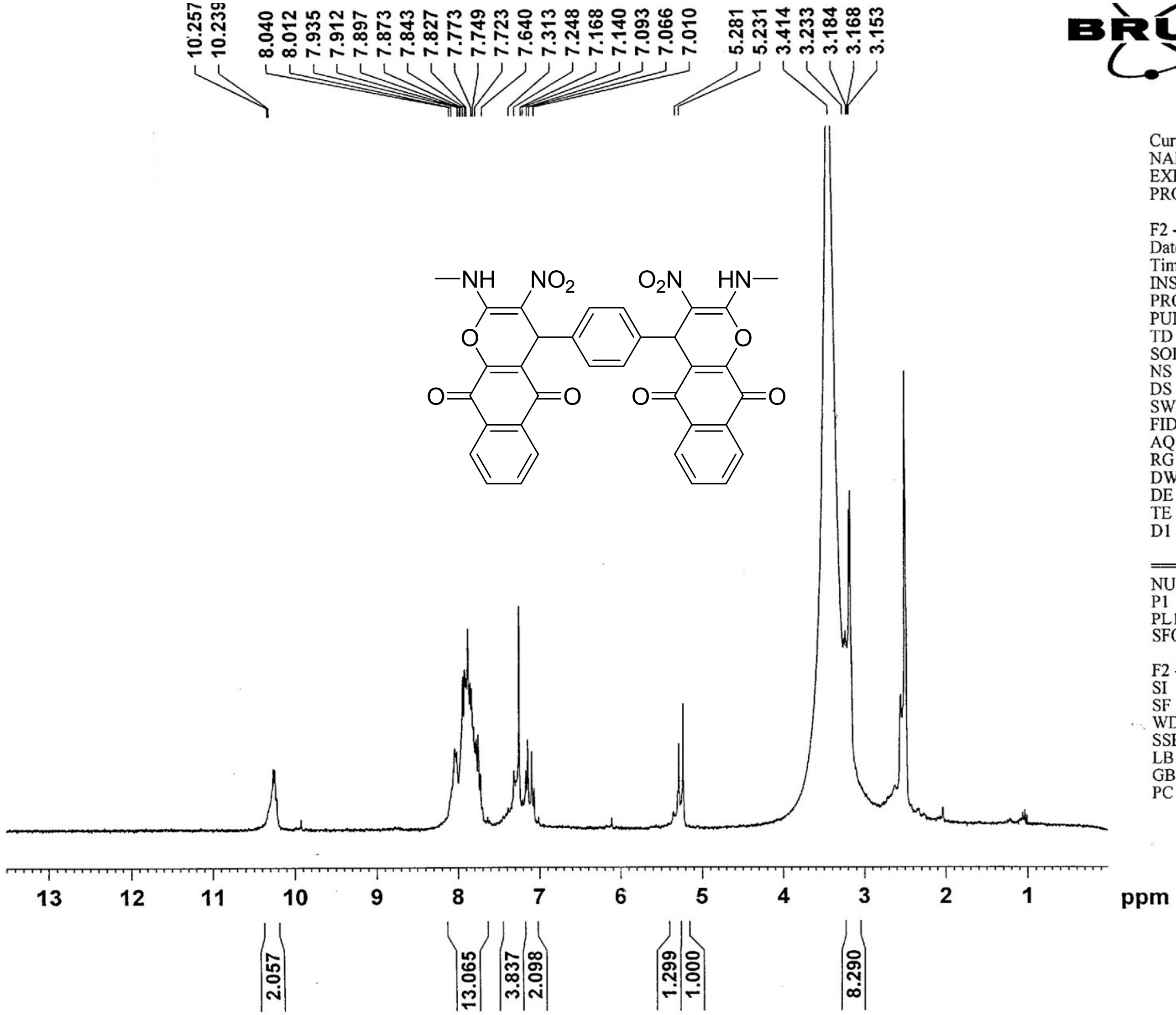
^{13}C NMR of 6a



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PULPROG            zg
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SOLVENT          DMSO
NS                 16
DS                  0
SWH       5995.204 Hz
FIDRES     0.365918 H
AQ       1.3664756 sec
RG                362
DW         83.400 usec
DE           6.00 usec
TE            300.0 K
D1      2.00000000 sec

======== CHANNEL f1
NUC1               1H
P1           9.00 usec
PL1           3.00 dB
SFO1      299.8729987 M

F2 - Processing parameter
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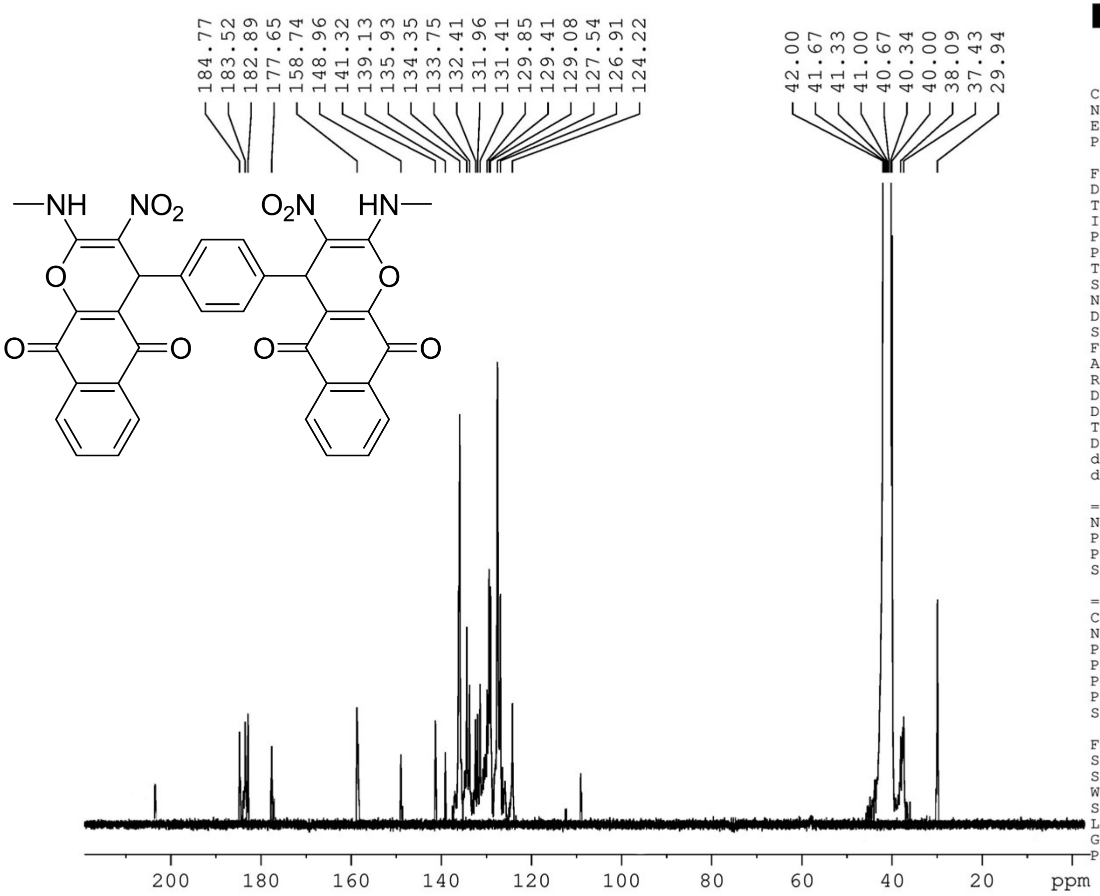
^{1}H NMR of 6b



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SFO1       62.9015280 MHz

======== CHANNEL f2 ========
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NUC2               1H
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PL2              3.00 dB
PL12            21.50 dB
PL13            23.00 dB
SFO2      250.1310005 MHz

F2 - Processing parameters
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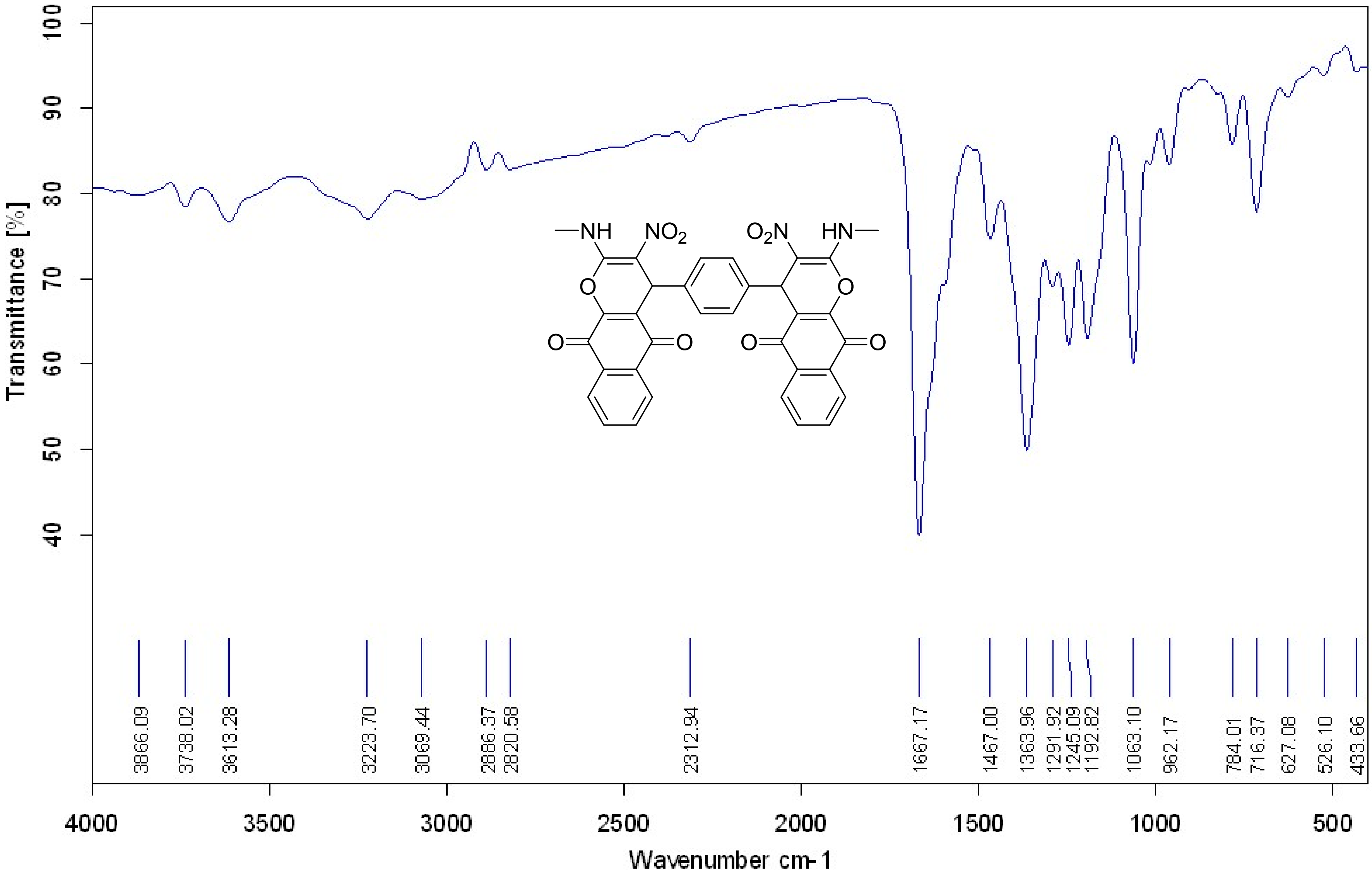
^{13}C NMR of 6b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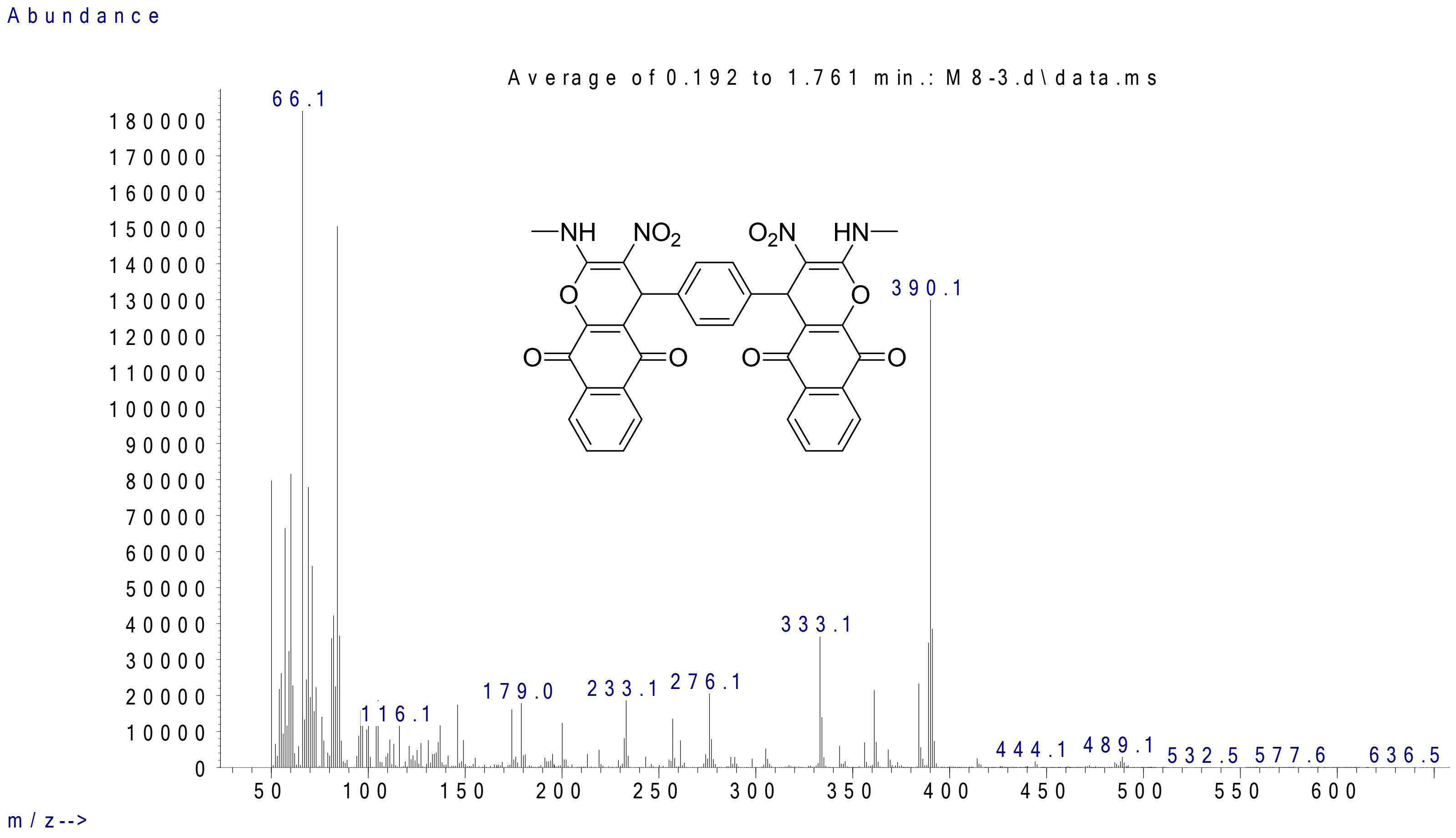
IR of 6b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m/z-->
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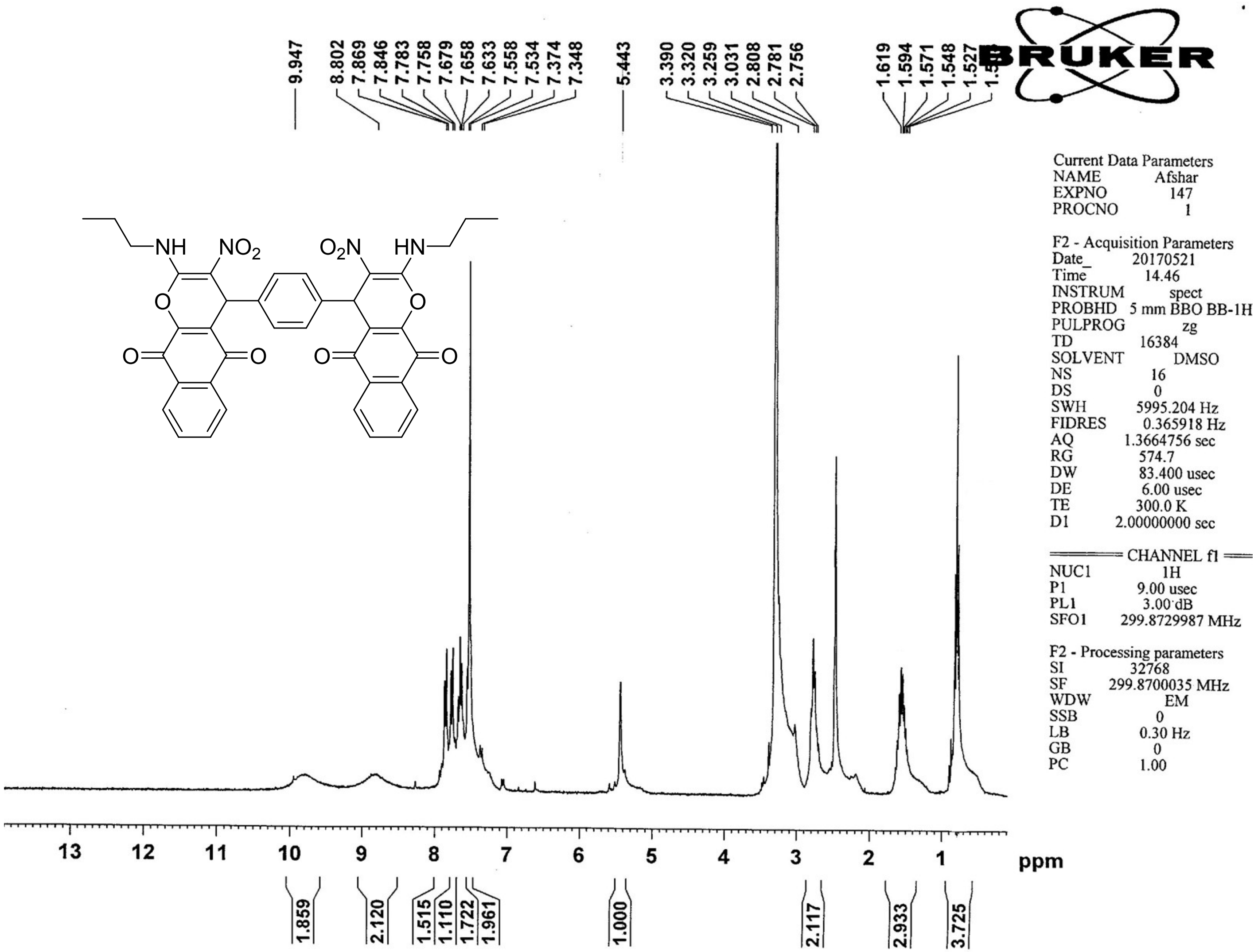
O

Mass of 6b



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PROCNO           1

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PROBHD   5 mm BBO BB-1H
PULPROG           zg
TD          16384
SOLVENT          DMSO
NS             16
DS              0
SWH         5995.204 Hz
FIDRES      0.365918 Hz
AQ        1.3664756 sec
RG             574.7
DW            83.400 usec
DE              6.00 usec
TE             300.0 K
D1        2.00000000 sec

======== CHANNEL f1 ========
NUC1             1H
P1             9.00 usec
PL1            3.00 dB
SFO1     299.8729987 MHz

F2 - Processing parameters
SI             32768
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WDW               EM
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GB                 0
PC              1.00
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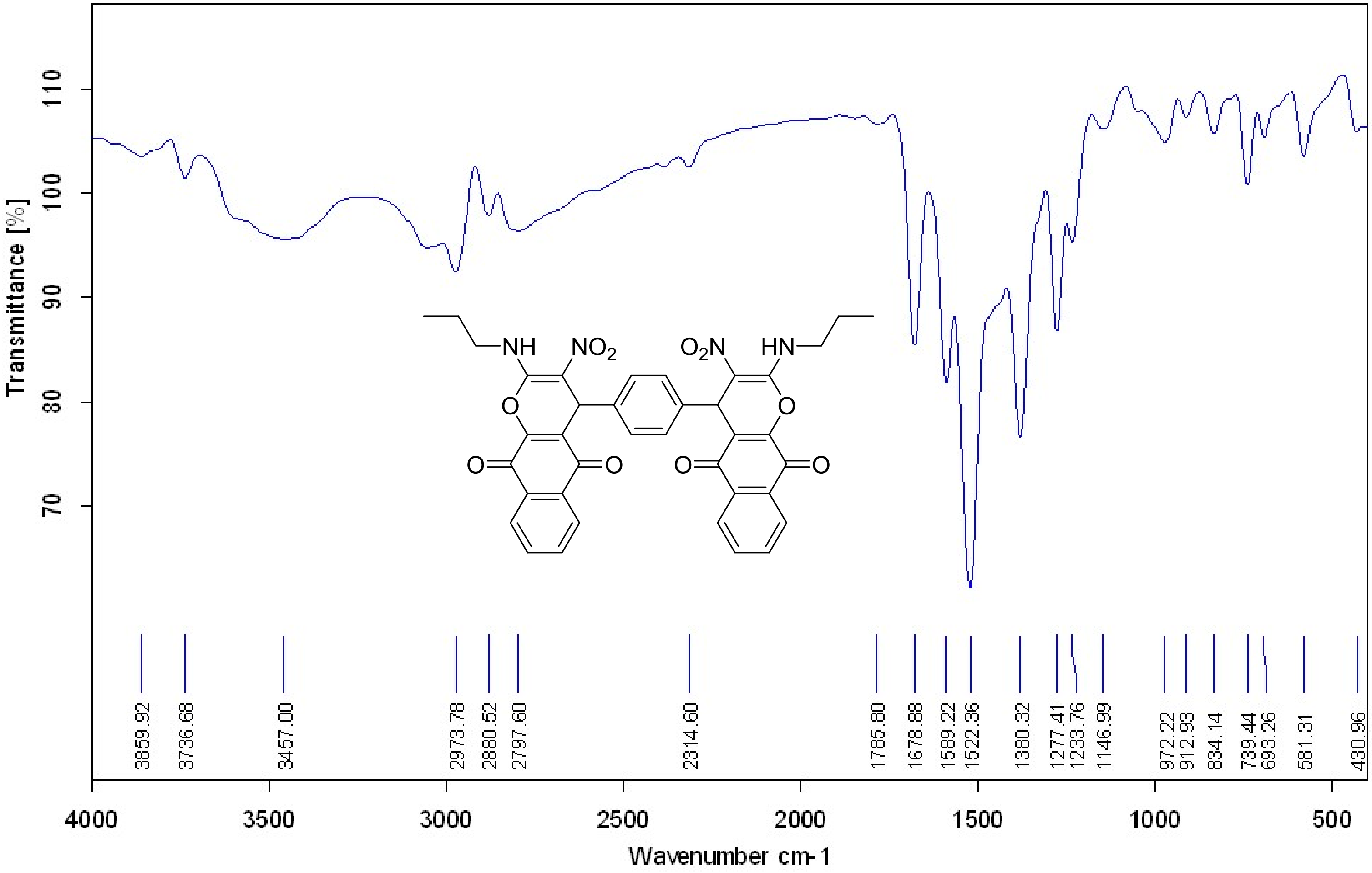
^{1}H NMR of 6c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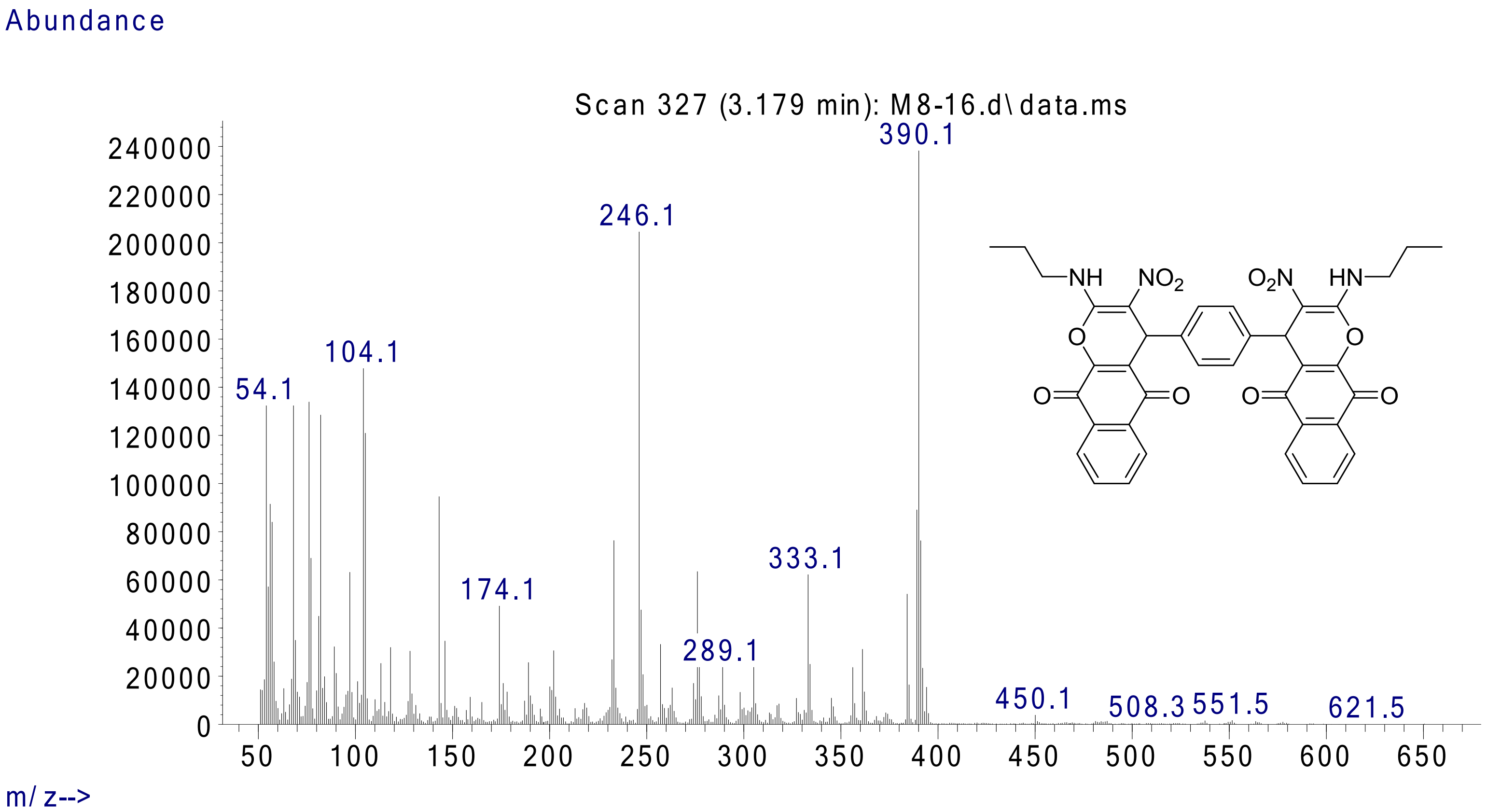
IR of 6c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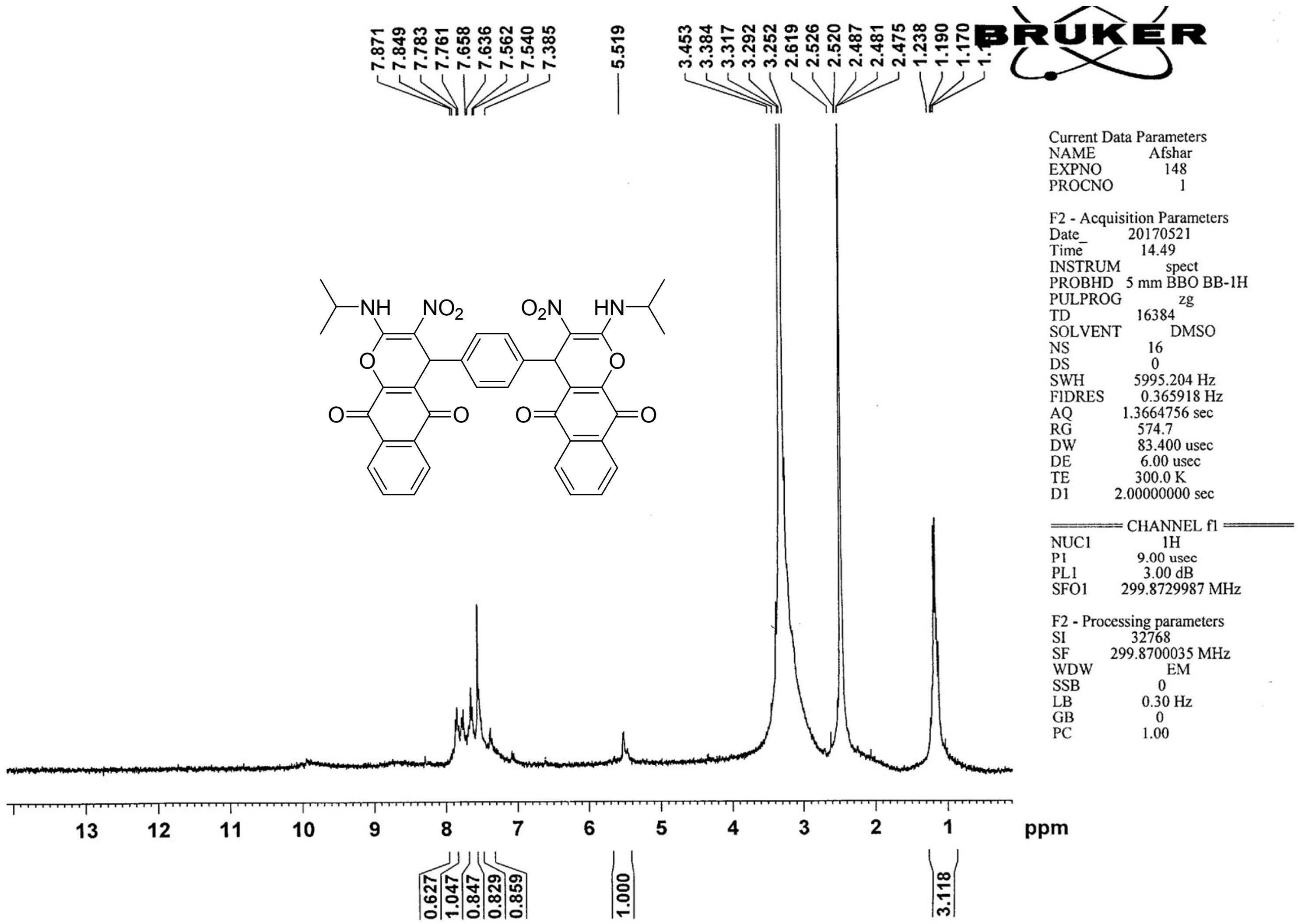
O

Mass of 6c



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PULPROG zg
TD 16384
SOLVENT DMSO
NS 16
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SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 574.7
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 3.00 dB
SFO1 299.8729987 MHz

F2 - Processing parameters
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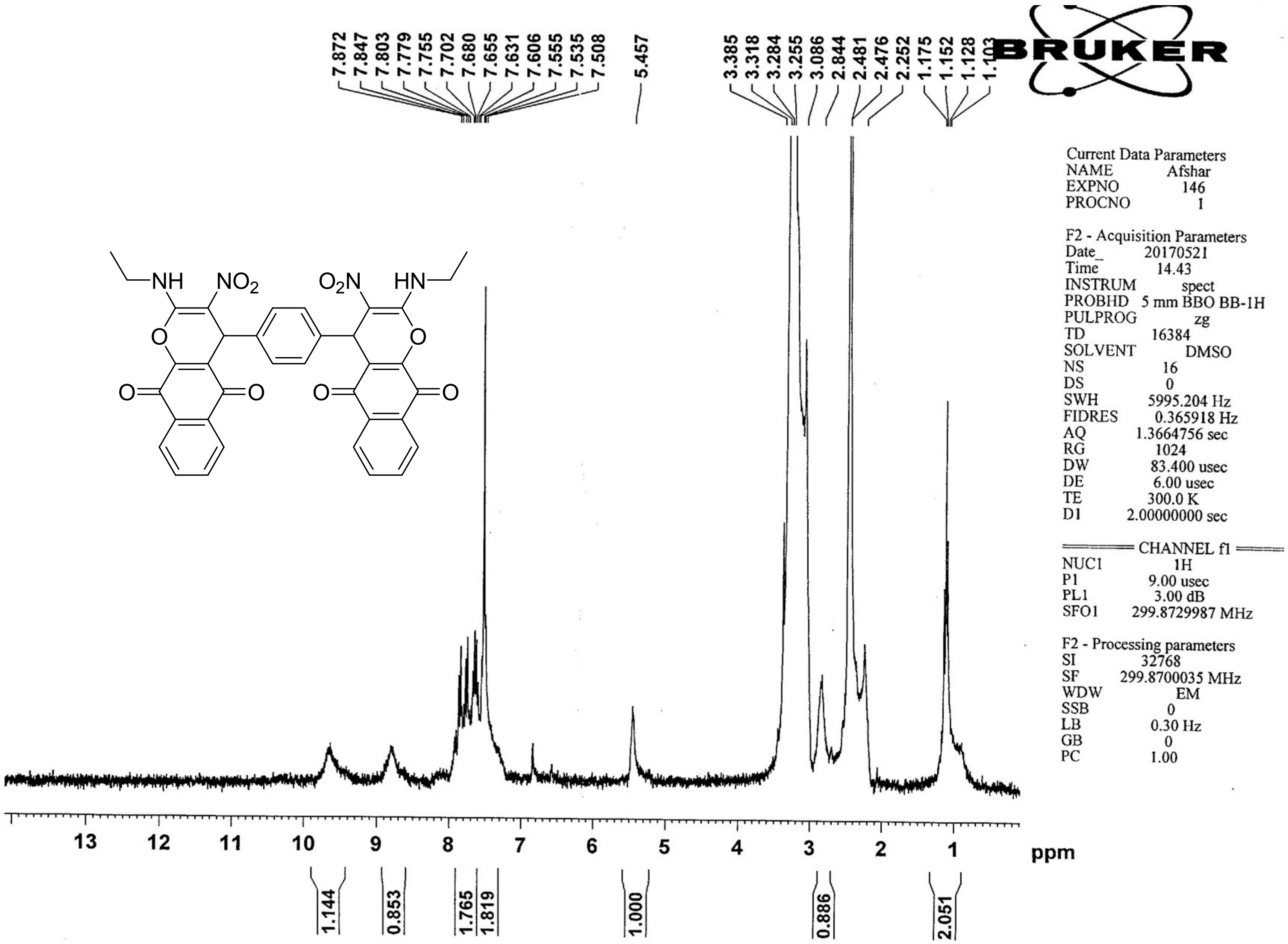
SF 299.8700035 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR of 6d



Current Data Parameters
NAME Afshar
EXPNO 146
PROCNO 1

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PULPROG zg
TD 16384
SOLVENT DMSO
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 1024
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec

CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 3.00 dB
SFO1 299.8729987 MHz

F2 - Processing parameters
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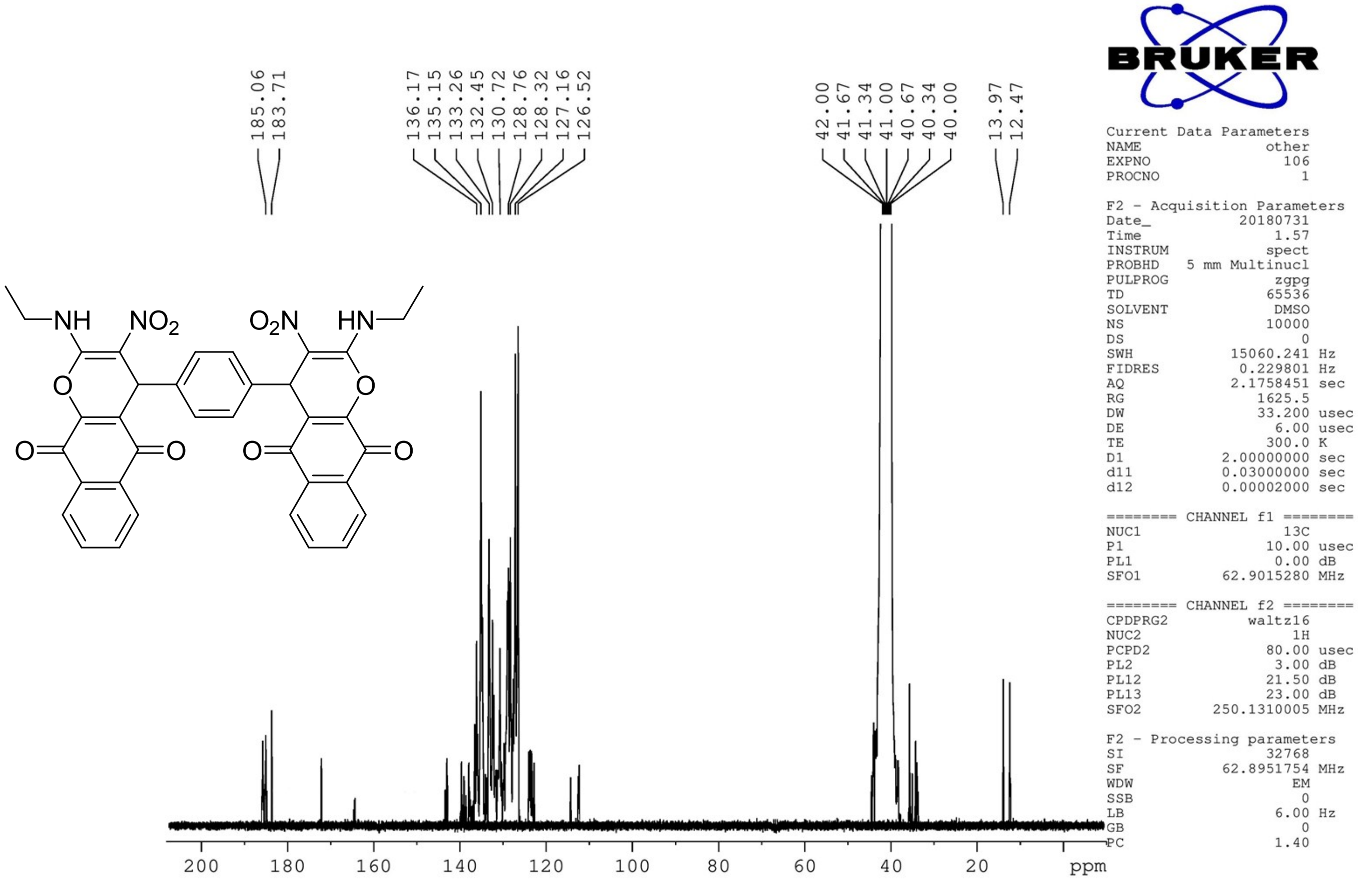
PC 1.00

^1H NMR of 6e



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TD                  65536
SOLVENT              DMSO
NS                  10000
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FIDRES        0.229801 Hz
AQ          2.1758451 sec
RG                 1625.5
DW            33.200 usec
DE              6.00 usec
TE                300.0 K
D1         2.00000000 sec
d11        0.03000000 sec
d12        0.00002000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1             10.00 usec
PL1               0.00 dB
SFO1         62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2          80.00 usec
PL2               3.00 dB
PL12             21.50 dB
PL13             23.00 dB
SFO2        250.1310005 MHz

F2 - Processing parameters
SI                  32768
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SSB                     0
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PC                   1.40
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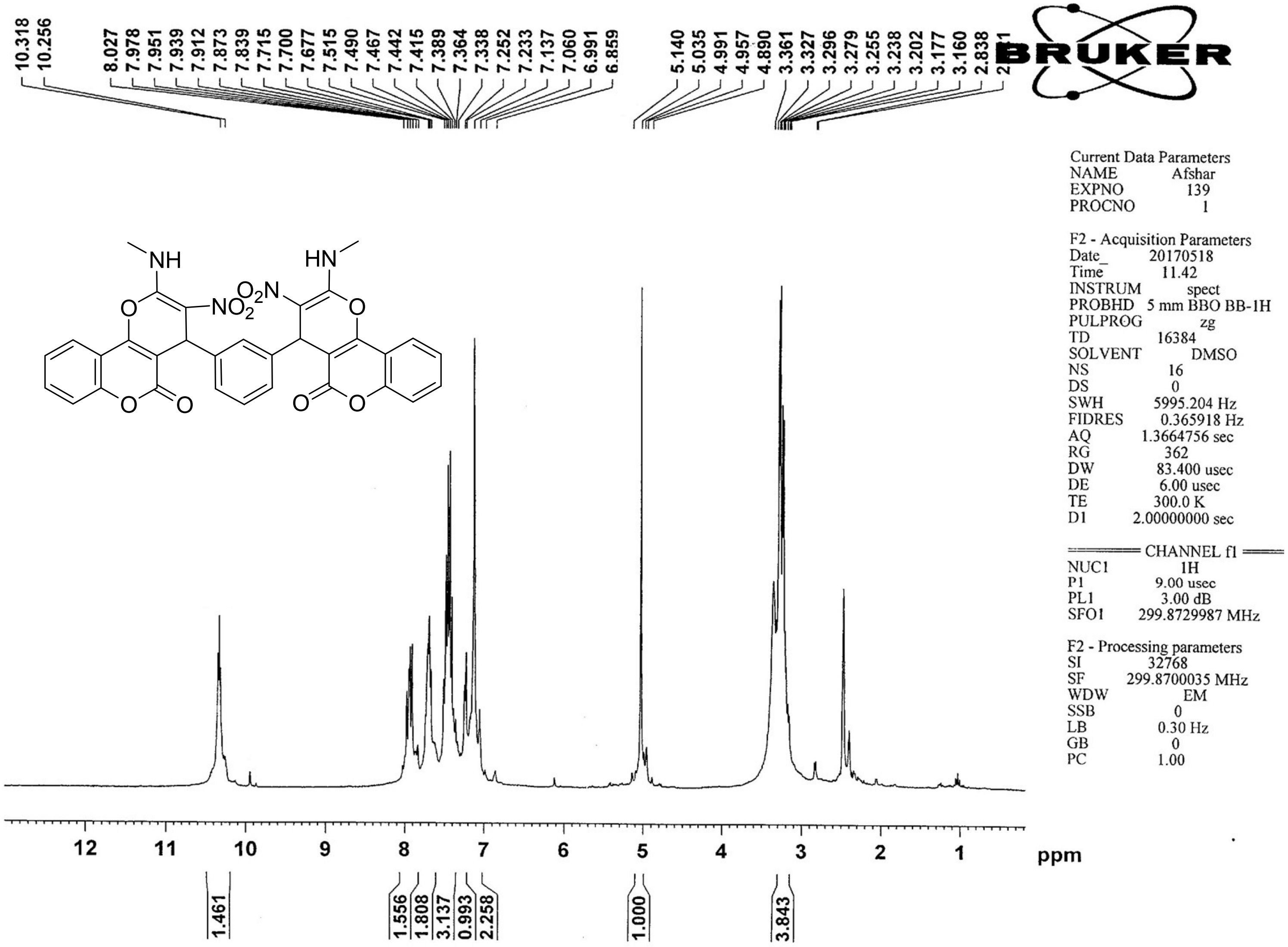
^{13}C NMR of 6e



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PULPROG zg
TD 16384
SOLVENT DMSO
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 362
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec

======== CHANNEL f1 ========
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P1 9.00 usec
PL1 3.00 dB
SFO1 299.8729987 MHz

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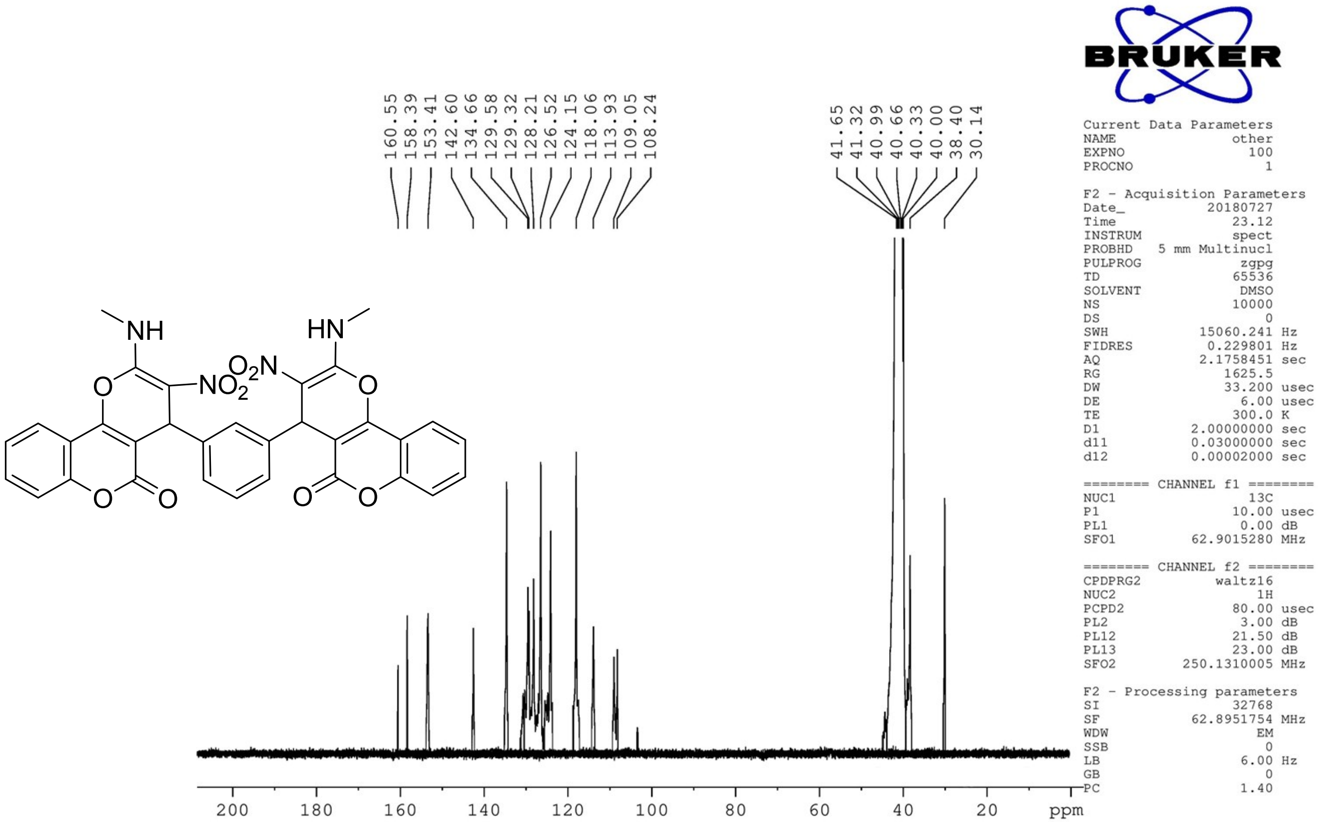
^{1}H NMR of 7a



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TD                  65536
SOLVENT              DMSO
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DS                      0
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FIDRES           0.229801 Hz
AQ              2.1758451 sec
RG                 1625.5
DW                 33.200 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
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======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  0.00 dB
SFO1           62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                21.50 dB
PL13                23.00 dB
SFO2          250.1310005 MHz

F2 - Processing parameters
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PC                   1.40
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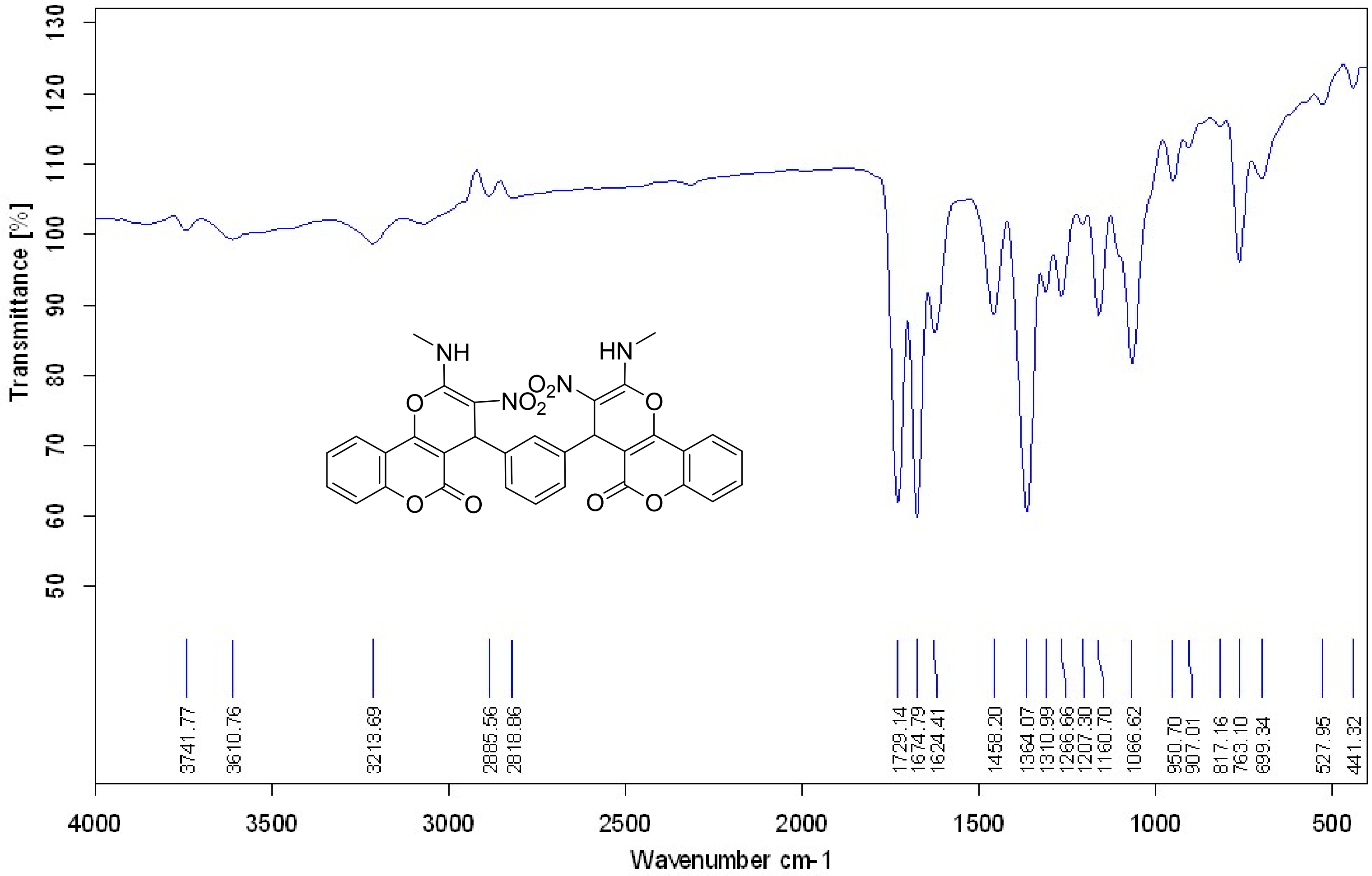
^{13}C NMR of 7a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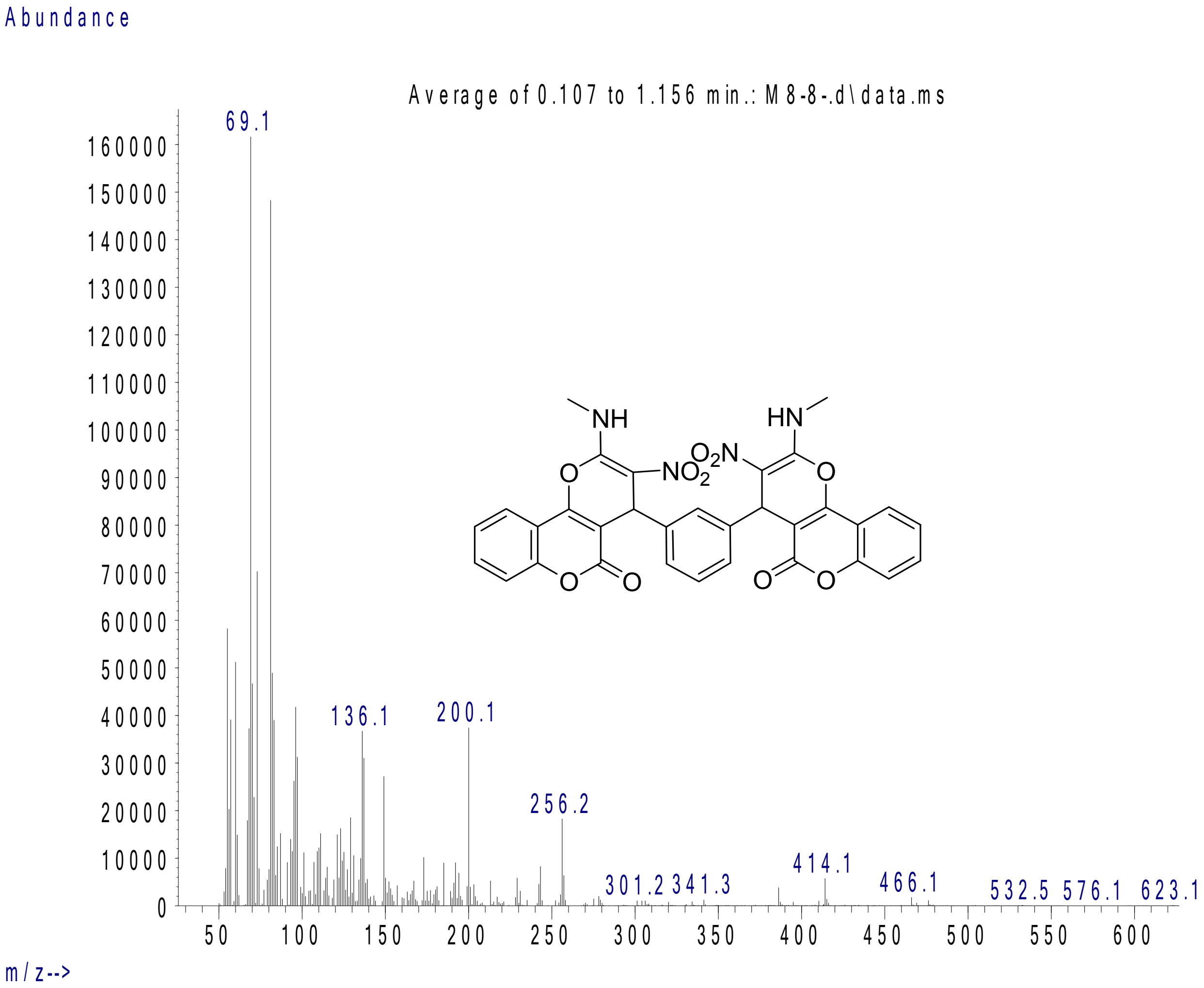
IR of 7a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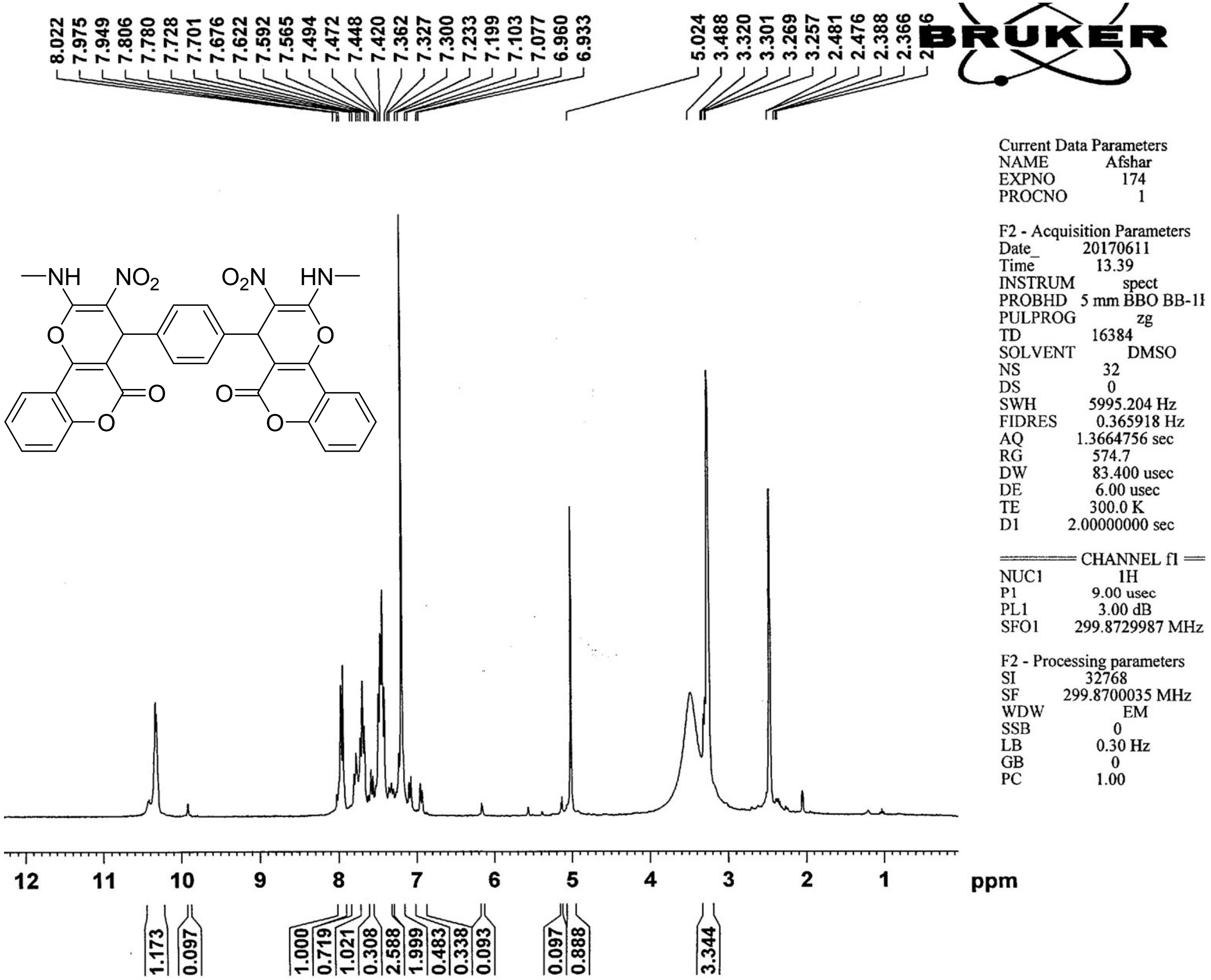
Mass of 7a



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PROCNO                1

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PULPROG              zg
TD                16384
SOLVENT            DMSO
NS                   32
DS                    0
SWH          5995.204 Hz
FIDRES       0.365918 Hz
AQ         1.3664756 sec
RG                574.7
DW           83.400 usec
DE             6.00 usec
TE              300.0 K
D1       2.00000000 sec

======== CHANNEL f1 ==
NUC1                 1H
P1             9.00 usec
PL1             3.00 dB
SFO1     299.8729987 MHz

F2 - Processing parameters
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WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.00
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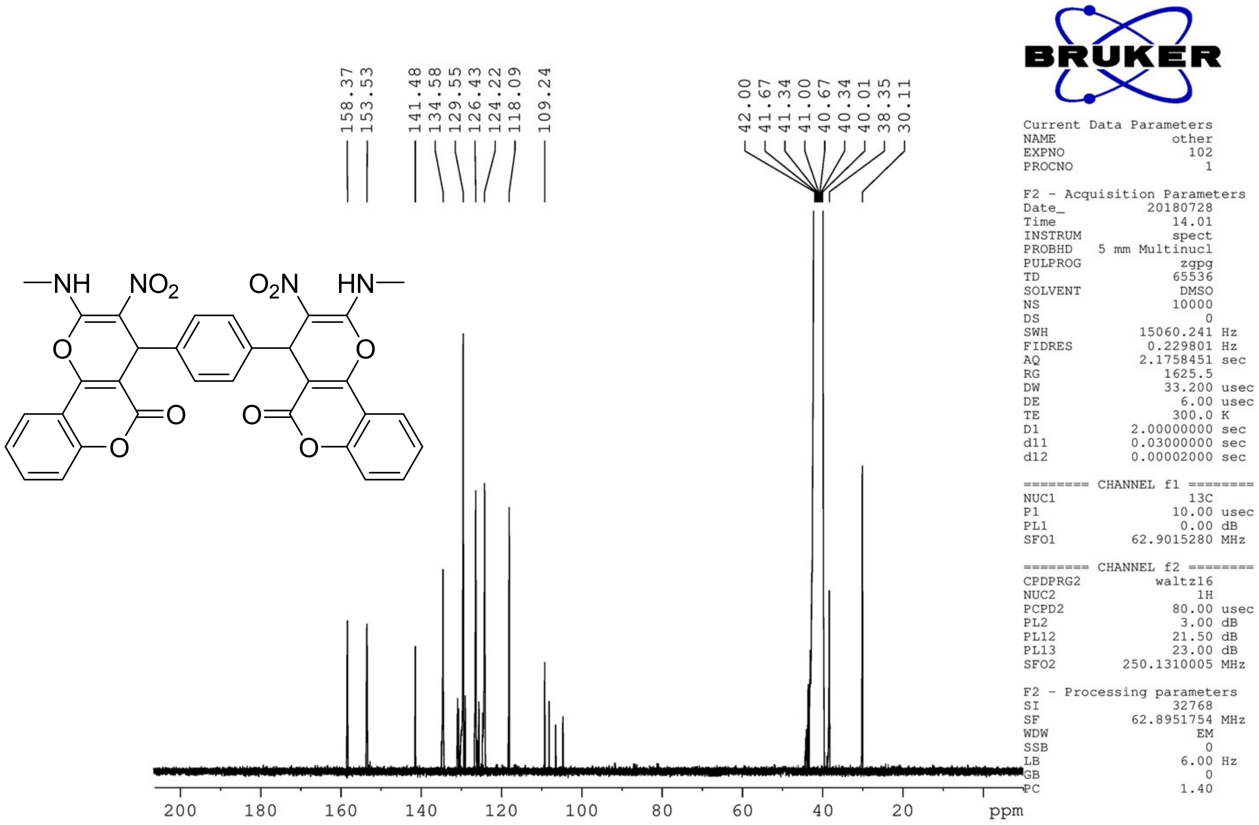
^{1}H NMR of 7b



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PULPROG             zgpg
TD                 65536
SOLVENT             DMSO
NS                 10000
DS                     0
SWH            15060.241 Hz
FIDRES          0.229801 Hz
AQ             2.1758451 sec
RG                1625.5
DW                33.200 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 0.00 dB
SFO1          62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               21.50 dB
PL13               23.00 dB
SFO2         250.1310005 MHz

F2 - Processing parameters
SI                 32768
SF            62.8951754 MHz
WDW                   EM
SSB                    0
LB                  6.00 Hz
GB                     0
PC                  1.40
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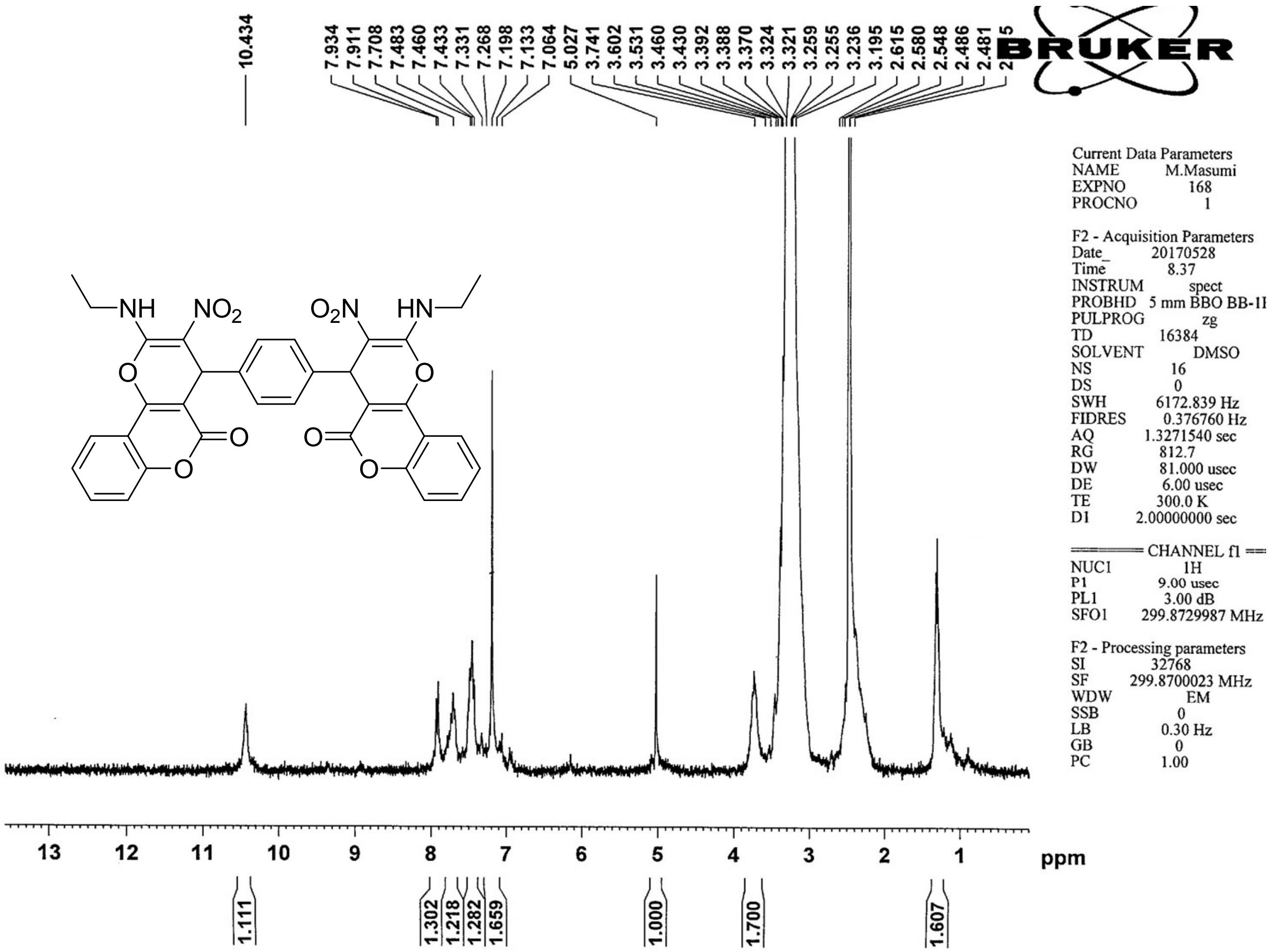
^{13}C NMR of 7b



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PROCNO               1

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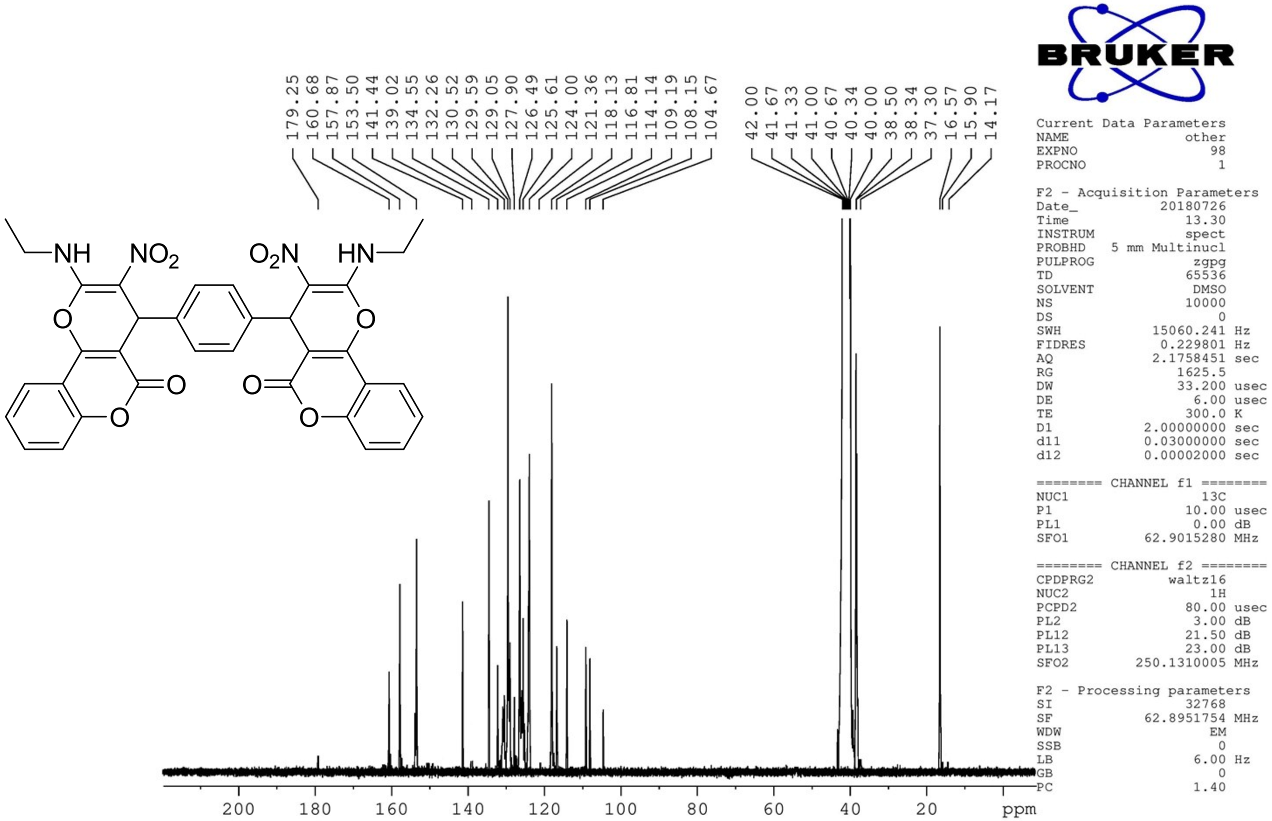
PROBHD   5 mm BBO BB-1
PULPROG             zg
TD               16384
SOLVENT           DMSO
NS                  16
DS                   0
SWH        6172.839 Hz
FIDRES     0.376760 Hz
AQ        1.3271540 sec
RG               812.7
DW          81.000 usec
DE            6.00 usec
TE             300.0 K
D1      2.00000000 sec

======== CHANNEL f1 ==
NUC1                1H
P1           9.00 usec
PL1            3.00 dB
SFO1    299.8729987 MHz

F2 - Processing parameters
SI               32768
SF      299.8700023 MHz
WDW                 EM
SSB                  0
LB             0.30 Hz
GB                   0
PC                1.00
```

^{1}H NMR of 7c



```
Current Data Parameters
NAME               other
EXPNO                 98
PROCNO                 1

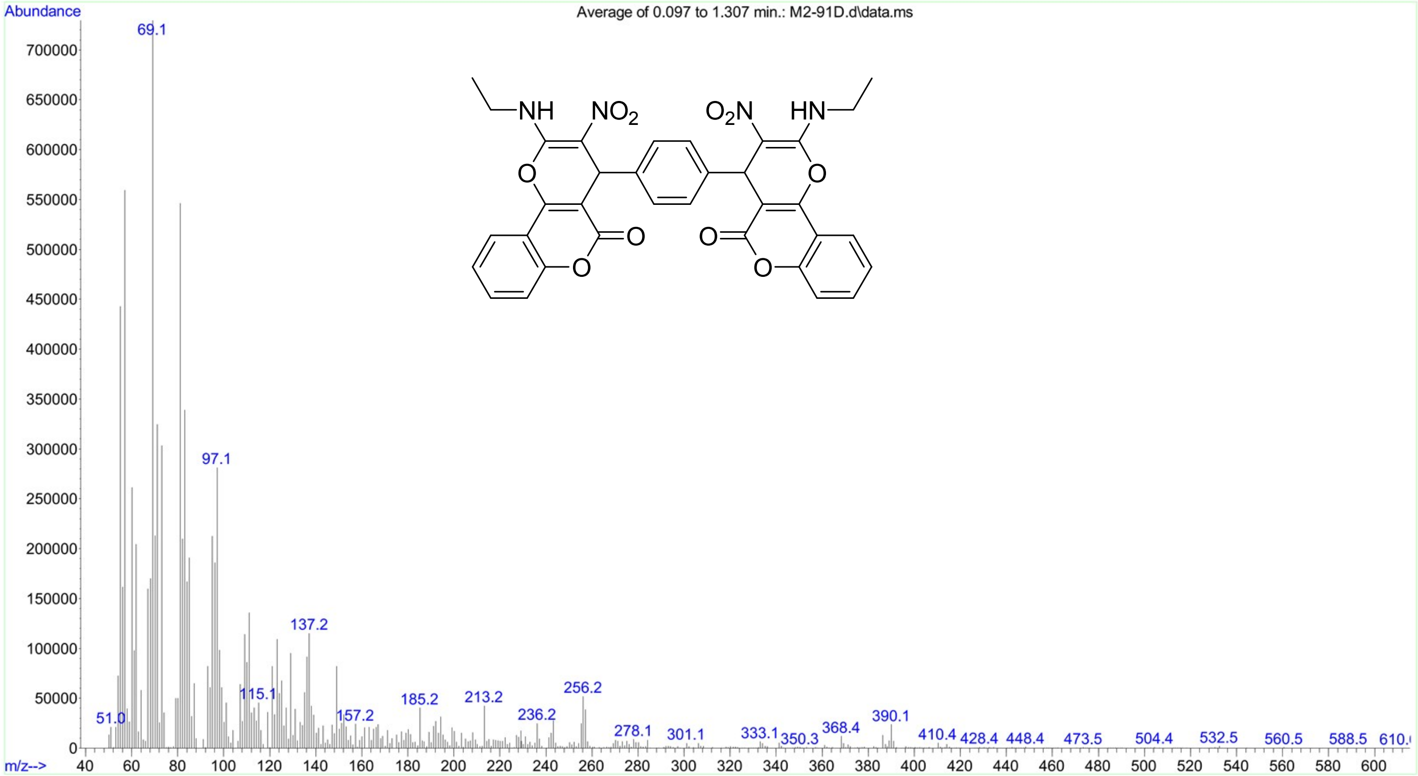
F2 - Acquisition Parameters
Date_           20180726
Time               13.30
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG             zgpg
TD                 65536
SOLVENT             DMSO
NS                 10000
DS                     0
SWH            15060.241 Hz
FIDRES          0.229801 Hz
AQ             2.1758451 sec
RG                1625.5
DW                33.200 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 0.00 dB
SFO1          62.9015280 MHz

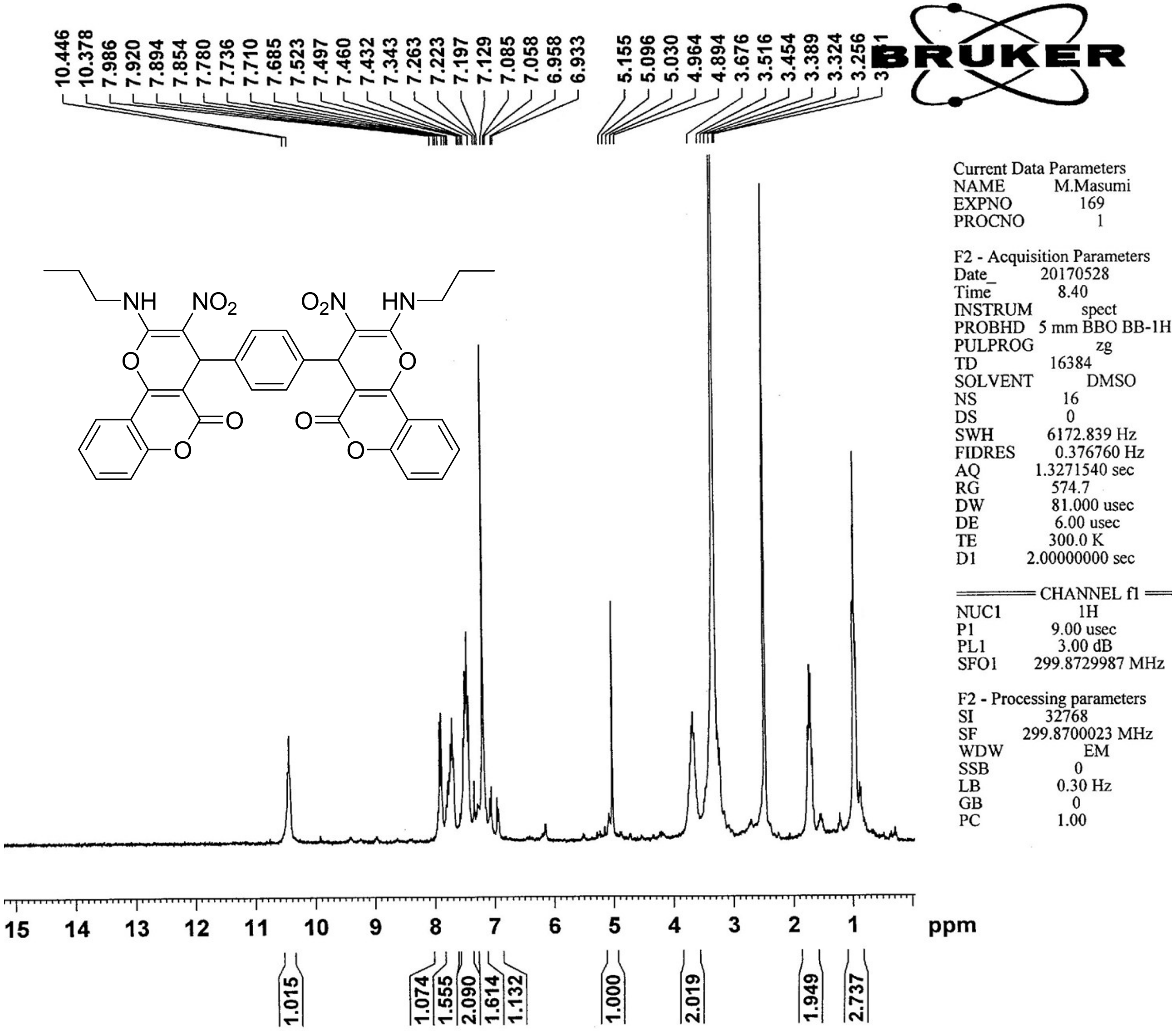
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               21.50 dB
PL13               23.00 dB
SFO2         250.1310005 MHz

F2 - Processing parameters
SI                 32768
SF            62.8951754 MHz
WDW                   EM
SSB                    0
LB                  6.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR of 7c


Abundance
Average of 0.097 to 1.307 min.: M2-91D.d\data.ms
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
69.1
97.1
137.2
51.0
115.1
157.2
185.2
213.2
236.2
256.2
278.1
301.1
333.1
350.3
368.4
390.1
410.4
428.4
448.4
473.5
504.4
532.5
560.5
588.5
610.
NH
NO2
O2N
HN
O
O
O
O
O
O

Mass of 7c



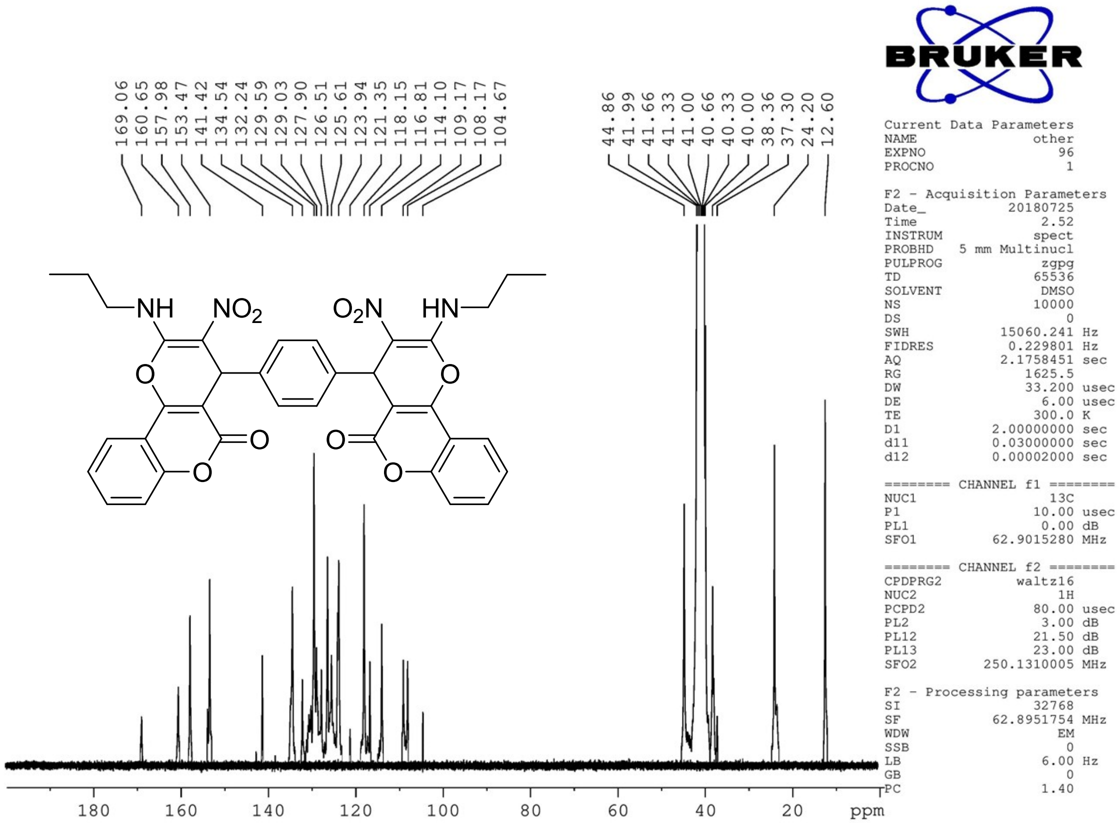
```
Current Data Parameters
NAME          M.Masumi
EXPNO              169
PROCNO               1

F2 - Acquisition Parameters
Date_         20170528
Time              8.40
INSTRUM          spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg
TD               16384
SOLVENT           DMSO
NS                  16
DS                   0
SWH        6172.839 Hz
FIDRES     0.376760 Hz
AQ       1.3271540 sec
RG               574.7
DW          81.000 usec
DE            6.00 usec
TE             300.0 K
D1      2.00000000 sec

======== CHANNEL f1 ========
NUC1                1H
P1            9.00 usec
PL1            3.00 dB
SFO1    299.8729987 MHz

F2 - Processing parameters
SI               32768
SF      299.8700023 MHz
WDW                 EM
SSB                  0
LB             0.30 Hz
GB                   0
PC                1.00
```

^{1}H NMR of 7d



```
Current Data Parameters
NAME              other
EXPNO                96
PROCNO                1

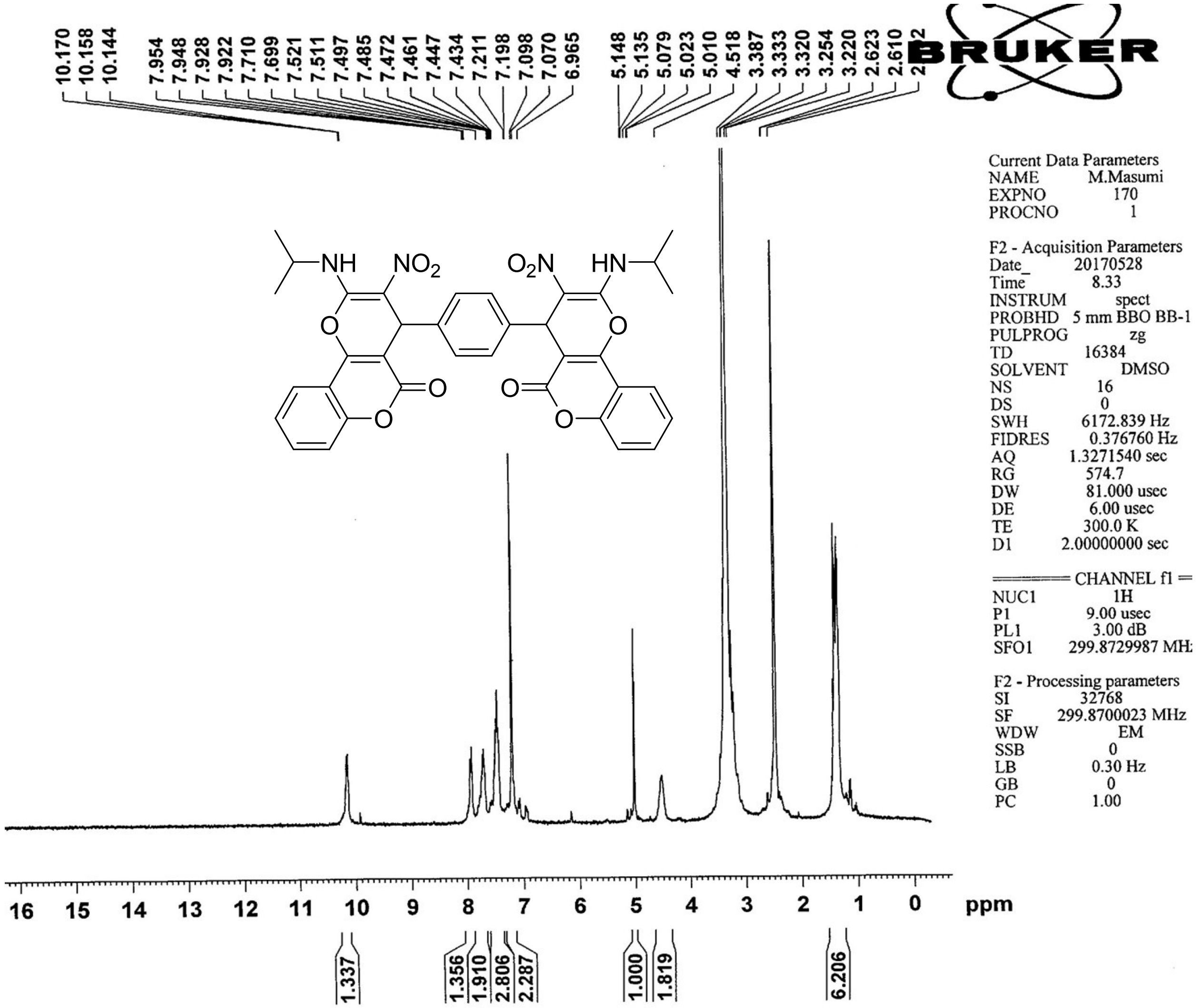
F2 - Acquisition Parameters
Date_          20180725
Time               2.52
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG            zgpg
TD                65536
SOLVENT            DMSO
NS                10000
DS                    0
SWH           15060.241 Hz
FIDRES         0.229801 Hz
AQ            2.1758451 sec
RG               1625.5
DW               33.200 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                0.00 dB
SFO1         62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                3.00 dB
PL12              21.50 dB
PL13              23.00 dB
SFO2        250.1310005 MHz

F2 - Processing parameters
SI                32768
SF           62.8951754 MHz
WDW                  EM
SSB                   0
LB                 6.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR of 7d



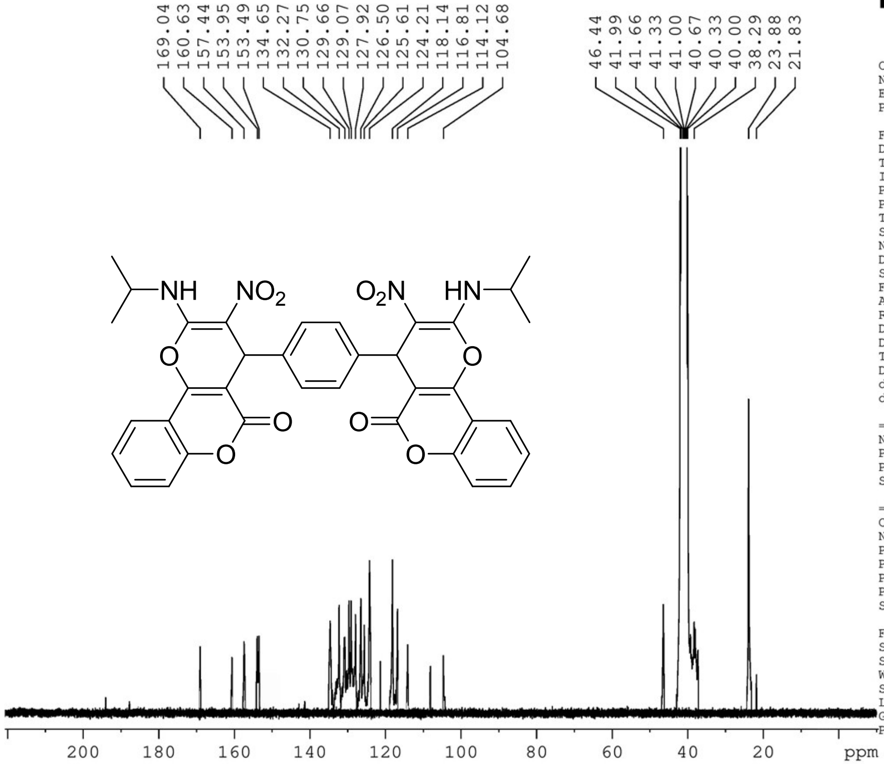
```
Current Data Parameters
NAME          M.Masumi
EXPNO              170
PROCNO               1

F2 - Acquisition Parameters
Date_         20170528
Time              8.33
INSTRUM          spect
PROBHD   5 mm BBO BB-1
PULPROG             zg
TD               16384
SOLVENT           DMSO
NS                  16
DS                   0
SWH        6172.839 Hz
FIDRES     0.376760 Hz
AQ       1.3271540 sec
RG               574.7
DW          81.000 usec
DE           6.00 usec
TE             300.0 K
D1      2.00000000 sec

======== CHANNEL f1 =
NUC1                1H
P1           9.00 usec
PL1            3.00 dB
SFO1    299.8729987 MH

F2 - Processing parameters
SI               32768
SF      299.8700023 MHz
WDW                 EM
SSB                  0
LB             0.30 Hz
GB                   0
PC                1.00
```

^{1}H NMR of 7e



```
Current Data Parameters
NAME               other
EXPNO                 83
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180703
Time                5.09
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG             zgpg
TD                 65536
SOLVENT             DMSO
NS                 10000
DS                     0
SWH            15060.241 Hz
FIDRES          0.229801 Hz
AQ             2.1758451 sec
RG                1625.5
DW                33.200 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 0.00 dB
SFO1          62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               21.50 dB
PL13               23.00 dB
SFO2         250.1310005 MHz

F2 - Processing parameters
SI                 32768
SF            62.8951754 MHz
WDW                   EM
SSB                    0
LB                  6.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR of 7e