Supporting information

Total synthesis of the plant alkaloid racemic Microthecaline A: First example of a natural product bearing tricyclic quinoline-serrulatane scaffold

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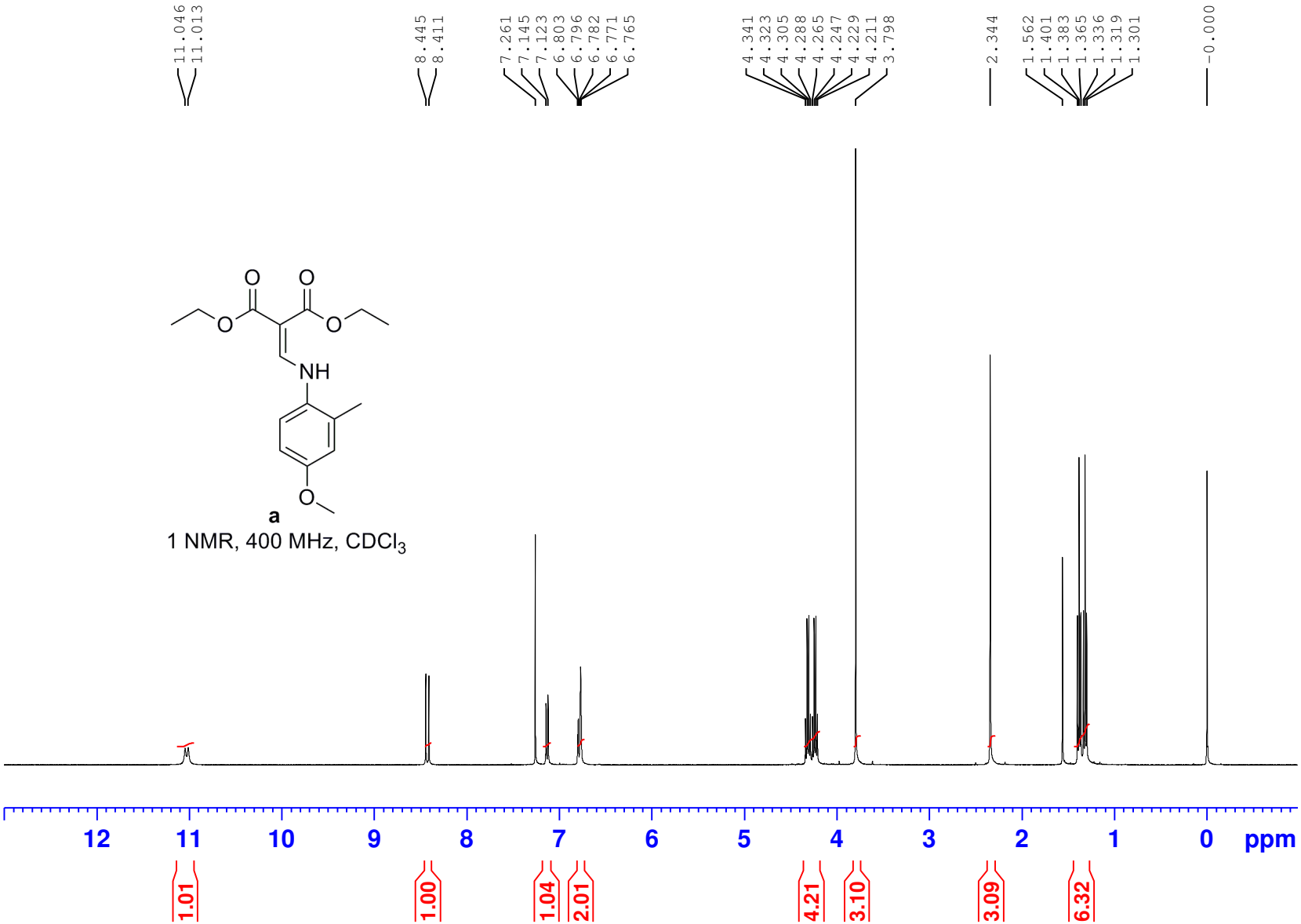
Contents:

Synthesis of ethyl 4-bromo-6-methoxy-8-methylquinoline-3-carboxylate (1) was accomplished in three steps as described below.

Diethyl 2-(((4-methoxy-2-methylphenyl)amino)methylene)malonate (a). To a stirred solution of 4-methoxy-2-methylaniline (5 g, 36.4 mmol) in dry toluene (50 mL) was added diethyl 2-(methoxymethylene)malonate (7.37 g, 36.4 mmol) and the reaction was refluxed for 12 h. On completion, the reaction mixture was cooled to room temperature, toluene was evaporated and the residue was taken in hexane and stirred for 1 hour. The solids thus obtained were filtered and dried to afford the required molecule in 94% yield (10.5 g); m.p. 99-101°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.04 – 11.01 (d, J = 13.2 Hz, 1H), 8.44 – 8.41 (d, J = 13.6 Hz, 1H), 7.14 – 7.12 (d, J = 8.8 Hz, 1H), 6.8 – 6.7 (m, 2H), 4.3 – 4.2 (q, 4H), 3.79 (s, 3H), 2.34 (s, 3H), 1.4 – 1.3 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.4, 165.9, 157, 153.3, 131.6, 129.4, 117.8, 116.5, 112.3, 92.5, 60.2, 59.8, 55.4, 17.7, 14.4, 14.3; ν_{max} (KBr)/cm^{-1}: 2944, 1721, 1427; HRMS-ESI (+) m/z: calcd for $C_{16}H_{22}NO_5$ $[M + H]^+$, 308.1492; found, 308.1496.

Ethyl 4-hydroxy-6-methoxy-8-methylquinoline-3-carboxylate (b). A stirred solution of **a** (10 g, 32.5 mmol) in diphenyl ether (100 mL) was heated to reflux for 2 hours. The reaction mixture was cooled to room temperature and diluted with hexane. The solids thus obtained were filtered and dried to afford **b** in 76% yield (6.5 g); m.p. 266-268°C.^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.93 (s, 1H), 7.47 – 7.46 (d, J = 2.8 Hz, 1H), 7.3 – 7.2 (m, 1H), 4.5 – 4.4 (q, J = 7.2 Hz, 2H), 3.96 (s, 3H), 2.75 (s, 3H), 1.47 – 1.44 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9, 164.9, 156.1, 143.2, 132.1, 130, 129.1, 128.8, 123.4, 122.6, 118.6, 108.6, 103.5, 59.5, 55.3, 16.9, 14.3; ν_{max} (KBr)/cm^{-1}: 3250, 2474, 1702; HRMS-ESI (+) m/z: calcd for $C_{14}H_{16}NO_4$ $[M + H]^+$, 262.1074; found, 262.1064.

Ethyl 4-bromo-6-methoxy-8-methylquinoline-3-carboxylate (1). To a stirred solution of **b** (5 g, 19.1 mmol) in DMF (50 mL) was added $POBr_3$ (2.33 mL, 22.9 mmol) drop wise at 0°C and the resulting mixture was left to stir at room temperature for 2 hours. On completion, the reaction mixture was diluted with water and solids obtained were filtered and dried to afford **1** in 84% yield (5.2 g); m.p. 117-119°C.^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.93 (s, 1H), 7.47 – 7.46 (d, J = 2.8 Hz, 1H), 7.3 – 7.2 (m, 1H), 7.26 (d, J = 2.4 Hz, 1H), 4.24 – 4.18 (q, J = 7.2 Hz, 2H), 3.8 (s, 3H), 2.5 (s, 3H), 1.29 – 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 158.9, 145.6, 144.7, 139.6, 132.9, 128.9, 126.3, 124.5, 103.6, 62, 55.5, 18.2, 14.2; ν_{max} (KBr)/cm^{-1}: 3414, 2946, 1720; HRMS-ESI (+) m/z: calcd for $C_{14}H_{15}BrNO_3$ $[M + H]^+$, 324.023; found, 324.022.

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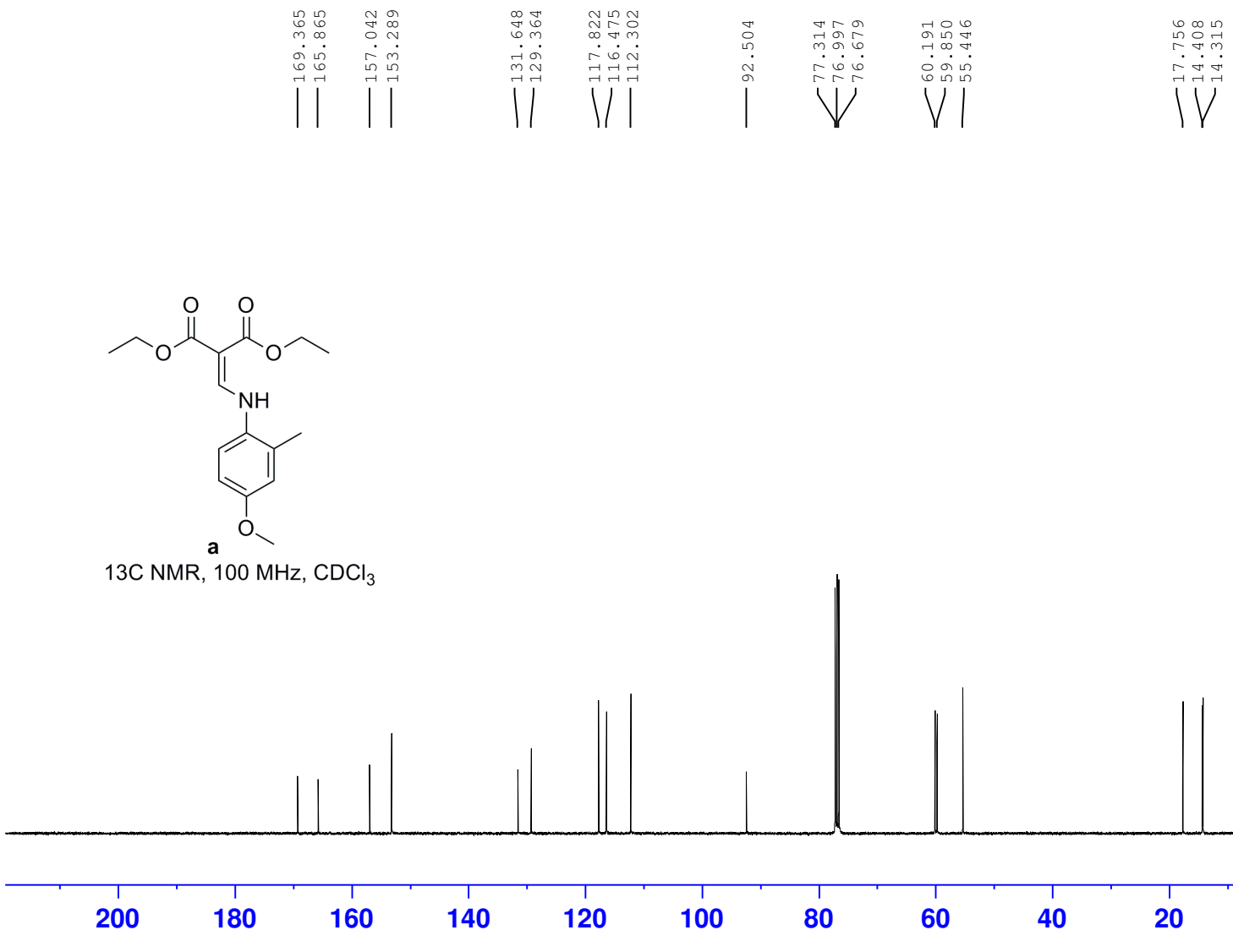


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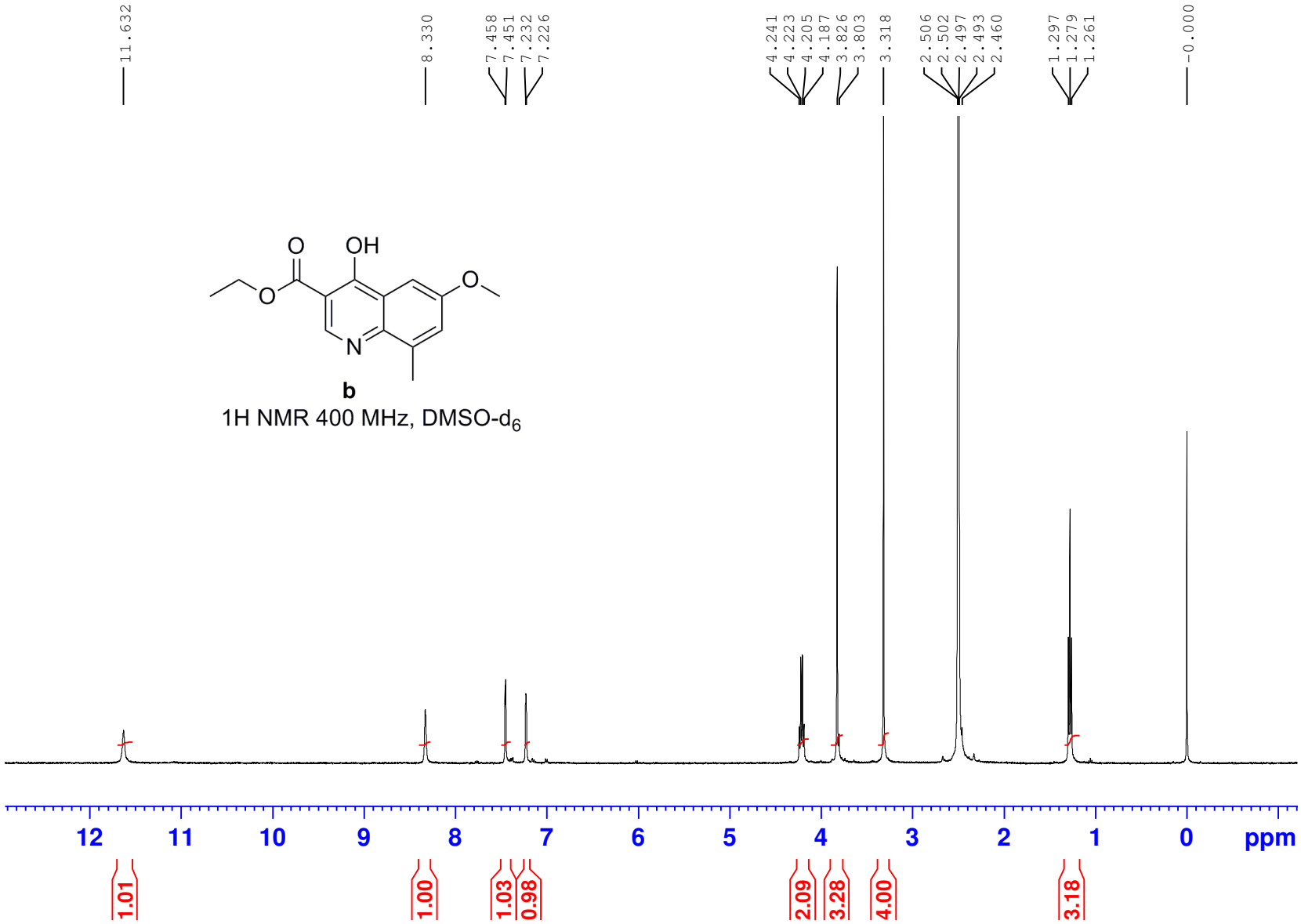


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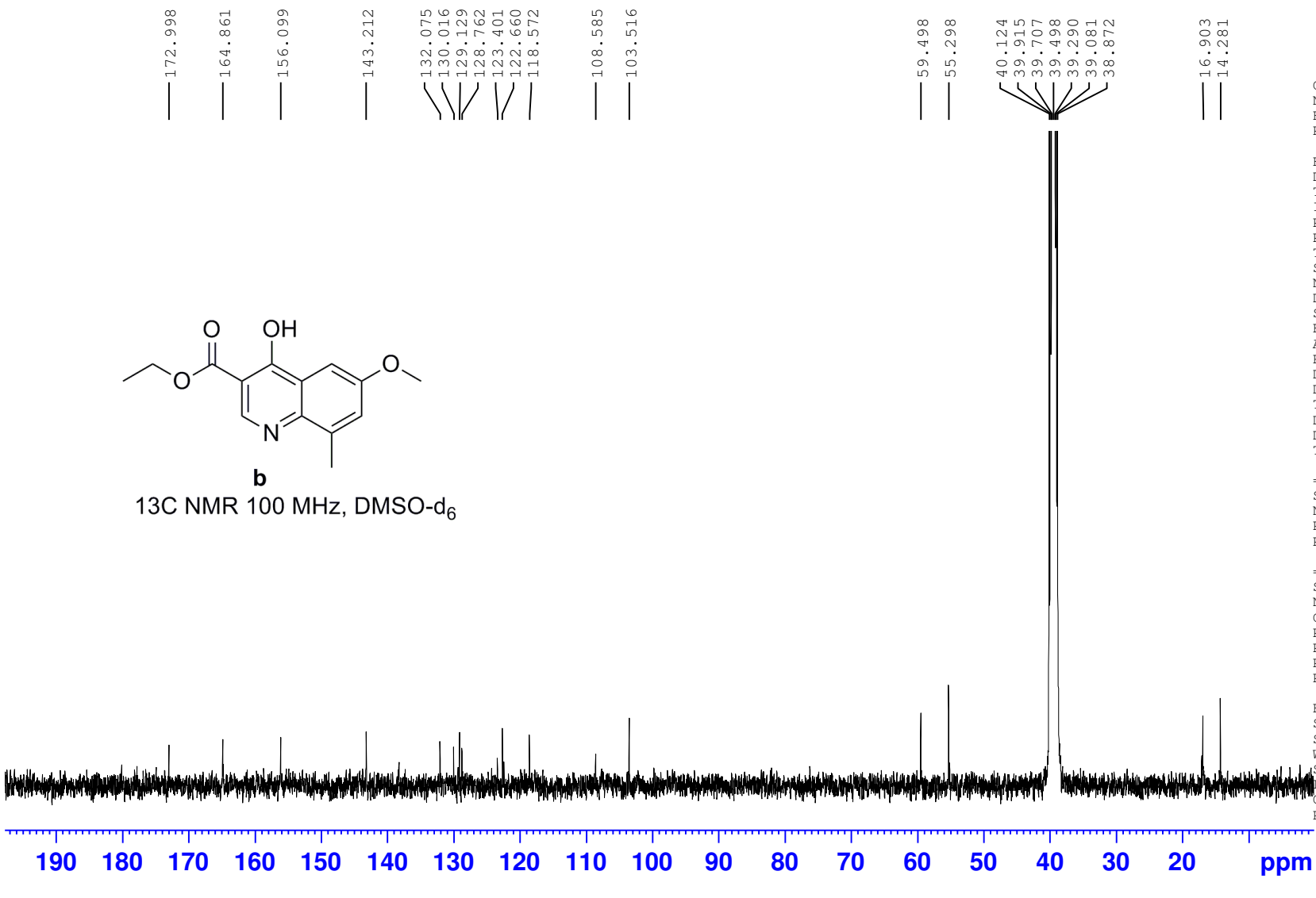


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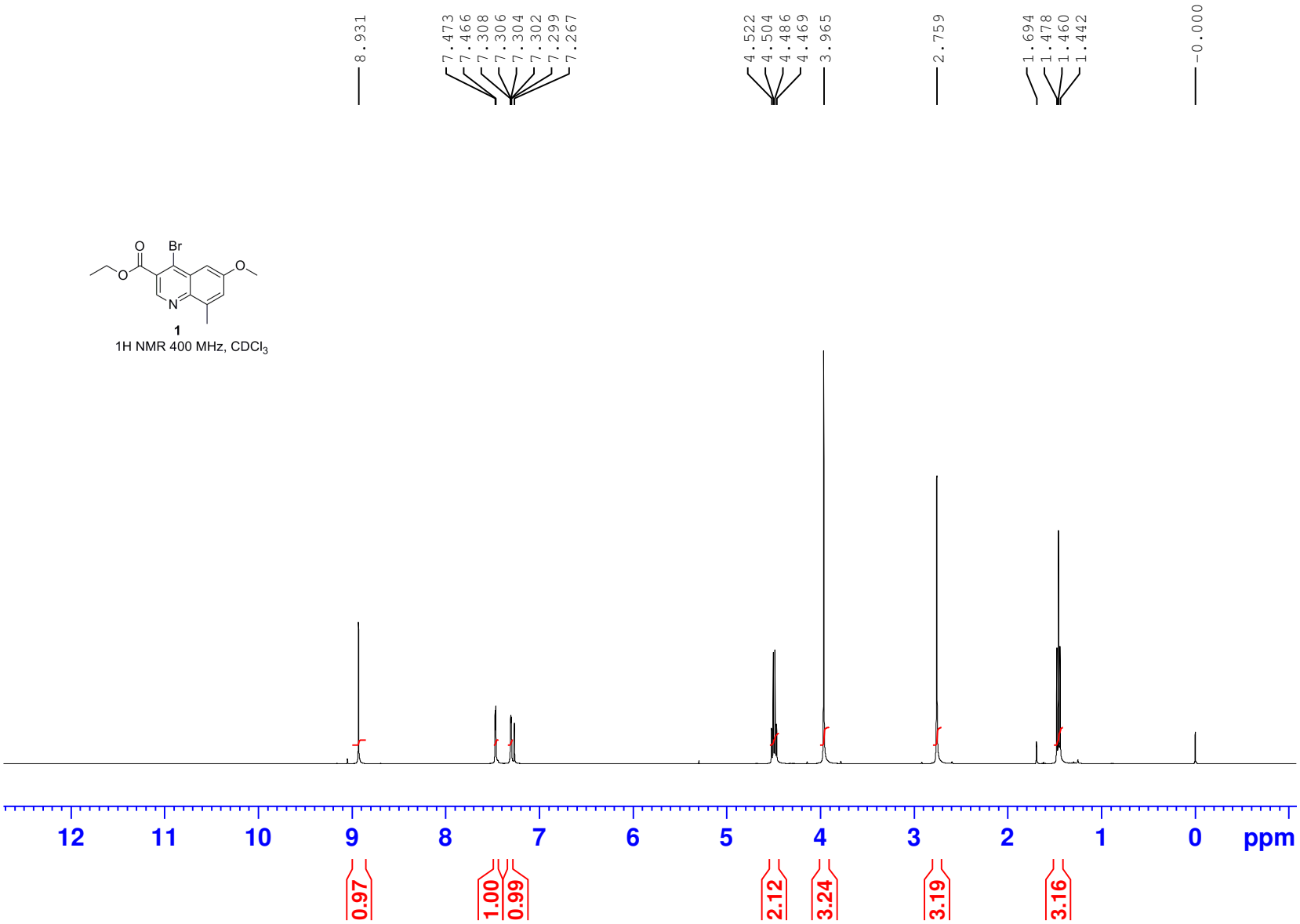


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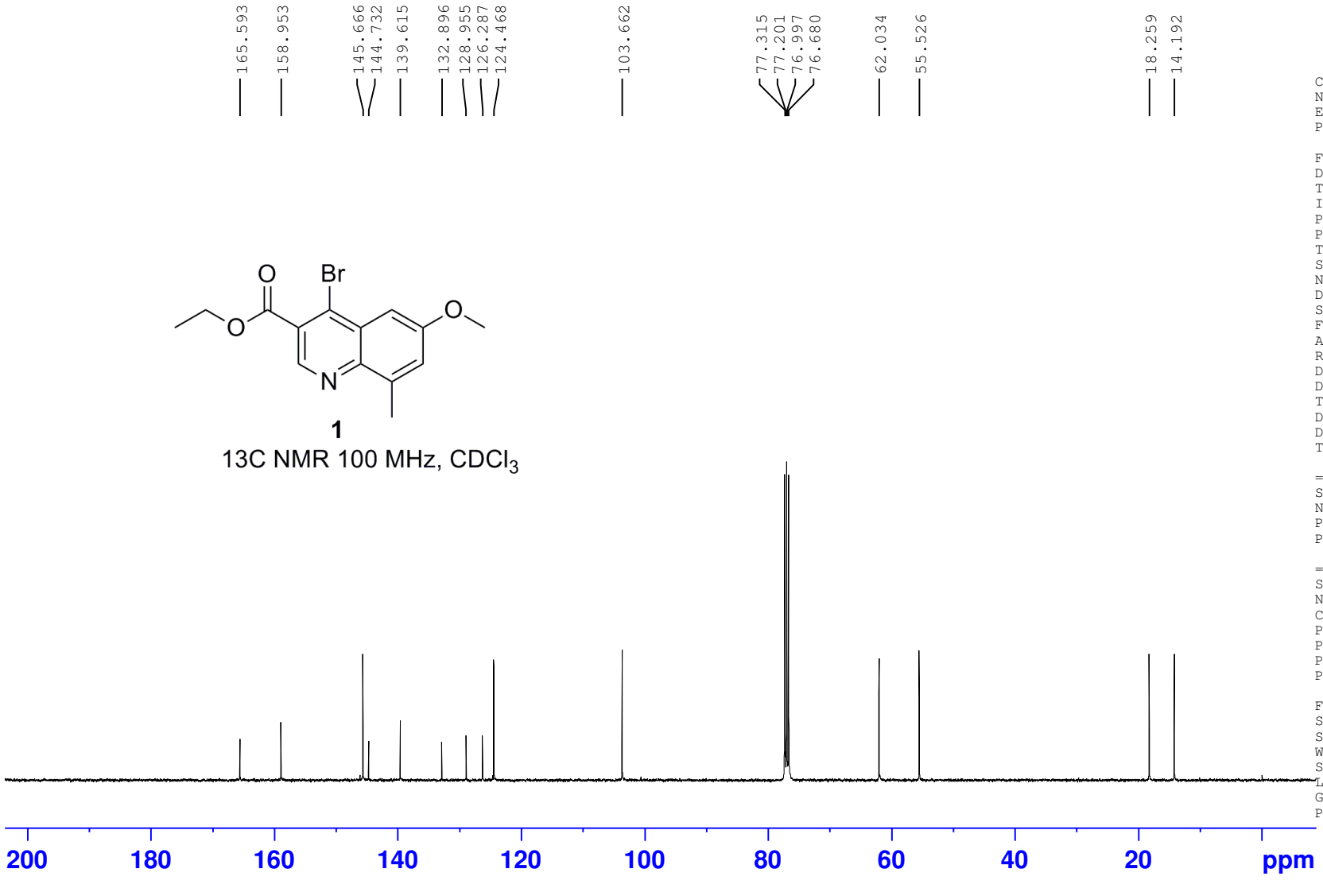


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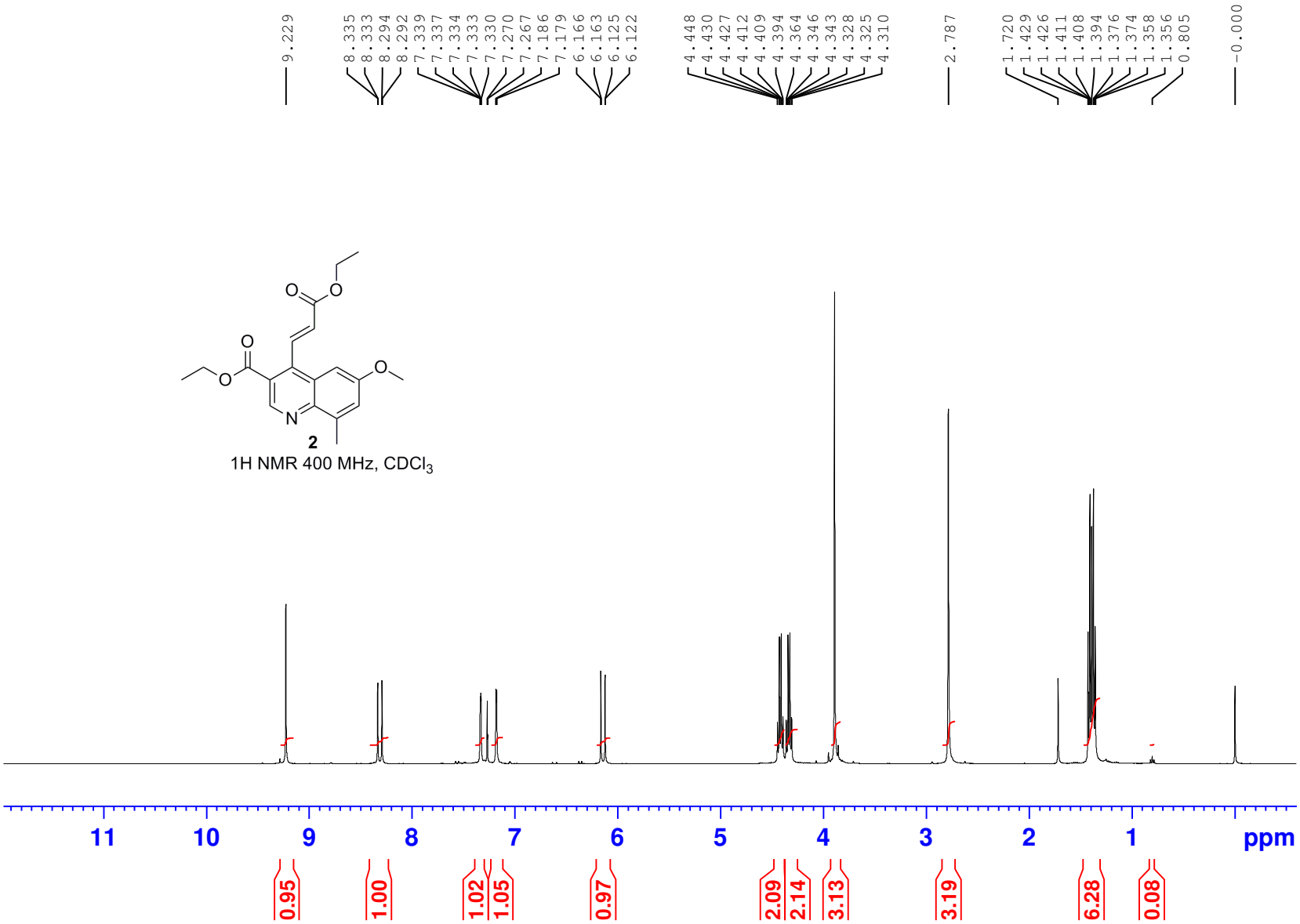


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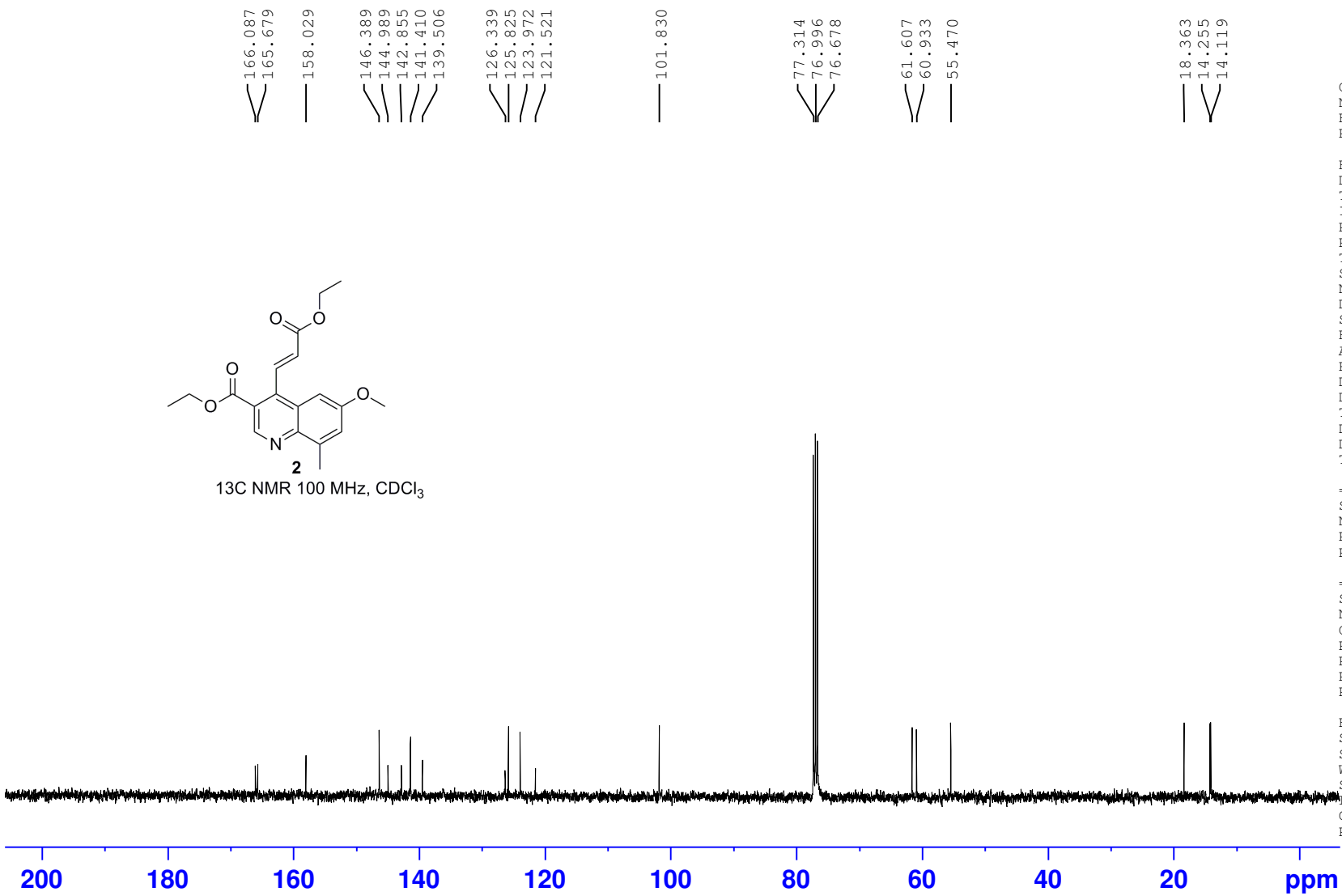


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PLW13        0.15210000 W

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ANL-MCL5-NMR-001

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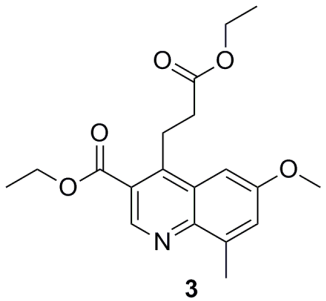

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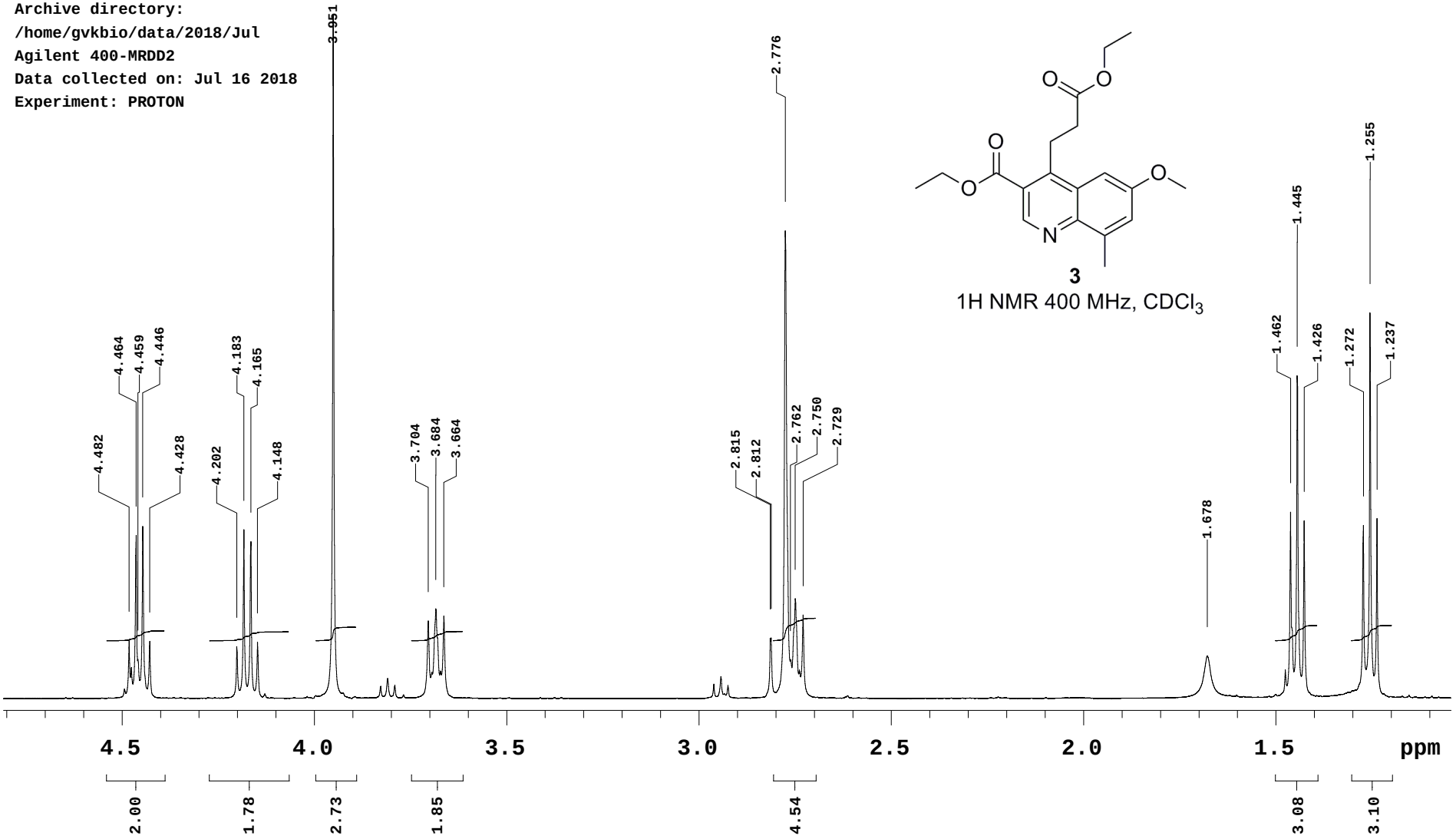

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TP-MA-01-05
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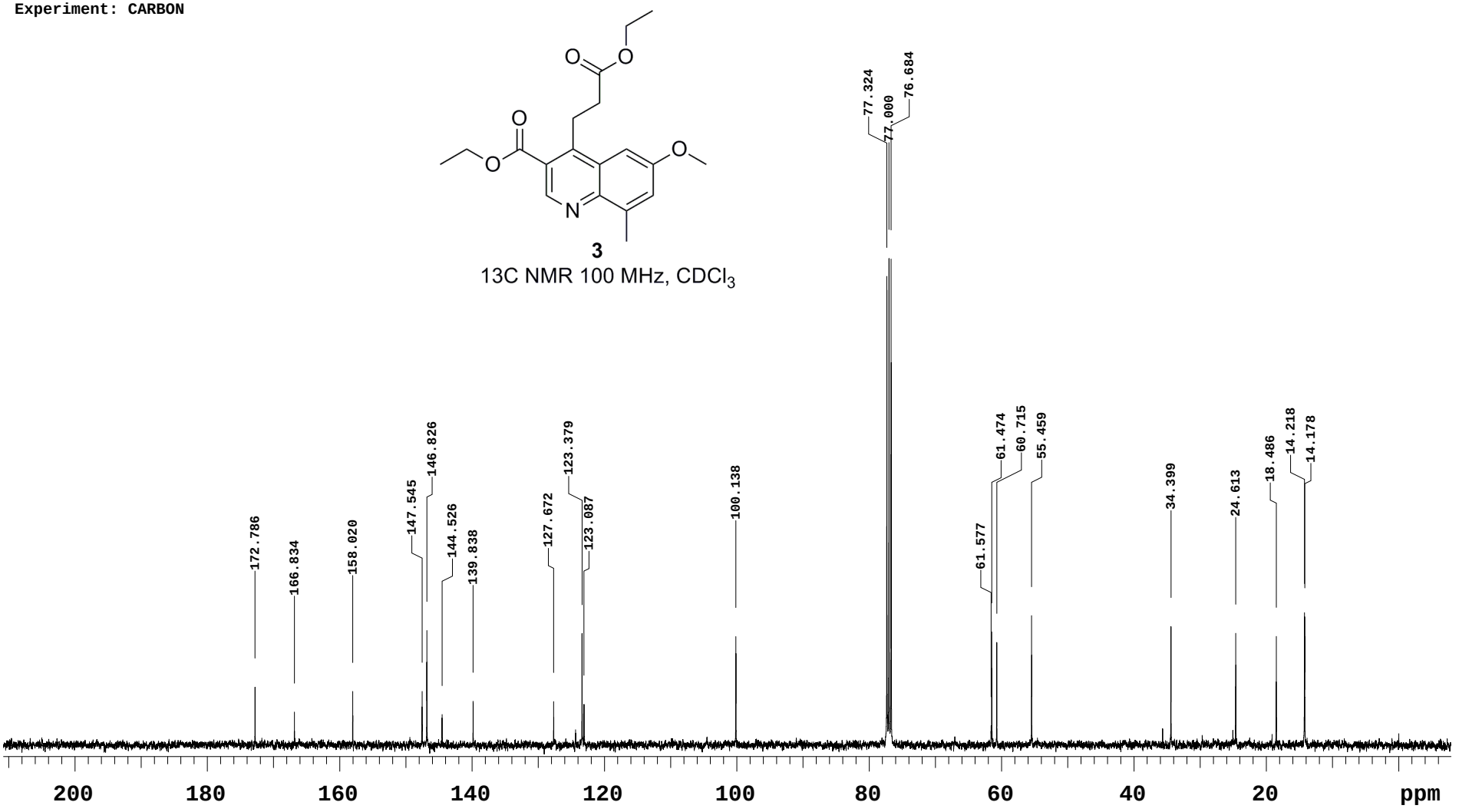

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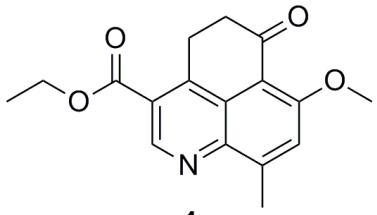

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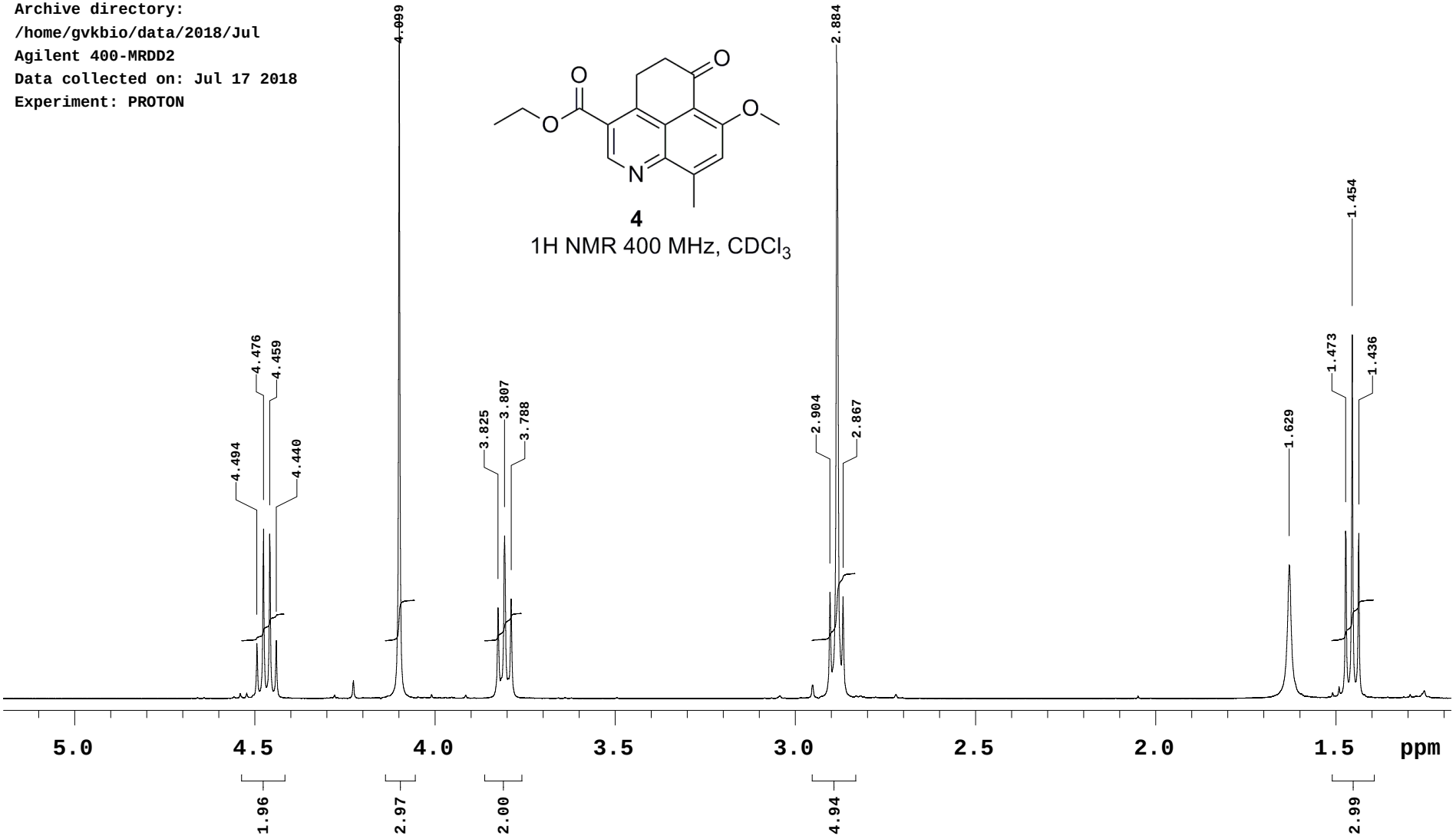

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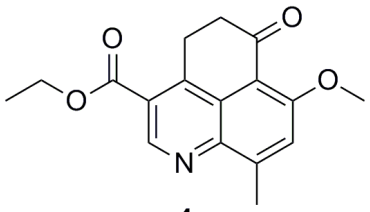

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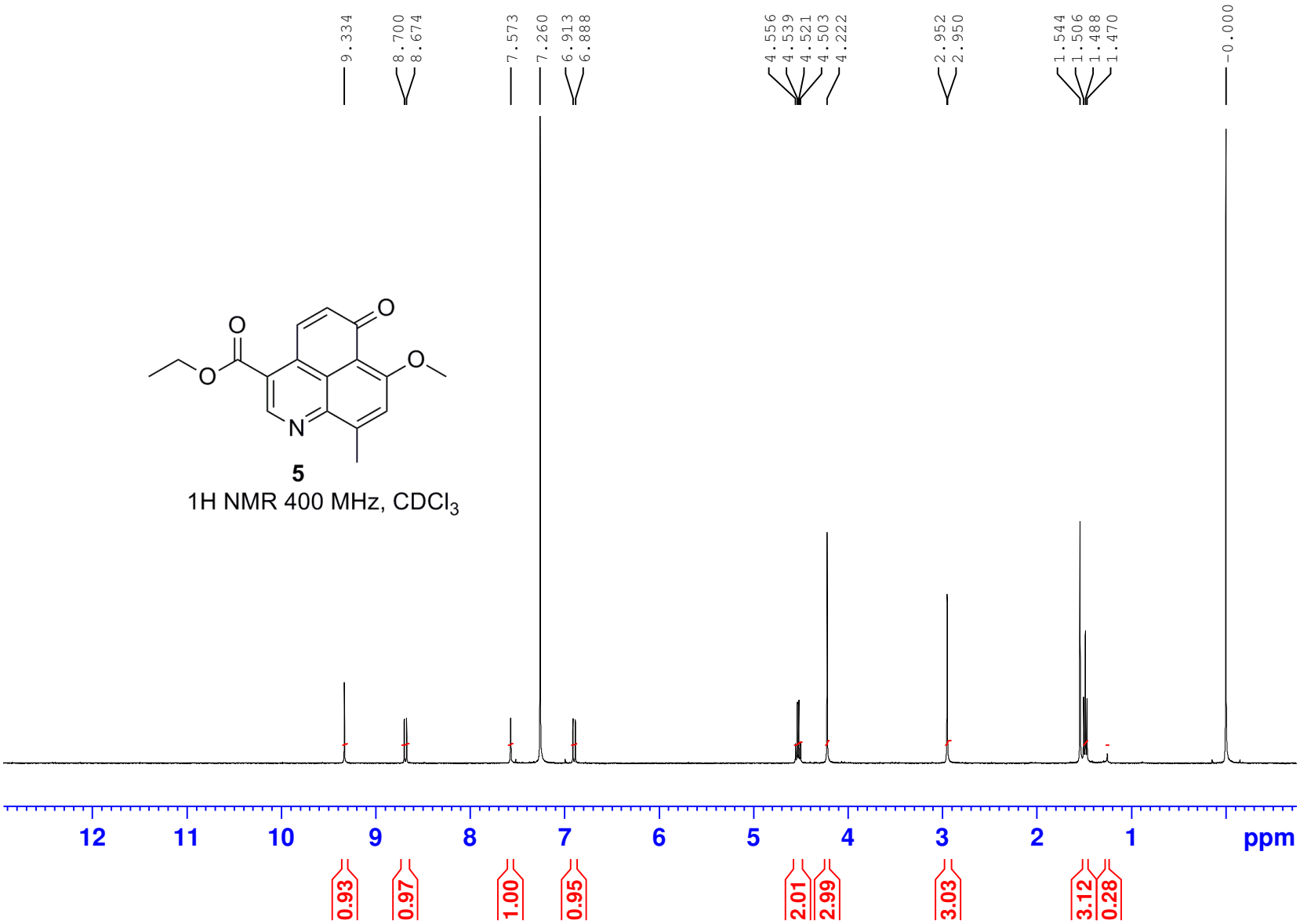


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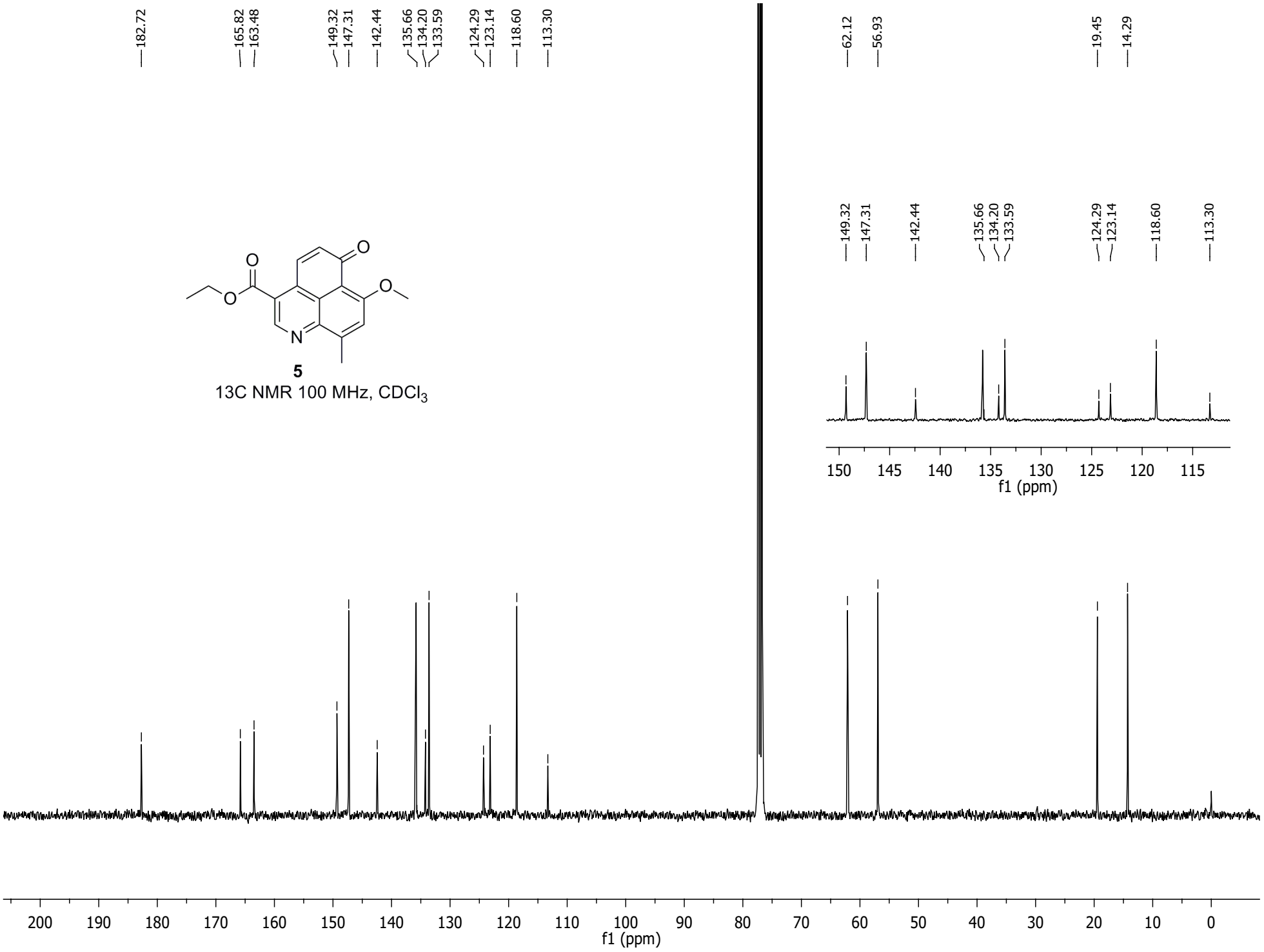
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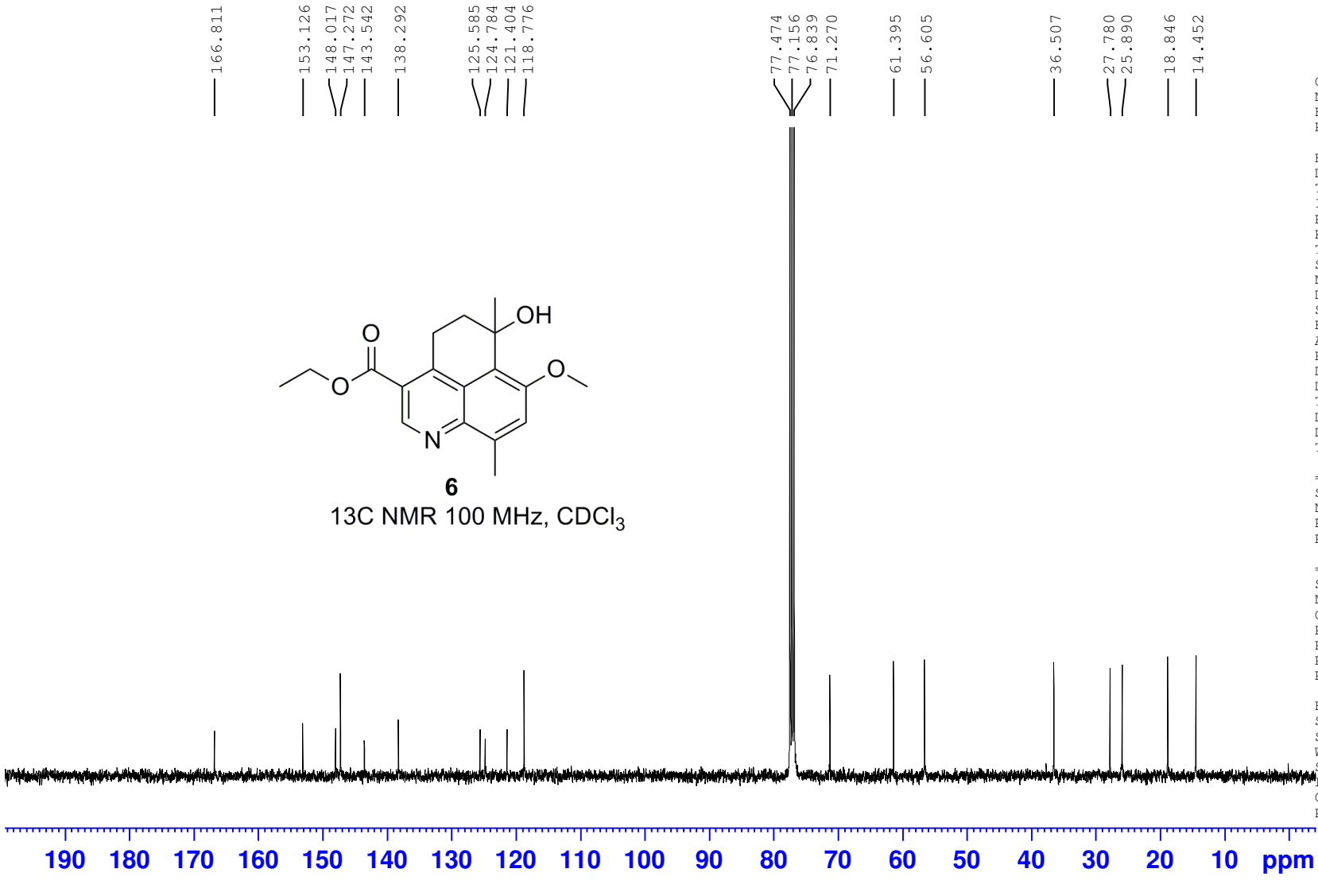
f1 (ppm)
f1 (ppm)



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NUC1                 13C
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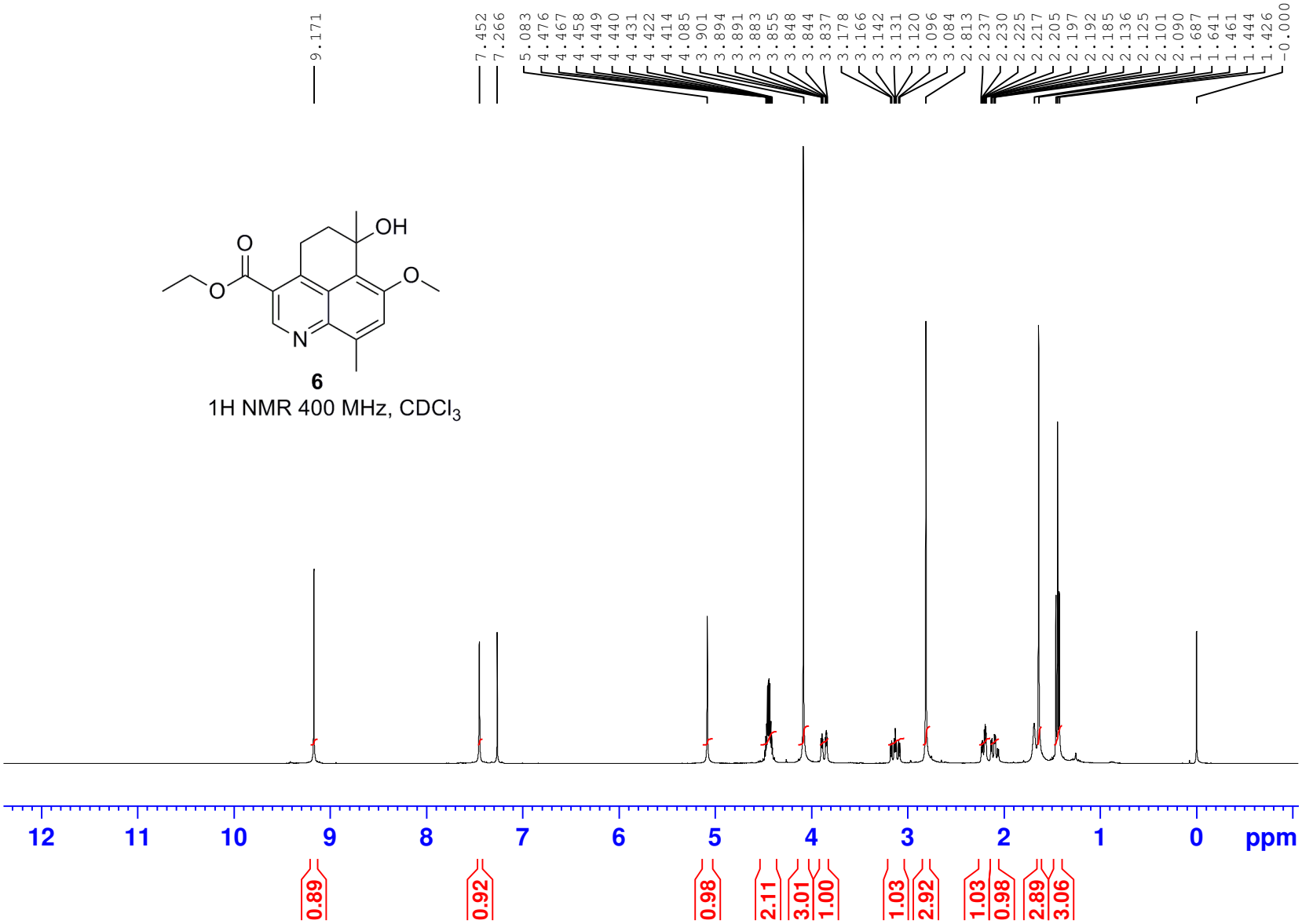
```

ANL-MCL5-NMR-001



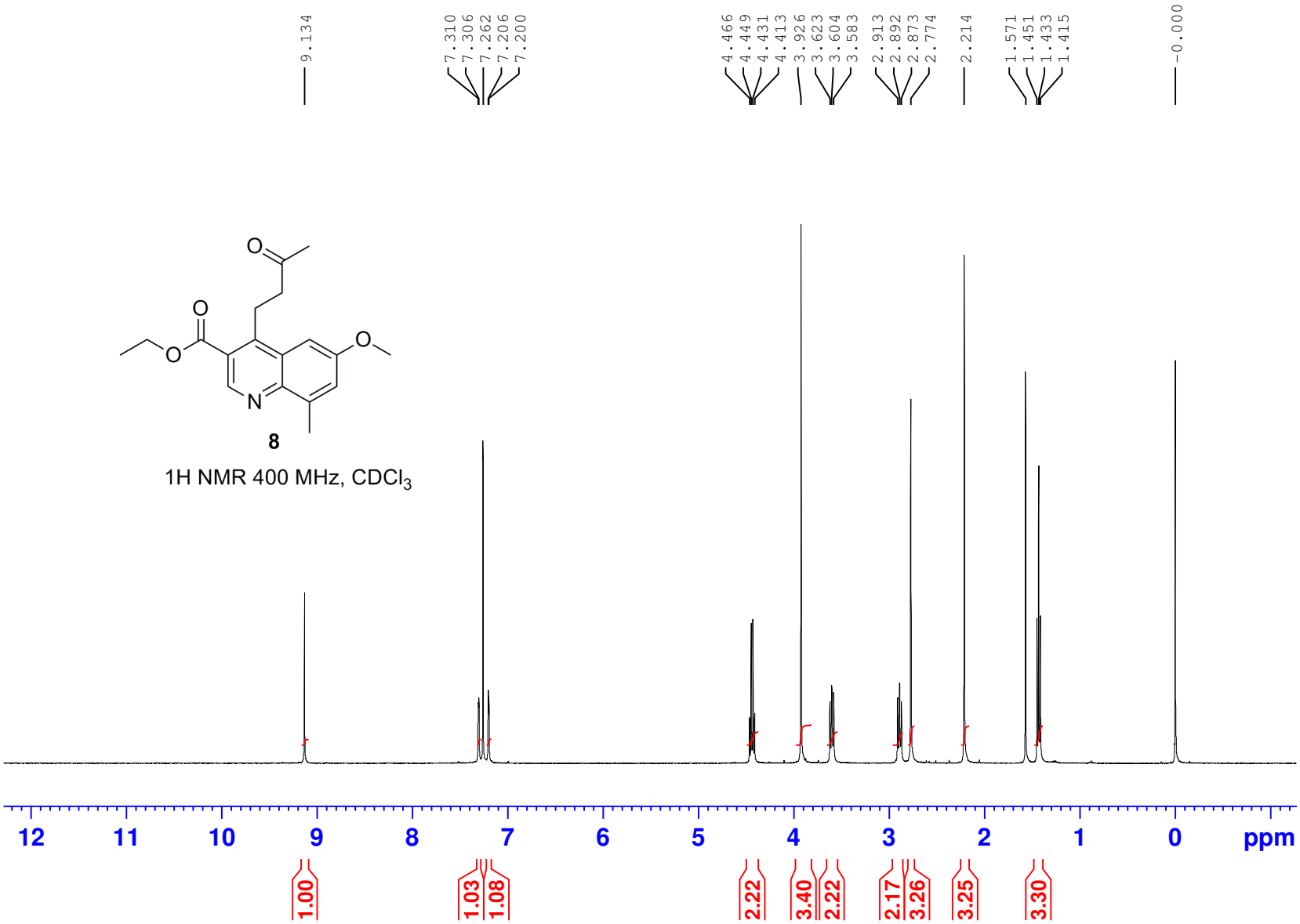

```
Current Data Parameters
NAME         511809A0037
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180903
Time                7.25
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 110.59
DW                62.400 usec
DE                 6.50 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  9.75 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                 65536
SF          400.1300072 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

ANL-MCL5-NMR-001



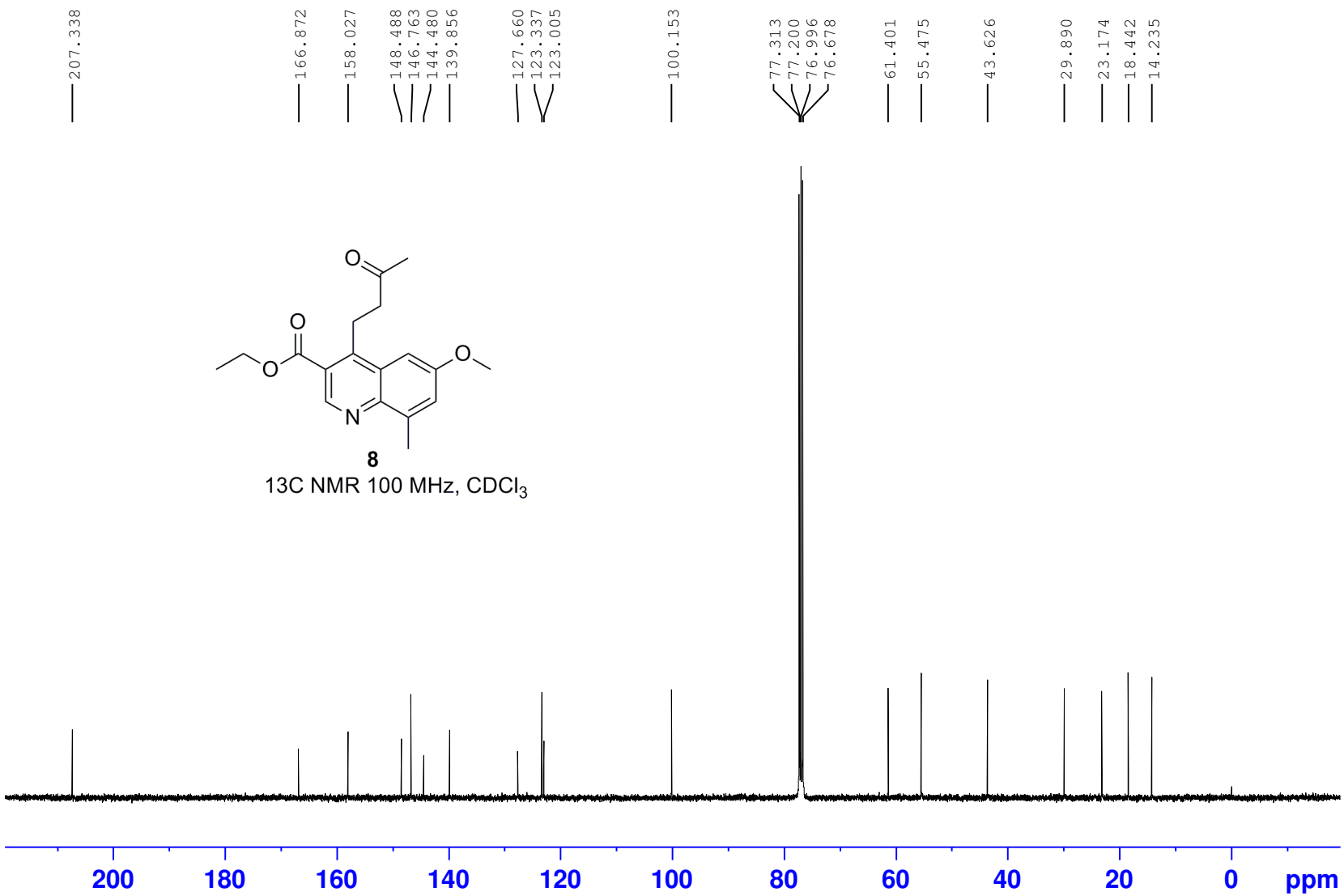

```
Current Data Parameters
NAME          511903B9690
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190322
Time                7.52
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                110.59
DW                62.400 usec
DE                 6.50 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                 9.75 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                 65536
SF            400.1300089 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

ANL-MCL5-NMR-001




```
Current Data Parameters
NAME         511903C0629
EXPNO                  2
PROCNO                 1

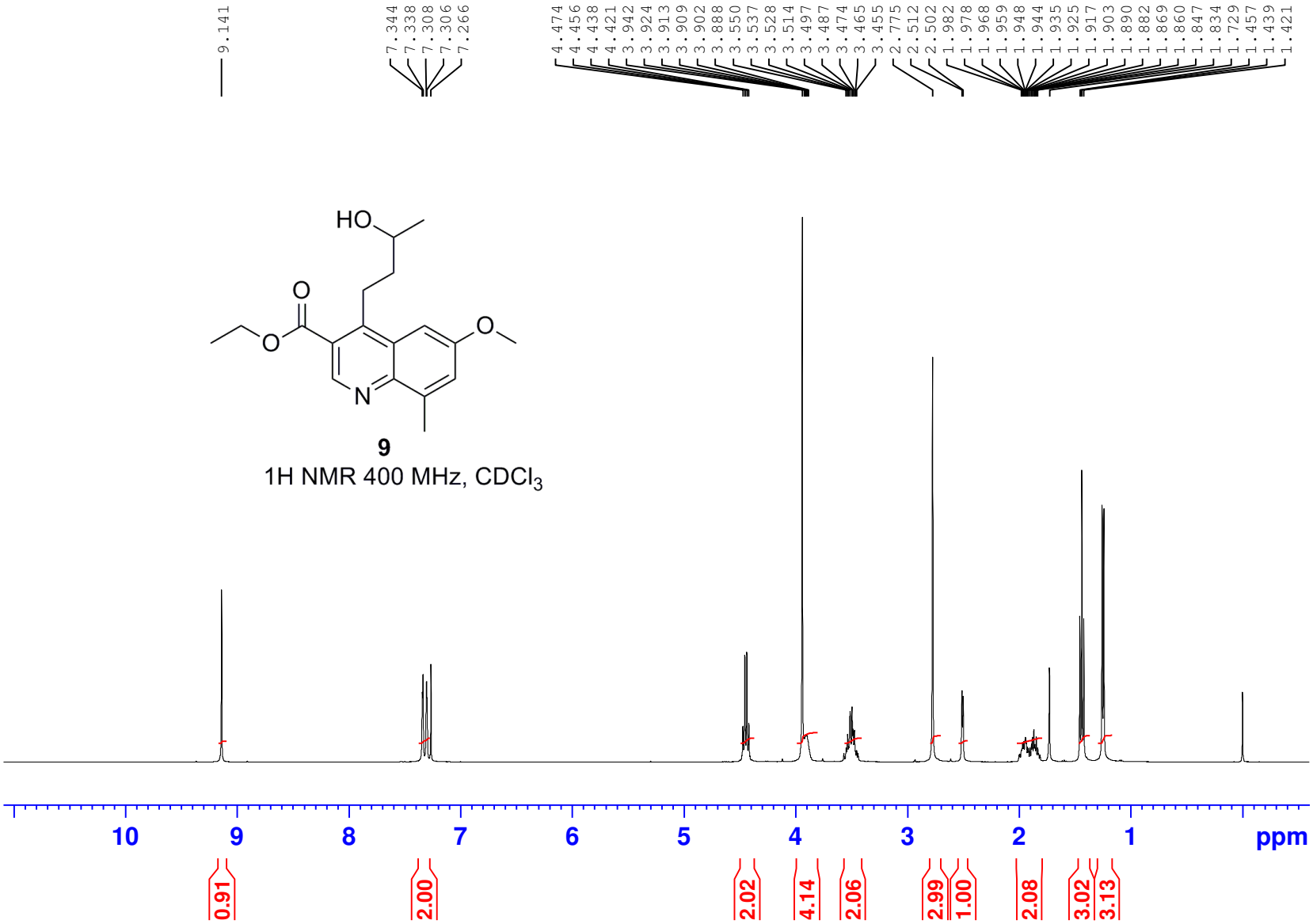
F2 - Acquisition Parameters
Date_           20190323
Time               22.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               195.29
DW               20.800 usec
DE                6.50 usec
TE               299.0 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1         78.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         16.00000000 W
PLW12         0.18777999 W
PLW13         0.15210000 W

F2 - Processing parameters
SI                 32768
SF           100.6127712 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

ANL-MCL5-NMR-001



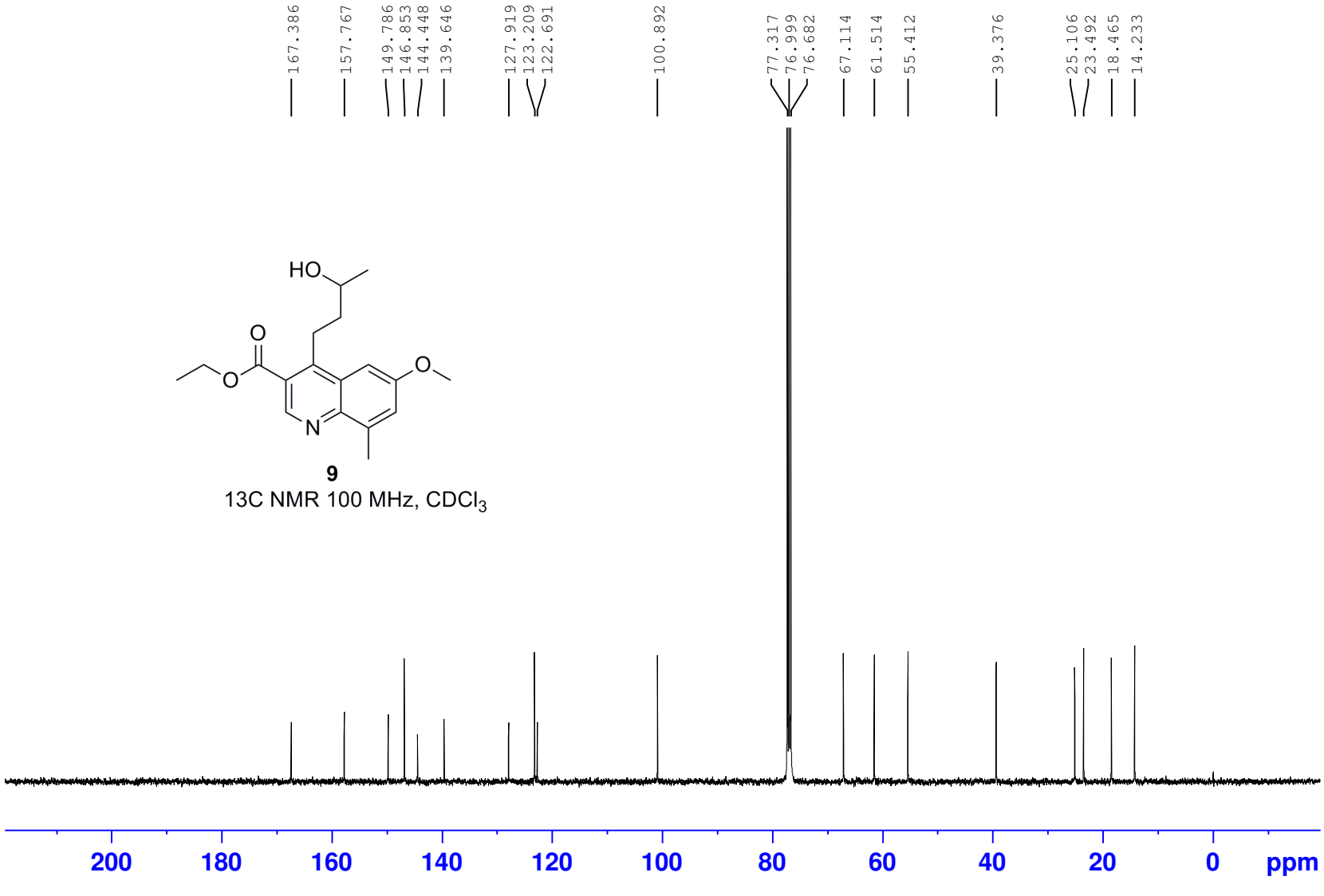

```
Current Data Parameters
NAME         511903C0627
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190323
Time                7.22
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 96.76
DW                62.400 usec
DE                 6.50 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                 9.75 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                 65536
SF          400.1300069 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

ANL-MCL5-NMR-001



9

13C NMR 100 MHz, $CDCl_3$

```
Current Data Parameters
NAME         511903C0627
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190323
Time                8.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                195.29
DW                20.800 usec
DE                 6.50 usec
TE                298.2 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                    1

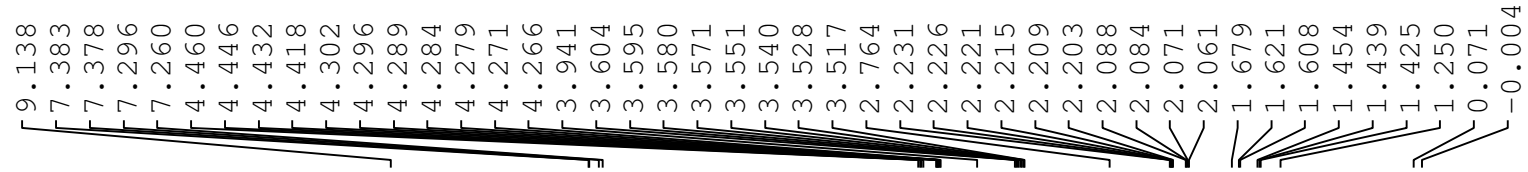
======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                10.00 usec
PLW1         78.00000000 W

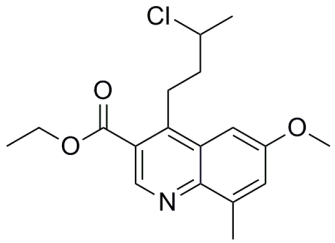
======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         16.00000000 W
PLW12         0.18777999 W
PLW13         0.15210000 W

F2 - Processing parameters
SI                 32768
SF           100.6127713 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

ANL-MCL5-NMR-001

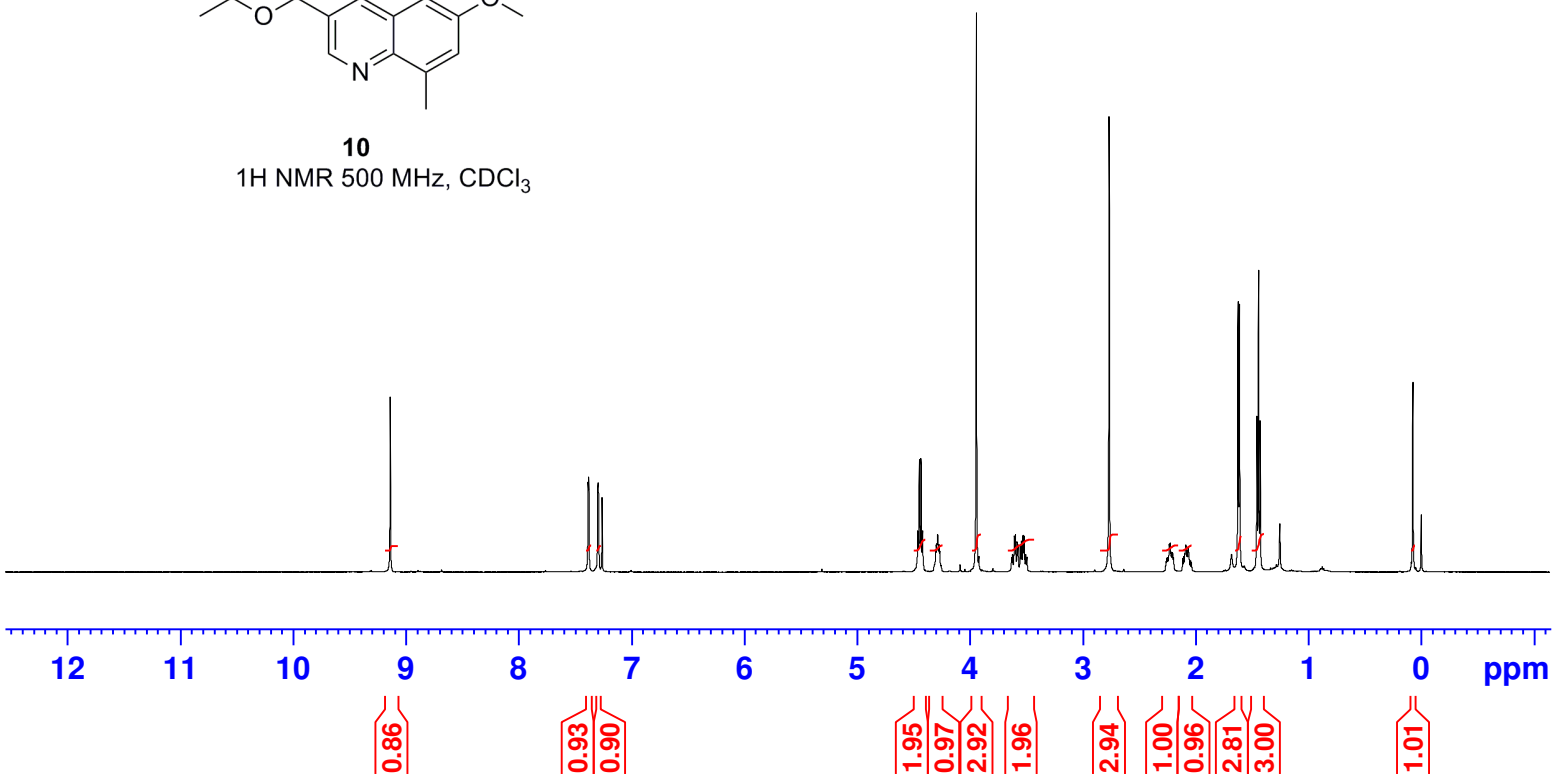
TP-MA-1158-13





10

1H NMR 500 MHz, $CDCl_3$

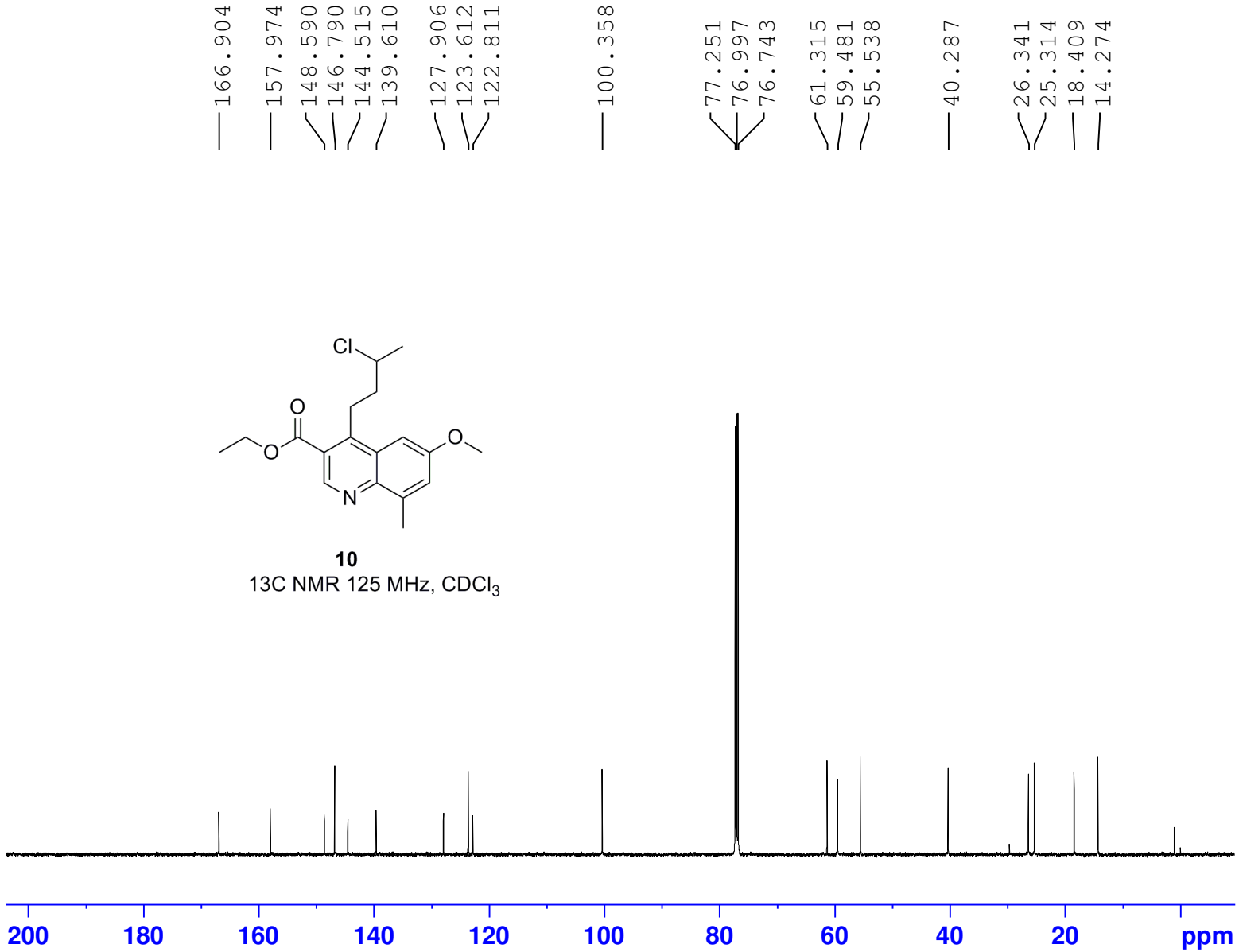



```
Current Data Parameters
NAME         511903C1076
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190325
Time              20.07 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                79.68
DW               50.000 usec
DE                6.50 usec
TE                300.2 K
D1           1.00000000 sec
TD0                    1
SFO1        500.1330885 MHz
NUC1                  1H
P1               10.00 usec
PLW1        20.38699913 W

F2 - Processing parameters
SI                 65536
SF          500.1300127 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

TP-MA-1158-13

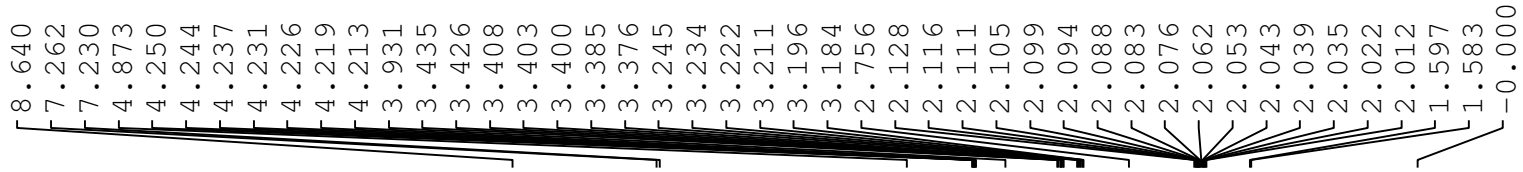


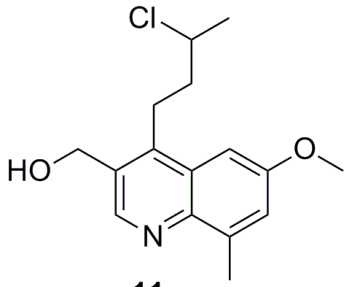

```
Current Data Parameters
NAME         511903C1076
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190325
Time              20.10 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  591
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.72
DW               16.800 usec
DE                6.50 usec
TE               300.3 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7703643 MHz
NUC1               13C
P1               10.00 usec
PLW1        79.88800049 W
SFO2        500.1320005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2        20.38699913 W
PLW12        0.25169000 W
PLW13        0.16023000 W

F2 - Processing parameters
SI                32768
SF          125.7577920 MHz
WDW                EM
SSB       0
LB               2.00 Hz
GB        0
PC               1.40
```

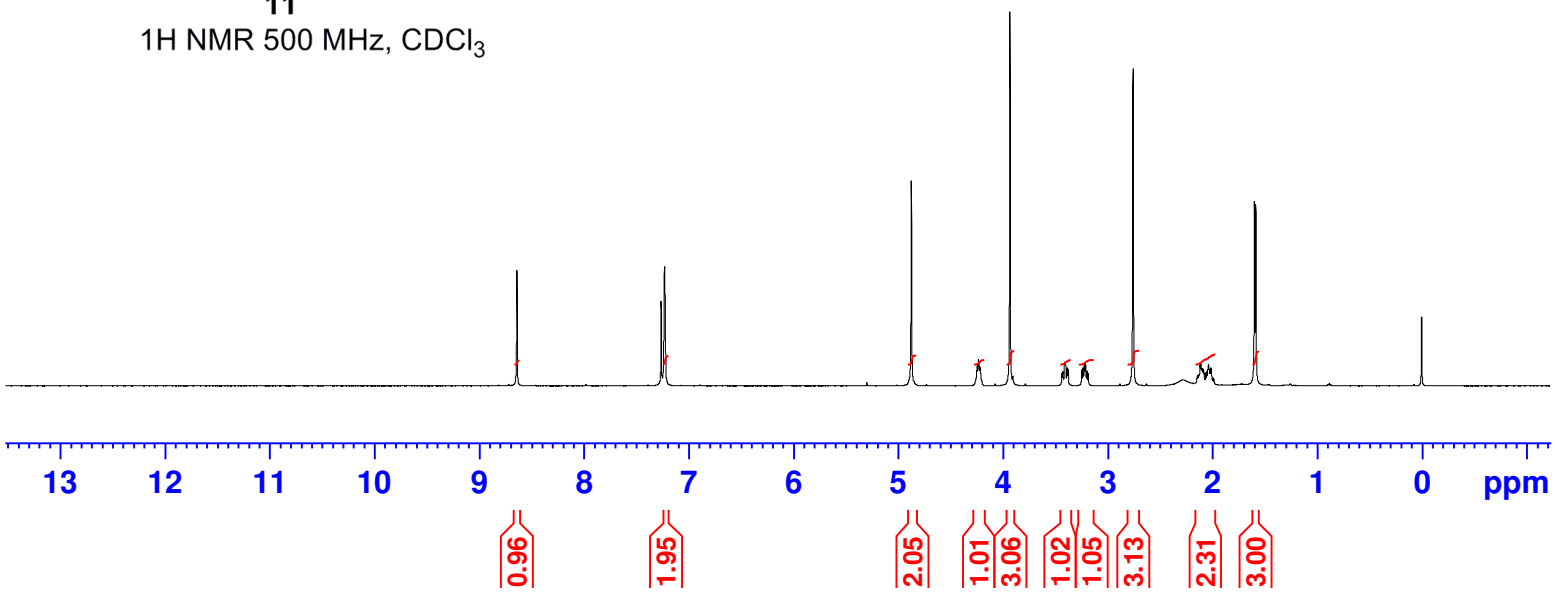
TP--MA-1158-14





11

1H NMR 500 MHz, $CDCl_3$

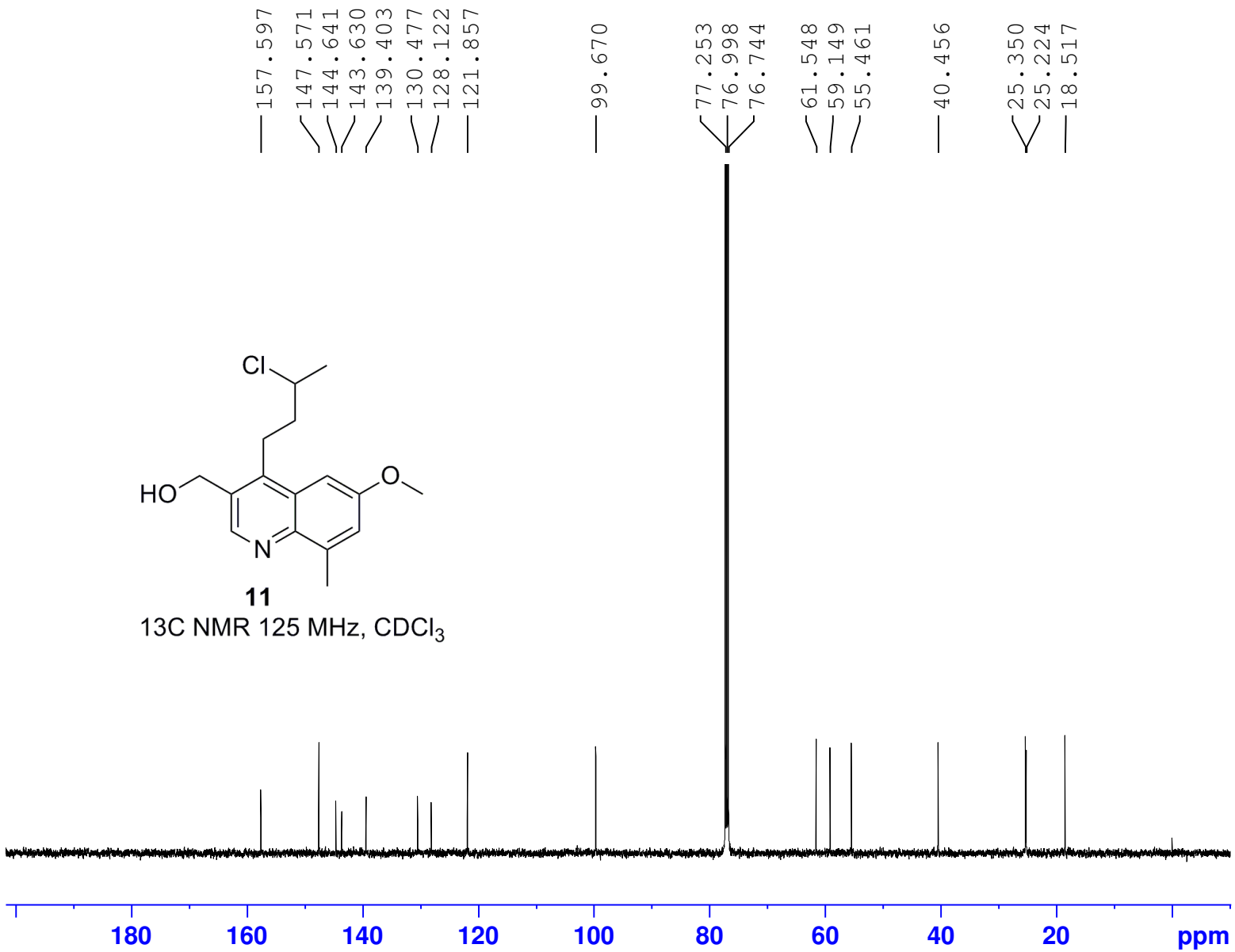



```
Current Data Parameters
NAME         511903C1077
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190325
Time              20.55 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG               111.07
DW                50.000 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1
SFO1        500.1330885 MHz
NUC1                  1H
P1                10.00 usec
PLW1        20.38699913 W

F2 - Processing parameters
SI                 65536
SF          500.1300117 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

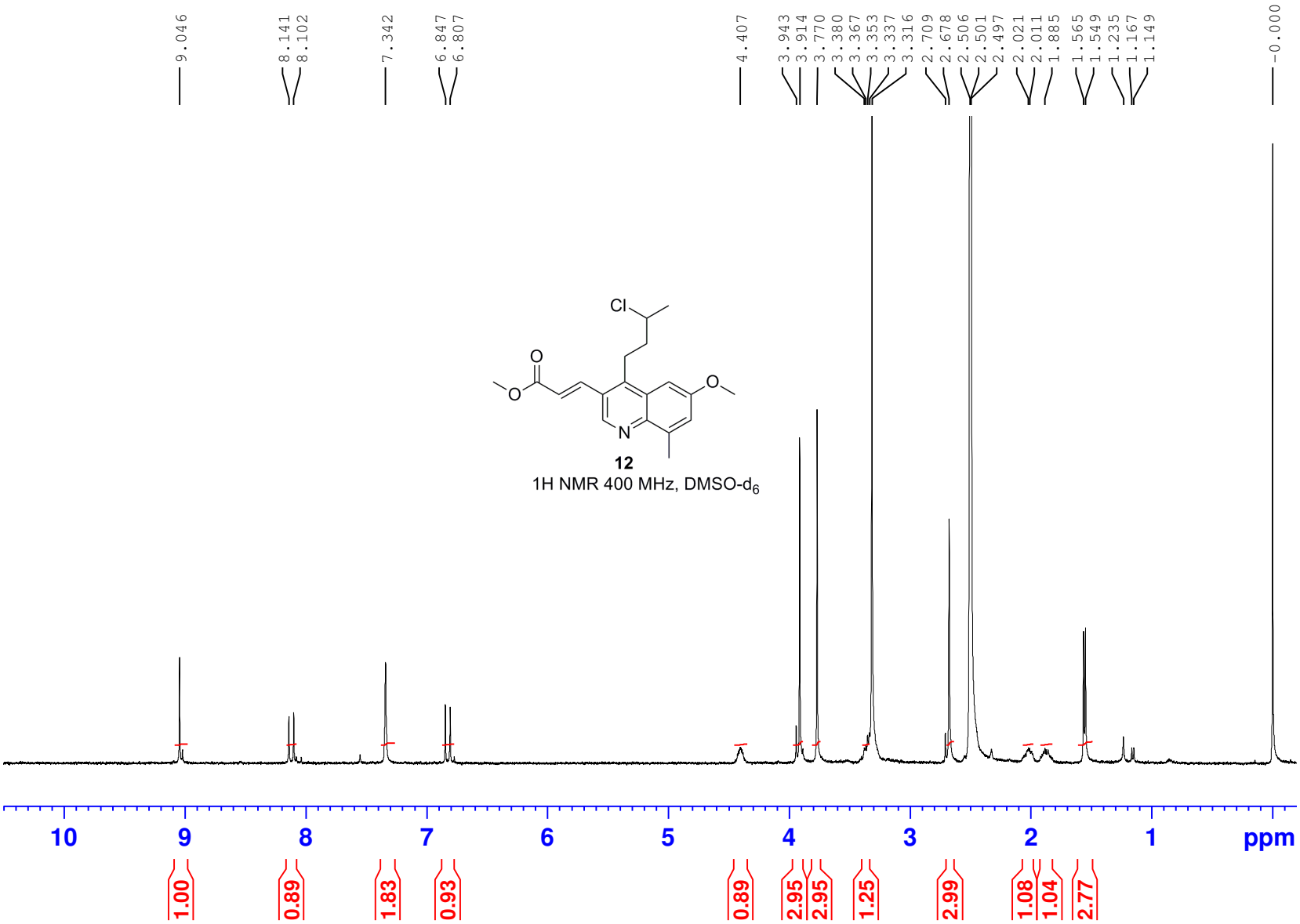
TP--MA-1158-14




```
Current Data Parameters
NAME         511903C1077
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190325
Time              21.01 h
INSTRUM             spect
PROBHD   Z119470_0294 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                  380
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.72
DW               16.800 usec
DE                6.50 usec
TE               298.1 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7703643 MHz
NUC1               13C
P1               10.00 usec
PLW1        79.88800049 W
SFO2        500.1320005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2        20.38699913 W
PLW12        0.25169000 W
PLW13        0.16023000 W

F2 - Processing parameters
SI                32768
SF          125.7577920 MHz
WDW                 EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.40
```



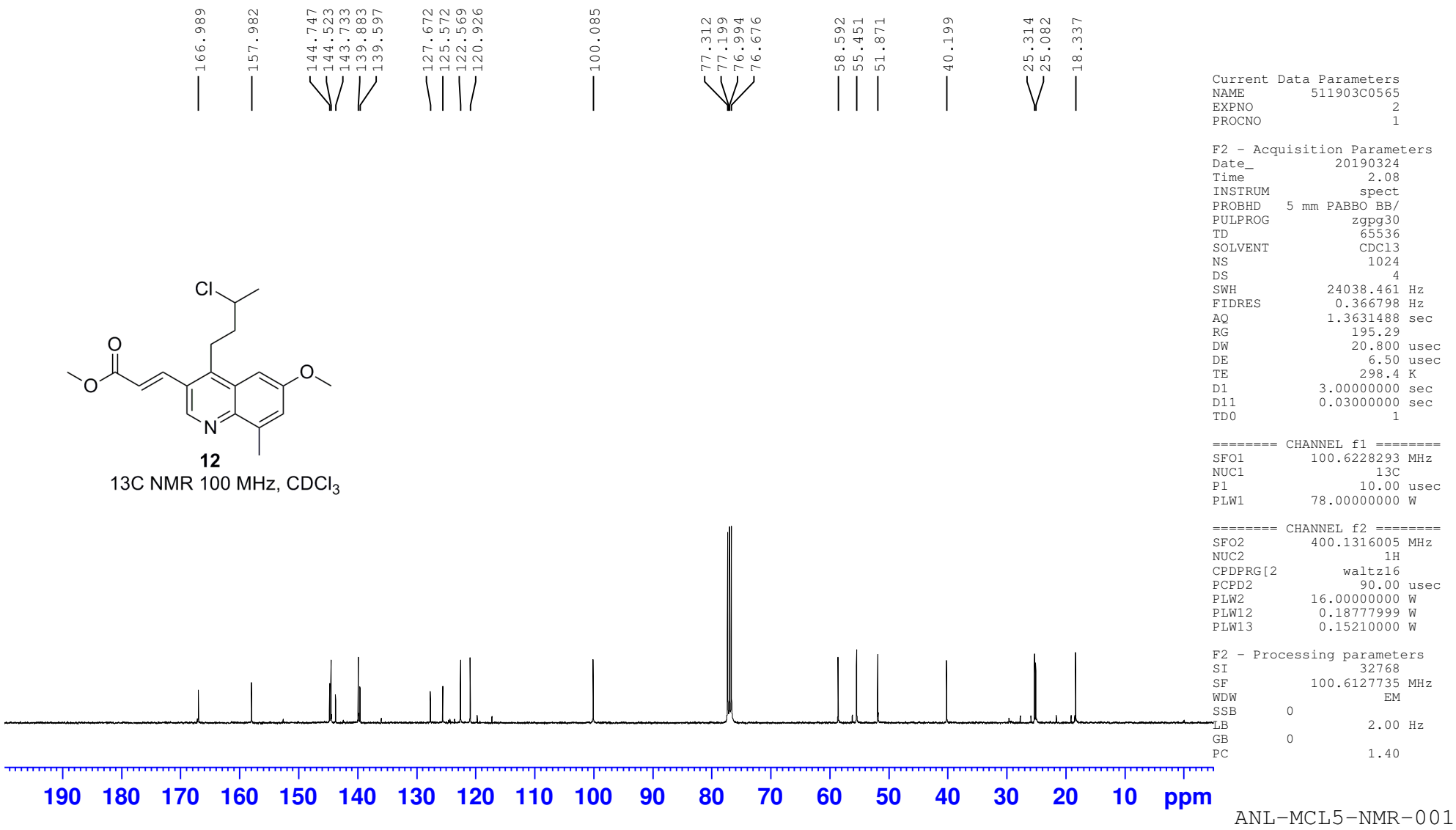

```
Current Data Parameters
NAME         511903B9686
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190322
Time                9.20
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 195.29
DW                 62.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  9.75 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                 65536
SF          400.1300025 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

ANL-MCL5-NMR-001




```
Current Data Parameters
NAME         511903C0565
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190324
Time                2.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               195.29
DW               20.800 usec
DE                6.50 usec
TE                298.4 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1

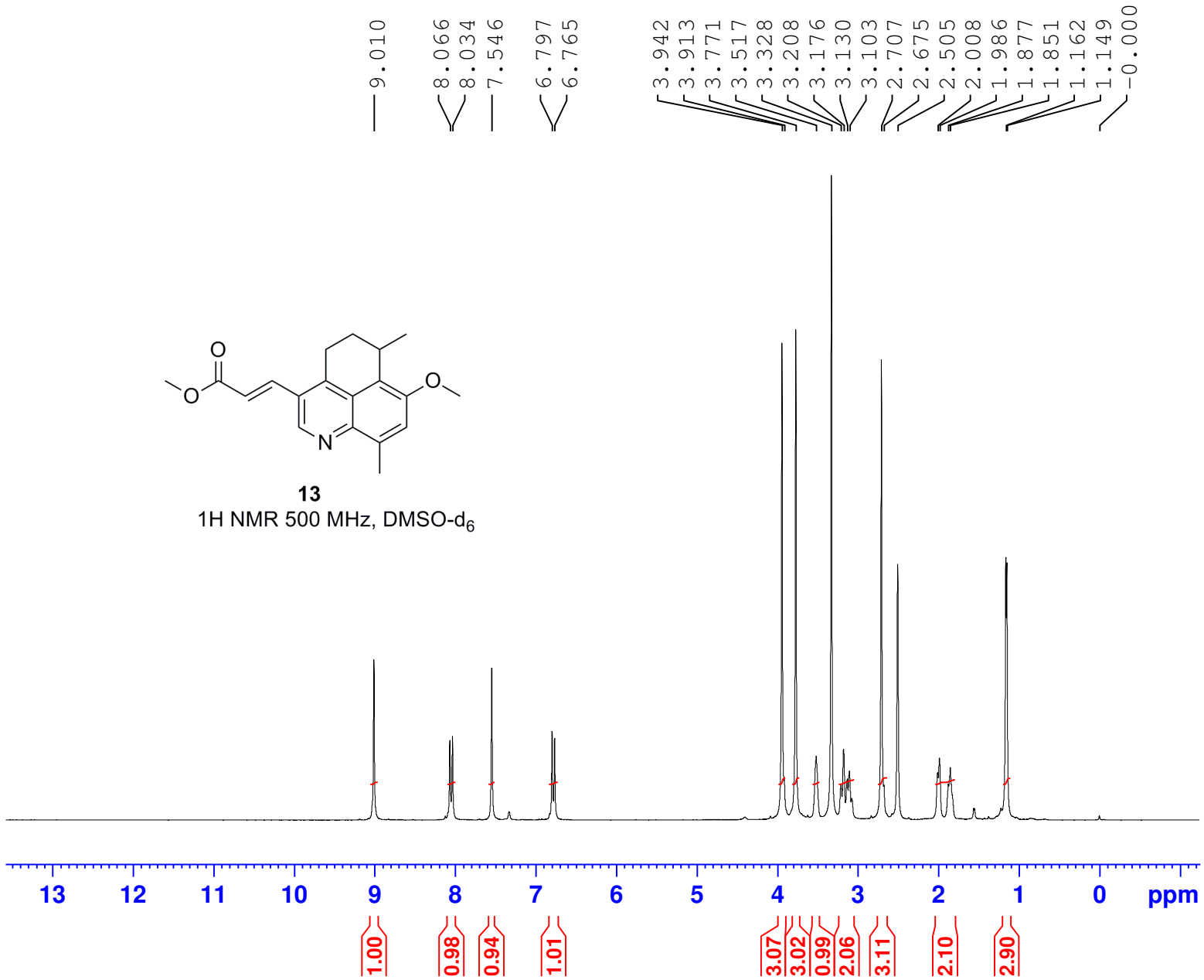
======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        78.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.18777999 W
PLW13        0.15210000 W

F2 - Processing parameters
SI                 32768
SF          100.6127735 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

ANL-MCL5-NMR-001

TP-MA-1158-17

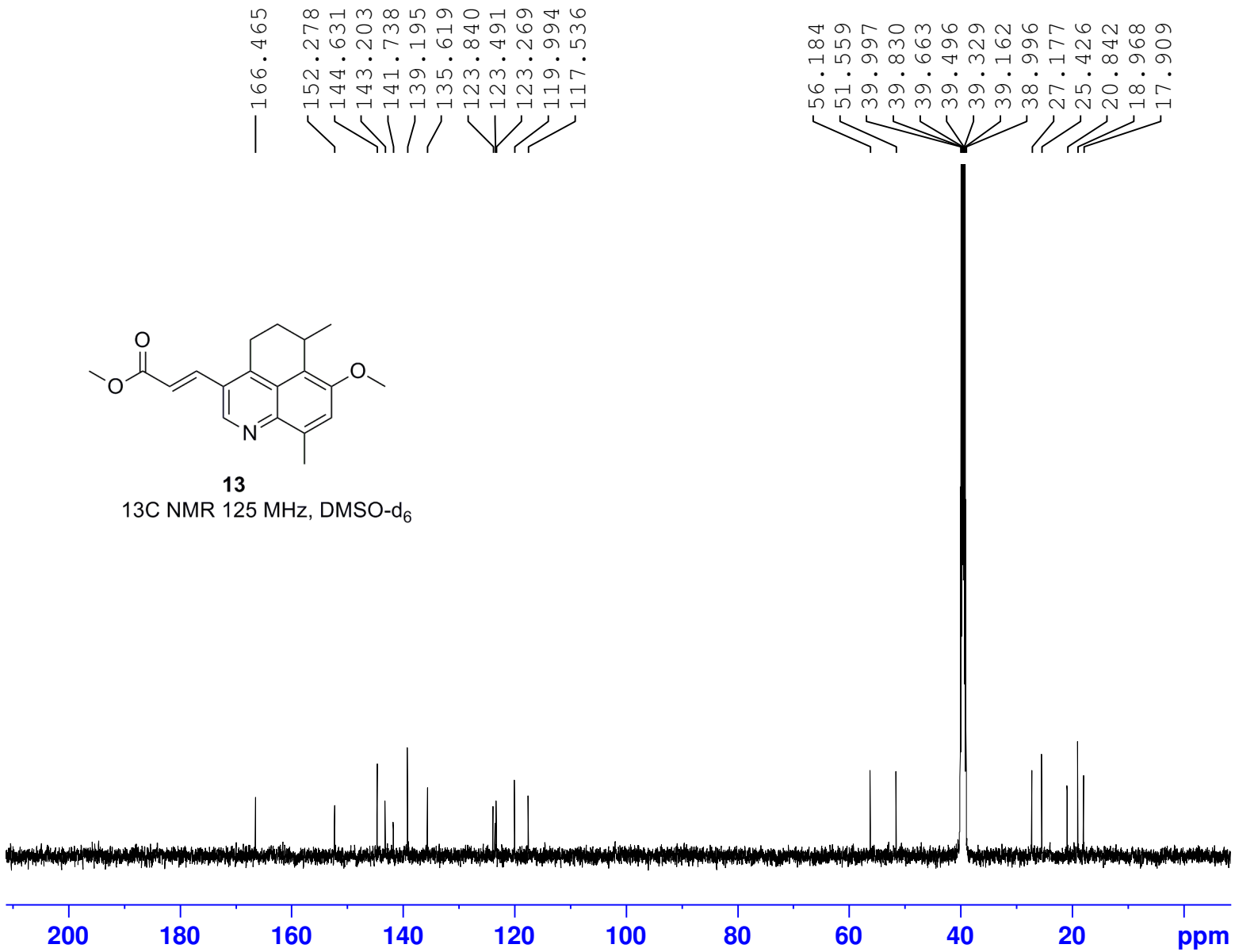



```
Current Data Parameters
NAME         511903B6921
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190319
Time              13.31 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                 79.68
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1
SFO1        500.1330883 MHz
NUC1                  1H
P1                10.00 usec
PLW1        20.38699913 W

F2 - Processing parameters
SI                 65536
SF          500.1300020 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

TP-MA-1158-17



13

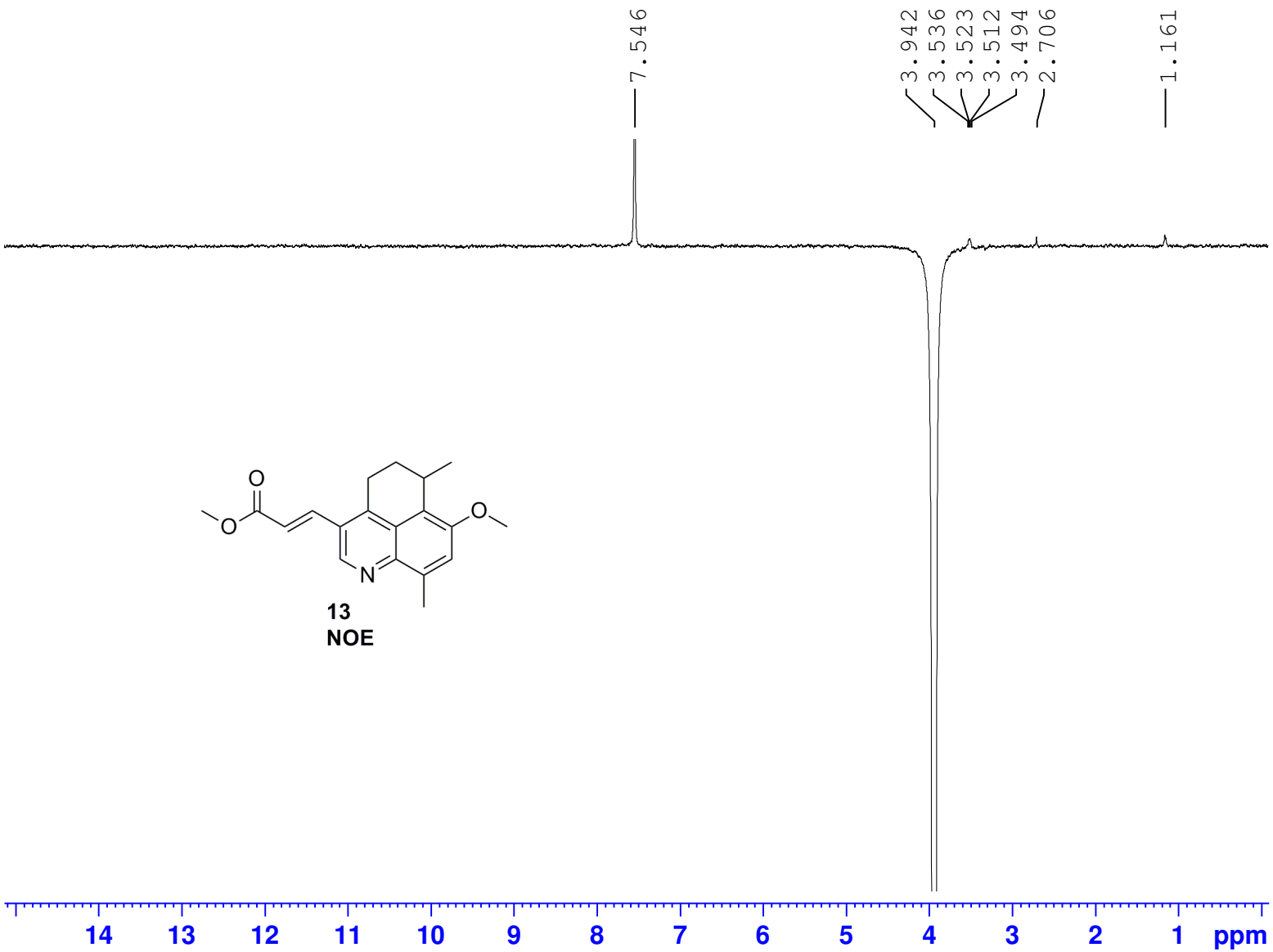
13C NMR 125 MHz, DMSO-d_6

```
Current Data Parameters
NAME         511903B7553
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190320
Time              19.40 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG           zgpg30
TD                65536
SOLVENT             DMSO
NS                    290
DS                      4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010048 sec
RG                197.72
DW                16.800 usec
DE                 6.50 usec
TE                303.2 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        125.7703643 MHz
NUC1                13C
P1                10.00 usec
PLW1         79.88800049 W
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         20.38699913 W
PLW12         0.25169000 W
PLW13         0.16023000 W

F2 - Processing parameters
SI                 32768
SF          125.7578535 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

TP-MA-1158-17

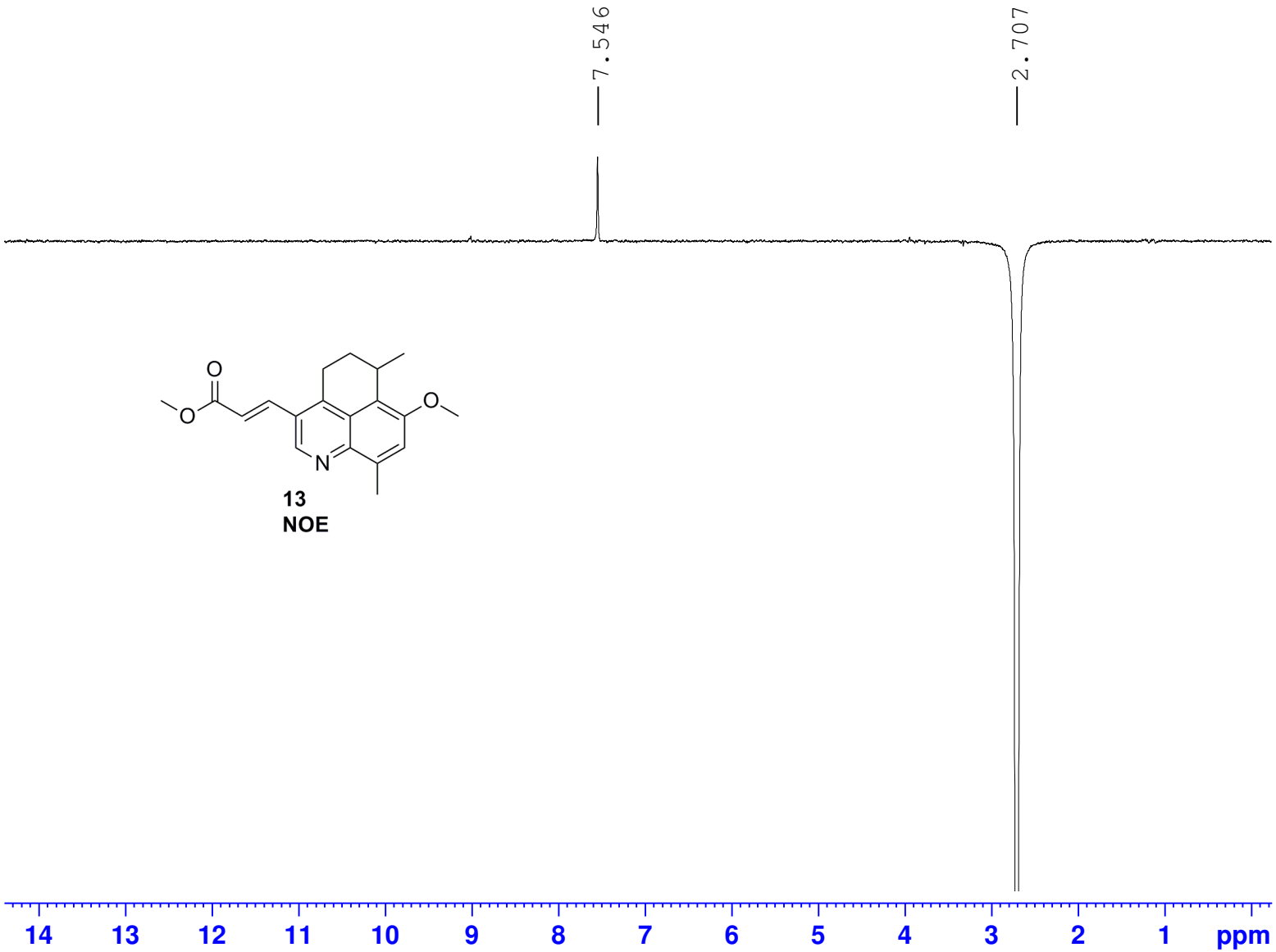



```
Current Data Parameters
NAME         511903B6921
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190319
Time              13.49 h
INSTRUM             spect
PROBHD   Z119470_0294 (
PULPROG          selrogp
TD                 65536
SOLVENT              DMSO
NS                     64
DS                      4
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                 197.72
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D16          0.00020000 sec
TD0                    1
ZGOPTNS
SFO1         500.1330883 MHz
NUC1                  1H
P1                10.00 usec
P12            80000.00 usec
P15           200000.00 usec
PLW0      0 W
PLW1        20.38699913 W
PLW11        0.16848999 W
SPNAM[2] Gaus1_180r.1000
SPOAL2             0.500
SPOFFS2         -1114.96 Hz
SPW2          0.00000752 W
GPNAM[1]      SMSQ10.100
GPZ1              15.00 %
P16             1000.00 usec

F2 - Processing parameters
SI                 32768
SF           500.1300026 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

TP-MA-1158-17

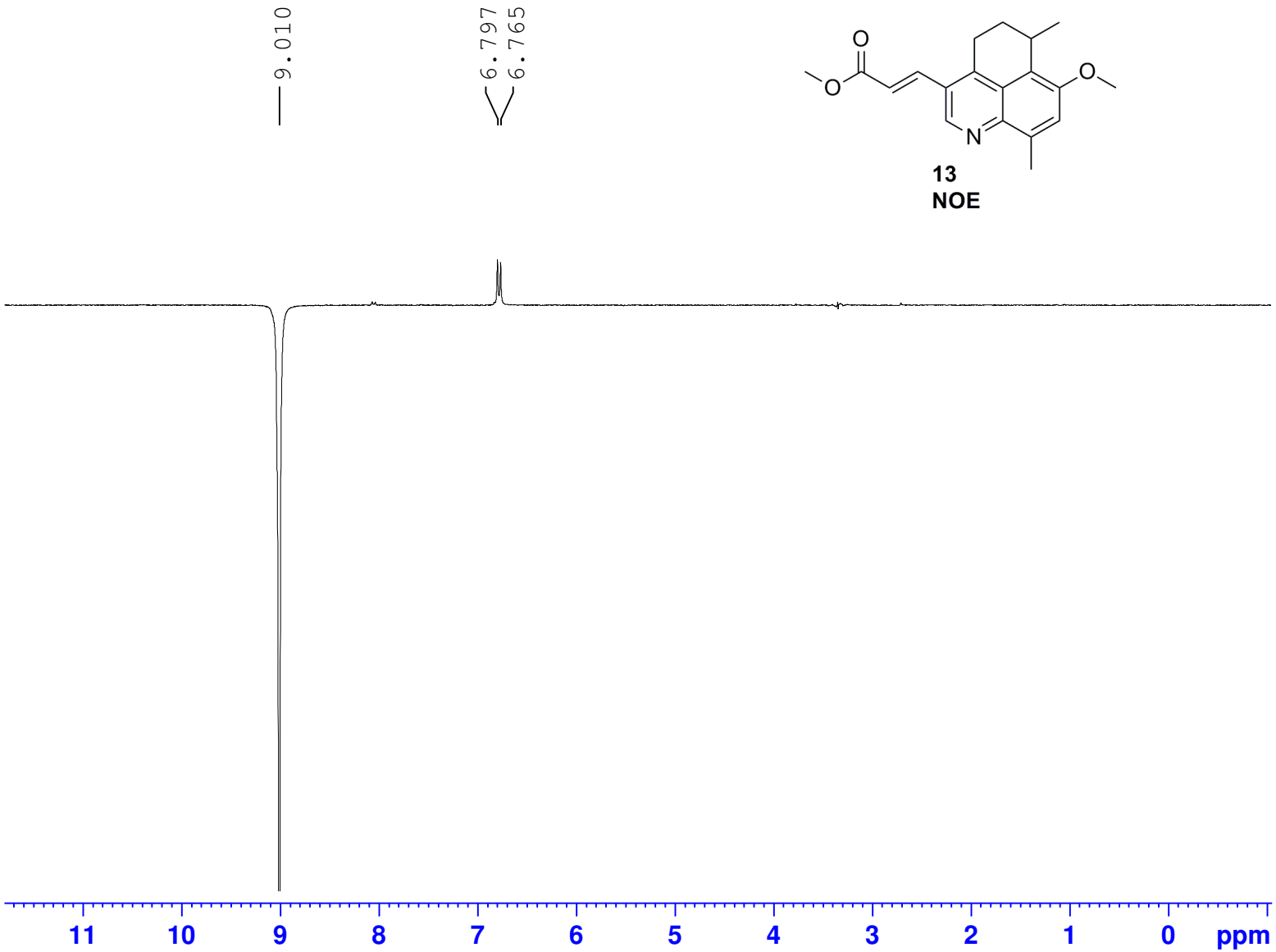



```
Current Data Parameters
NAME         511903B6921
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190319
Time              13.59 h
INSTRUM             spect
PROBHD   Z119470_0294 (
PULPROG          selrogp
TD                 65536
SOLVENT             DMSO
NS                    64
DS                     4
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                197.72
DW                50.000 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
D16          0.00020000 sec
TD0                    1
ZGOPTNS
SFO1         500.1330883 MHz
NUC1                  1H
P1                10.00 usec
P12            80000.00 usec
P15           200000.00 usec
PLW0      0 W
PLW1        20.38699913 W
PLW11        0.16848999 W
SPNAM[2] Gaus1_180r.1000
SPOAL2              0.500
SPOFFS2         -1732.48 Hz
SPW2          0.00000752 W
GPNAM[1]      SMSQ10.100
GPZ1               15.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 32768
SF           500.1300026 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

TP-MA-1158-17

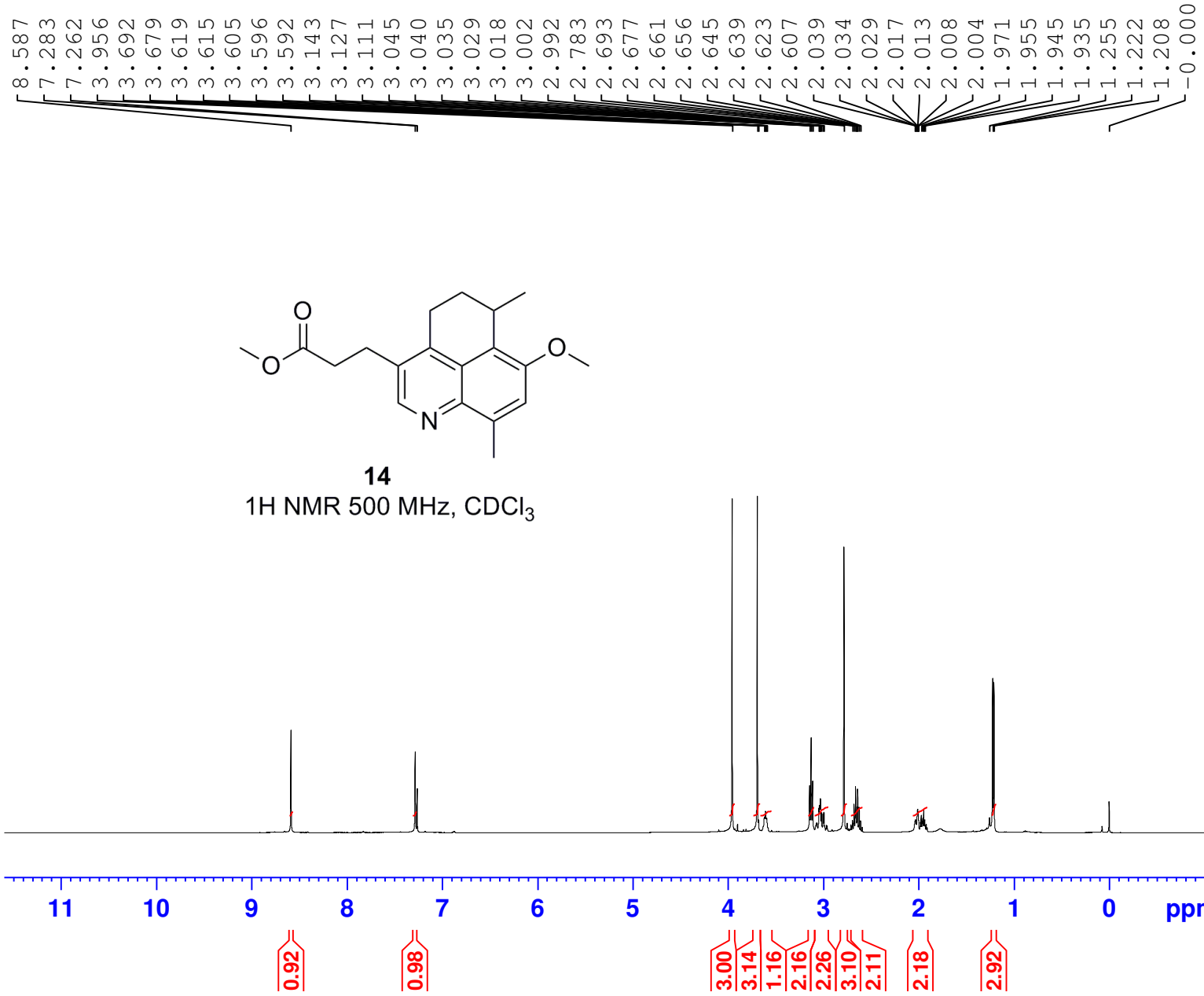



```
Current Data Parameters
NAME         511903B6921
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190319
Time              17.39 h
INSTRUM             spect
PROBHD   Z119470_0294 (
PULPROG          selrogp
TD                 65536
SOLVENT             DMSO
NS                    64
DS                     4
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                197.72
DW                 50.000 usec
DE                  6.50 usec
TE                 298.1 K
D1           2.00000000 sec
D16          0.00020000 sec
TD0                    1
ZGOPTNS   -DCALC_SPOFFS
SFO1         500.1330883 MHz
NUC1                1H
CNST21         9.0147018
P1                 10.00 usec
P12             25921.06 usec
P15            200000.00 usec
PLW0      0 W
PLW1         20.38699913 W
PLW11         0.16848999 W
SPNAM[2] Gaus1_180r.1000
SPOAL2             0.500
spoffs2          1420.22 Hz
SPW2          0.00007069 W
GPNAM[1]      SMSQ10.100
GPZ1               15.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 32768
SF           500.1300018 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

TP-MA-1158-19

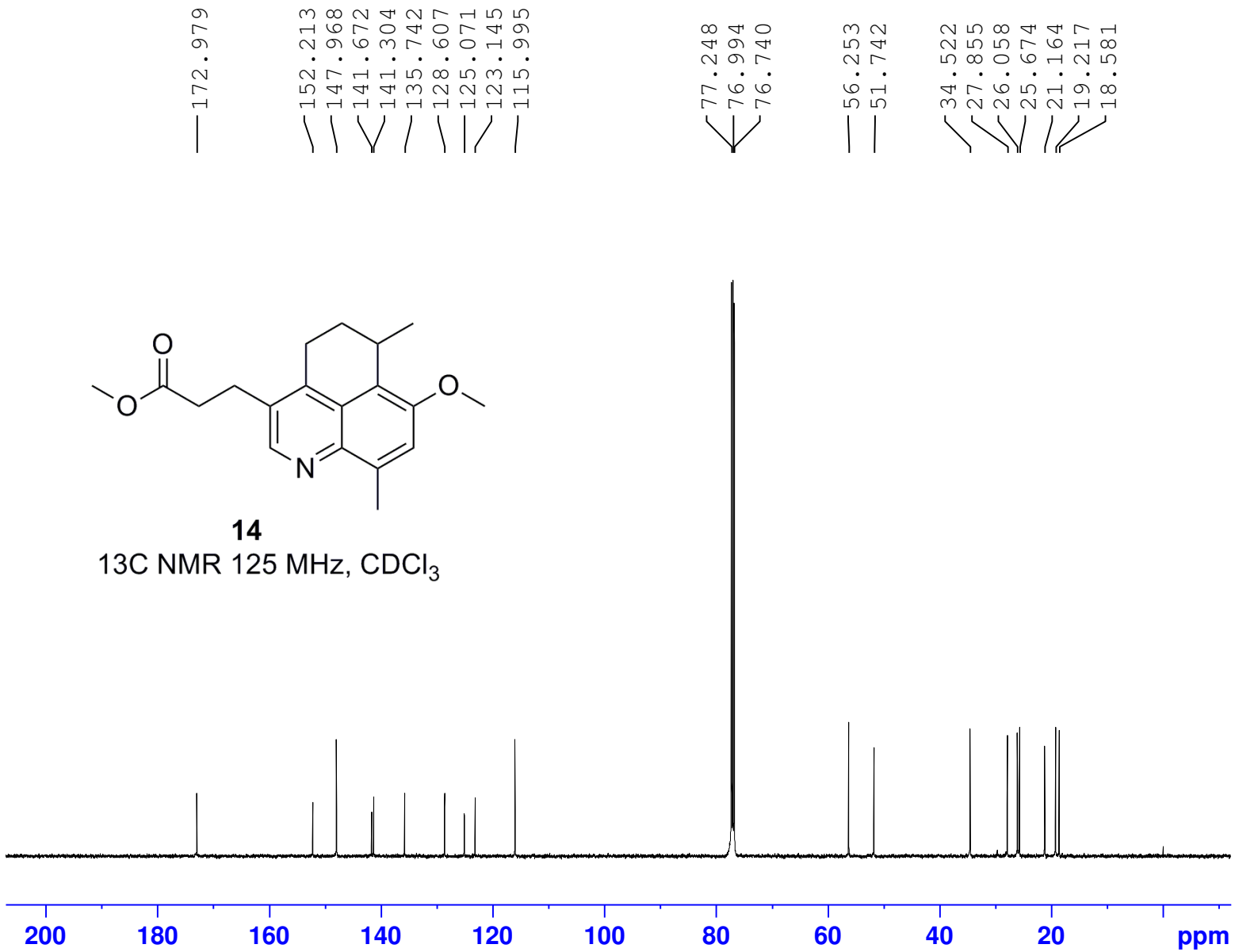



```
Current Data Parameters
NAME         511903C5249
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190327
Time              22.12 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                79.68
DW               50.000 usec
DE                6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1
SFO1        500.1330885 MHz
NUC1                  1H
P1               10.00 usec
PLW1        20.38699913 W

F2 - Processing parameters
SI                 65536
SF          500.1300113 MHz
WDW                   EM
SSB       0
LB                0.50 Hz
GB        0
PC                1.00
```

TP-MA-1158-19

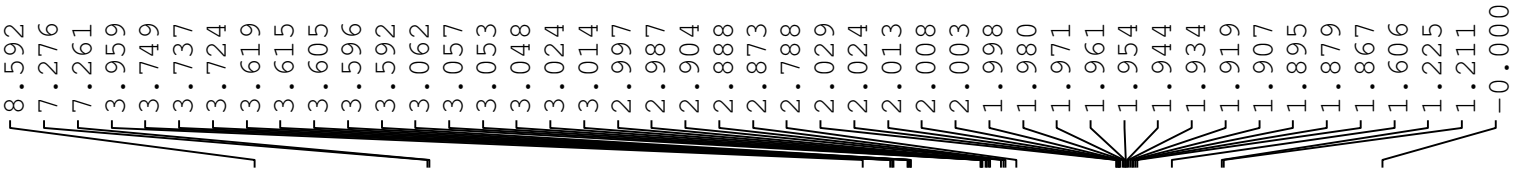


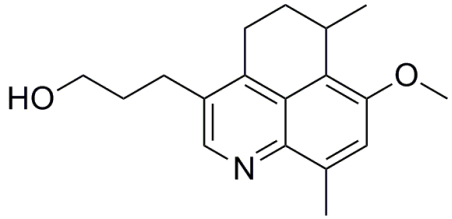

```
Current Data Parameters
NAME         511903C5249
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190327
Time              23.25 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.72
DW               16.800 usec
DE                6.50 usec
TE               298.1 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7703643 MHz
NUC1               13C
P1               10.00 usec
PLW1        79.88800049 W
SFO2        500.1320005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2        20.38699913 W
PLW12        0.25169000 W
PLW13        0.16023000 W

F2 - Processing parameters
SI                32768
SF          125.7577937 MHz
WDW                EM
SSB       0
LB               2.00 Hz
GB        0
PC               1.40
```

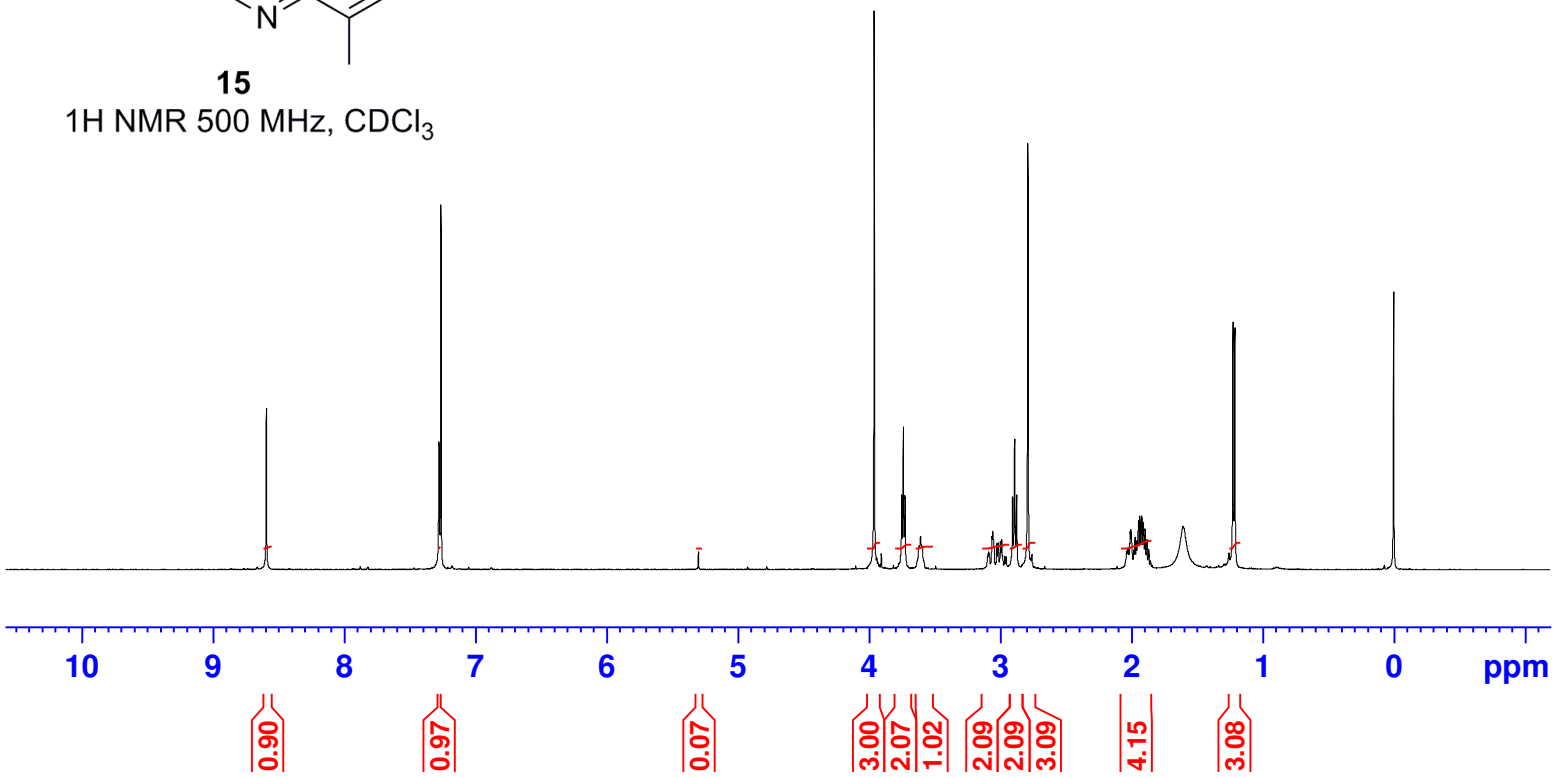
TP-MA-1158-20





15

1H NMR 500 MHz, $CDCl_3$

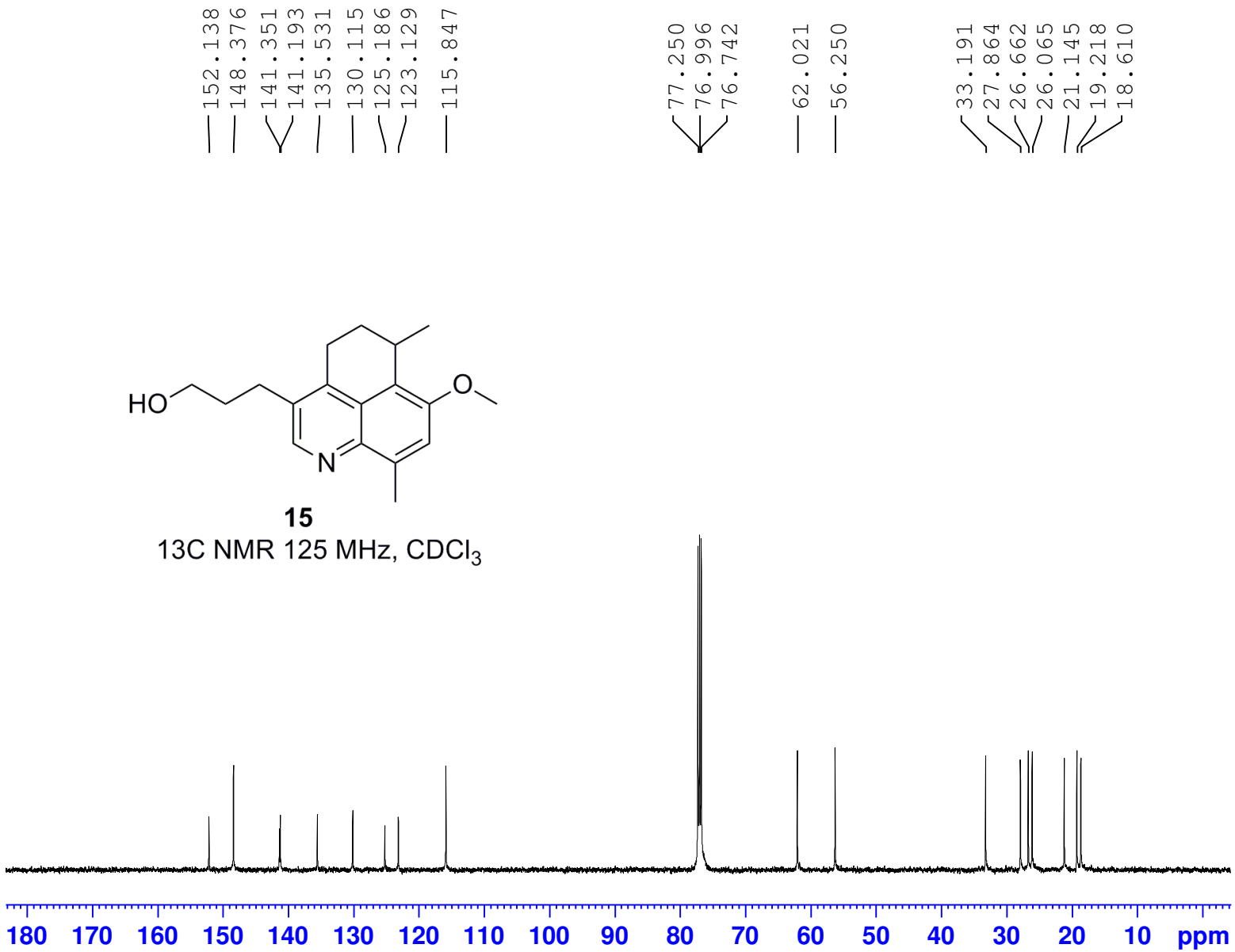



```
Current Data Parameters
NAME         511903C7023
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190329
Time               7.24 h
INSTRUM           spect
PROBHD   Z119470_0294 (
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG               132.94
DW                50.000 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                   1
SFO1        500.1330885 MHz
NUC1                 1H
P1                10.00 usec
PLW1        20.38699913 W

F2 - Processing parameters
SI                65536
SF          500.1300121 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

TP-MA-1158-20

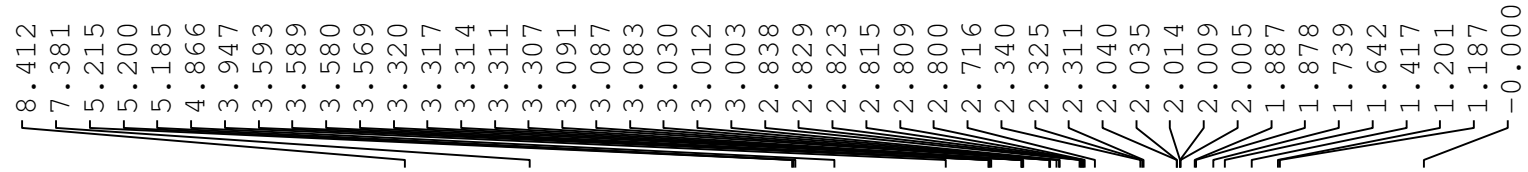


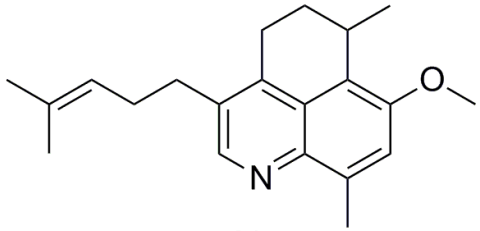

```
Current Data Parameters
NAME         511903C5252
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190327
Time              20.47 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  484
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.72
DW               16.800 usec
DE                6.50 usec
TE               298.2 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7703643 MHz
NUC1               13C
P1               10.00 usec
PLW1         79.88800049 W
SFO2        500.1320005 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2         20.38699913 W
PLW12         0.25169000 W
PLW13         0.16023000 W

F2 - Processing parameters
SI                32768
SF          125.7577967 MHz
WDW                EM
SSB       0
LB               2.00 Hz
GB        0
PC               1.40
```

TP-MA-1158-22





16

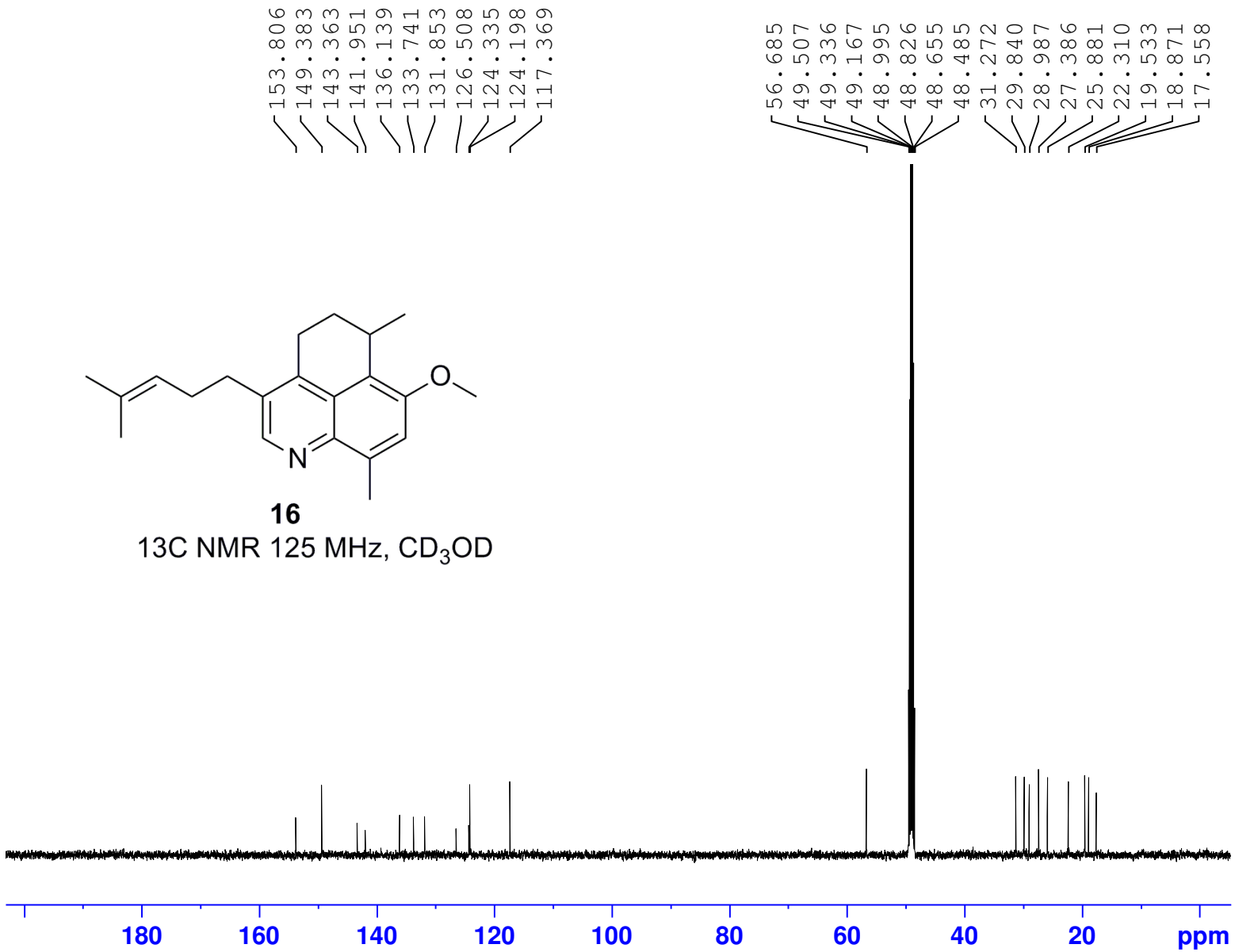
1H NMR 500 MHz, CD_3OD


```
Current Data Parameters
NAME         511903C3907
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190327
Time              17.45 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                69.27
DW               50.000 usec
DE                6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1
SFO1        500.1330885 MHz
NUC1                  1H
P1               10.00 usec
PLW1        20.38699913 W

F2 - Processing parameters
SI                 65536
SF          500.1300079 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

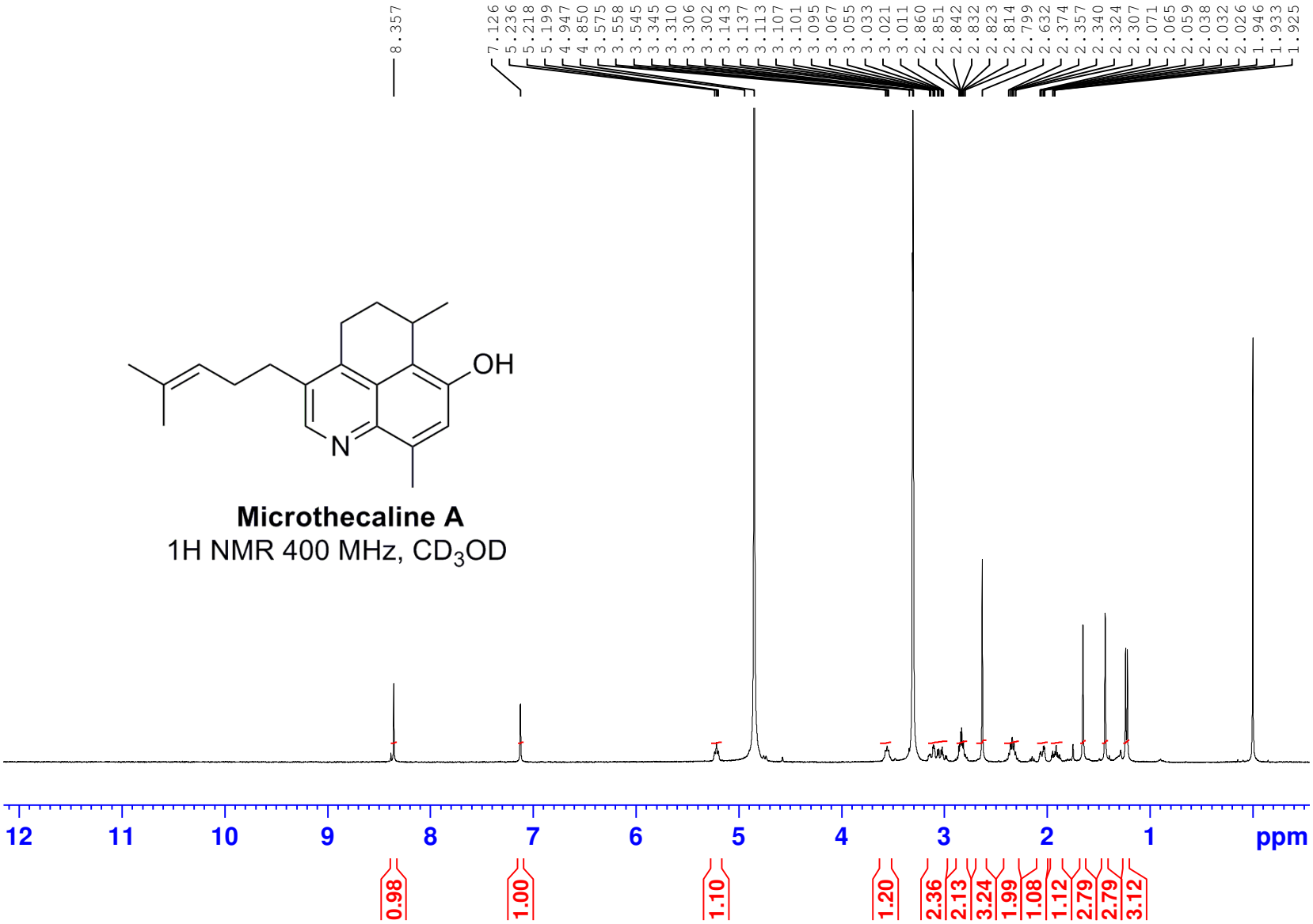
TP-MA-1158-22




```
Current Data Parameters
NAME         511903C3907
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190327
Time              17.50 h
INSTRUM             spect
PROBHD   Z119470_0294 (
PULPROG           zgpg30
TD                65536
SOLVENT             MeOD
NS                    84
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                197.72
DW                16.800 usec
DE                 6.50 usec
TE                298.2 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         125.7703643 MHz
NUC1                 13C
P1                10.00 usec
PLW1         79.88800049 W
SFO2         500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         20.38699913 W
PLW12         0.25169000 W
PLW13         0.16023000 W

F2 - Processing parameters
SI                 32768
SF           125.7576130 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```



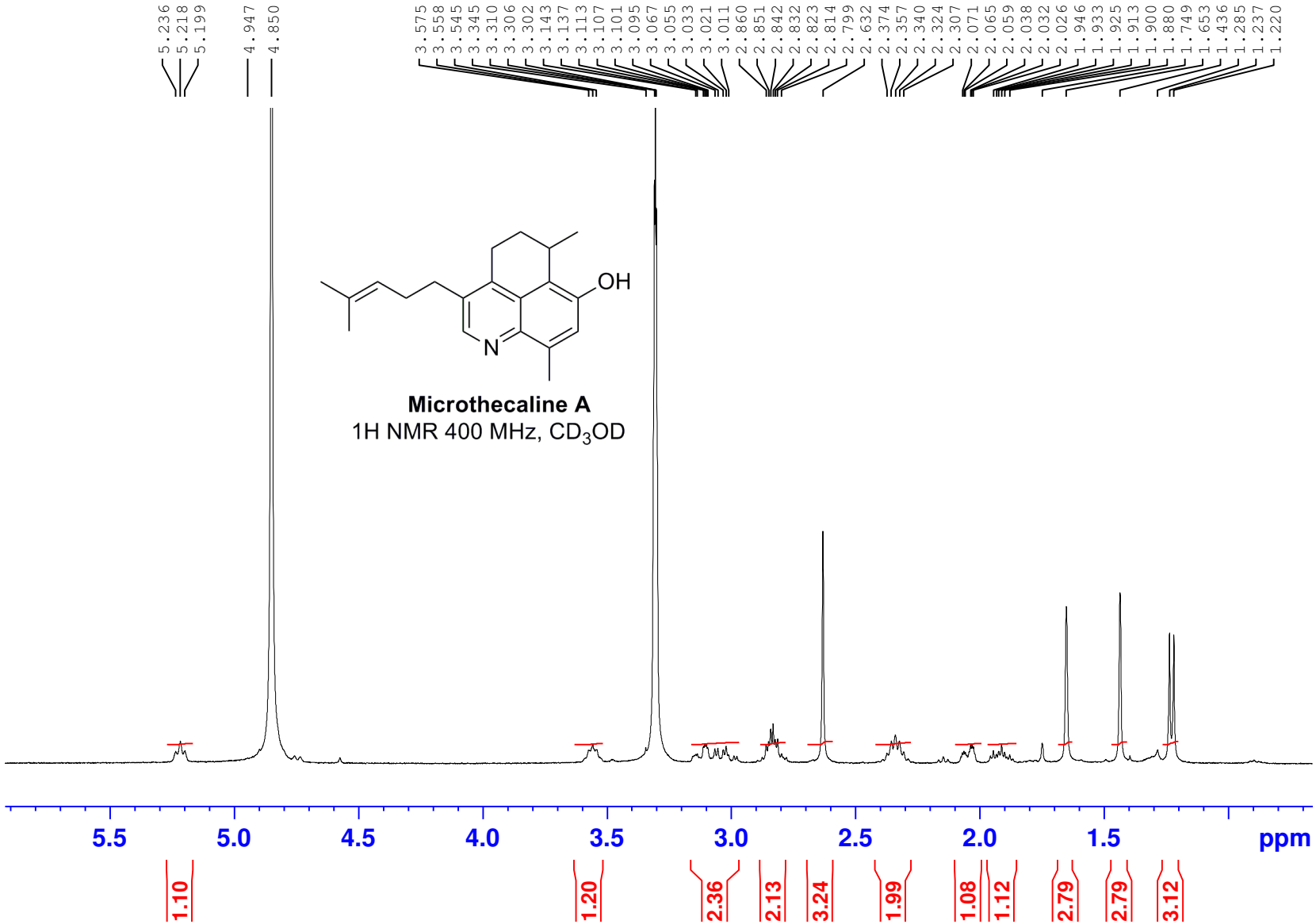

```
Current Data Parameters
NAME          511904A1427
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190402
Time                13.17
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894465 sec
RG                 110.59
DW                 62.400 usec
DE                  6.50 usec
TE                 298.5 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                   9.75 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.1300093 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

ANL-MCL5-NMR-001



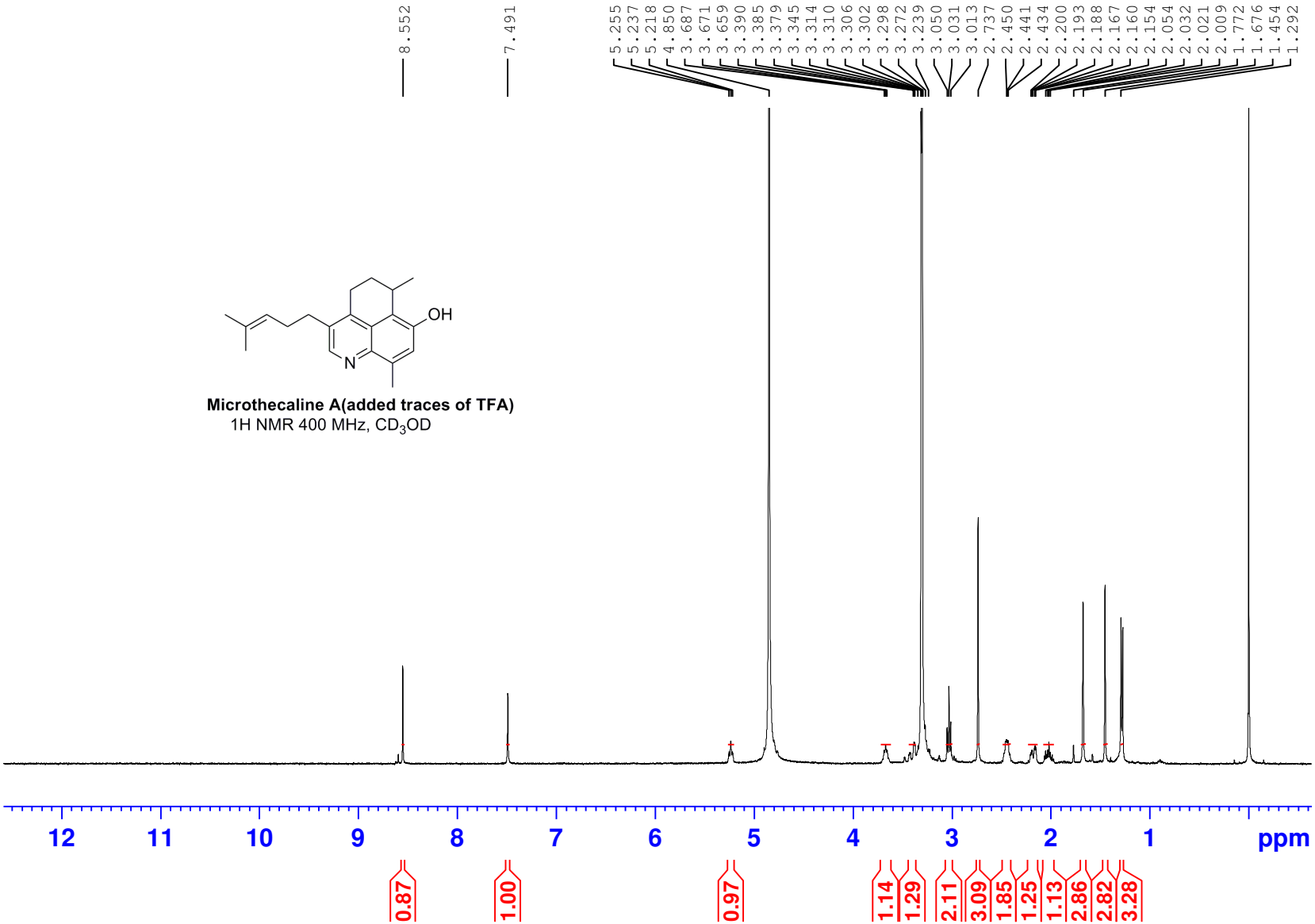

```
Current Data Parameters
NAME         511904A1427
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190402
Time               13.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                 110.59
DW                 62.400 usec
DE                  6.50 usec
TE                 298.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  9.75 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                 65536
SF          400.1300093 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

ANL-MCL5-NMR-001



Microthecaline A(added traces of TFA)
1H NMR 400 MHz, CD_3OD

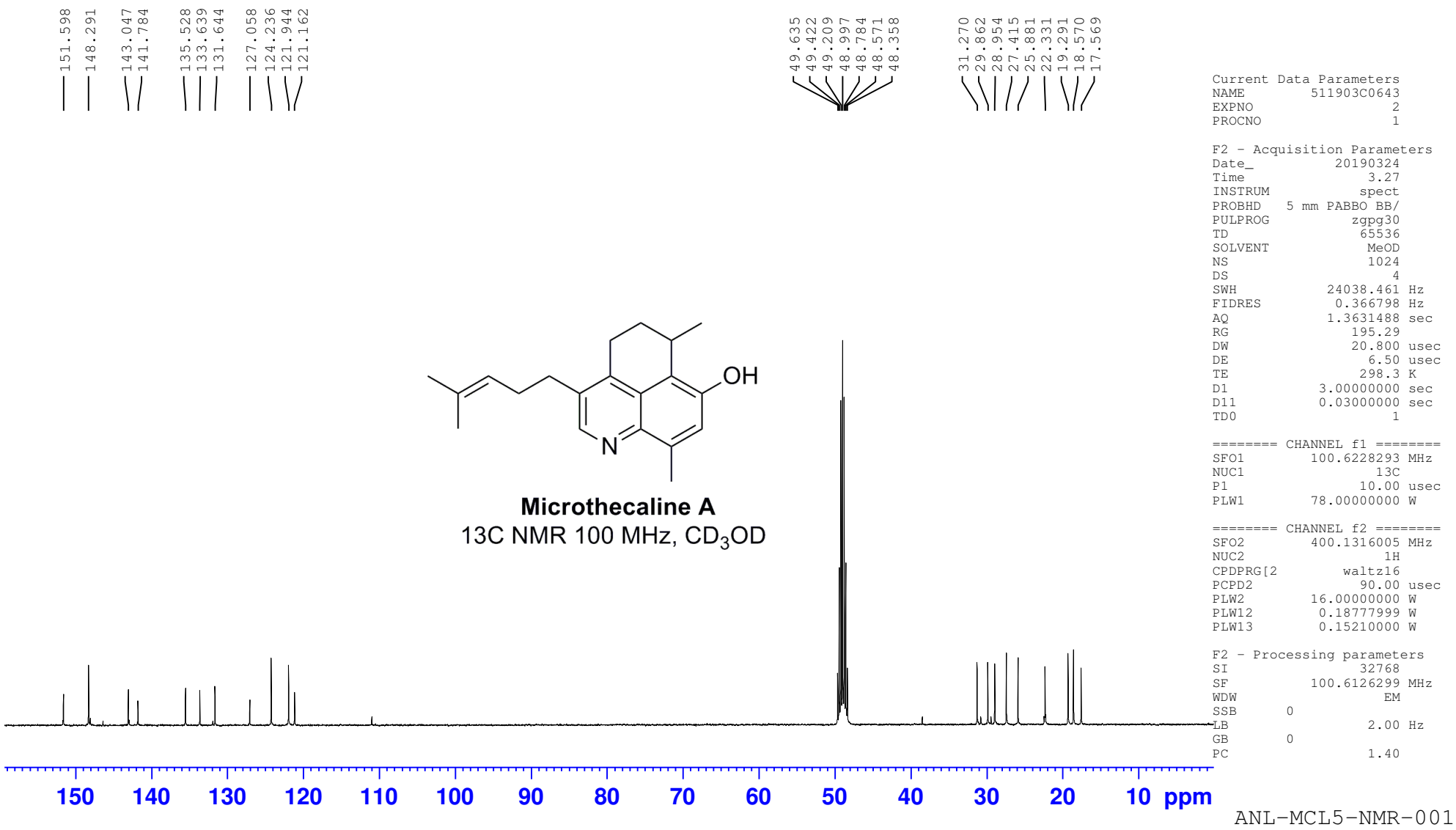
```
Current Data Parameters
NAME         511904A1428
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190402
Time               13.13
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894465 sec
RG                 195.29
DW                 62.400 usec
DE                  6.50 usec
TE                298.5 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 9.75 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300093 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

ANL-MCL5-NMR-001




```
Current Data Parameters
NAME         511903C0643
EXPNO                  2
PROCNO                 1

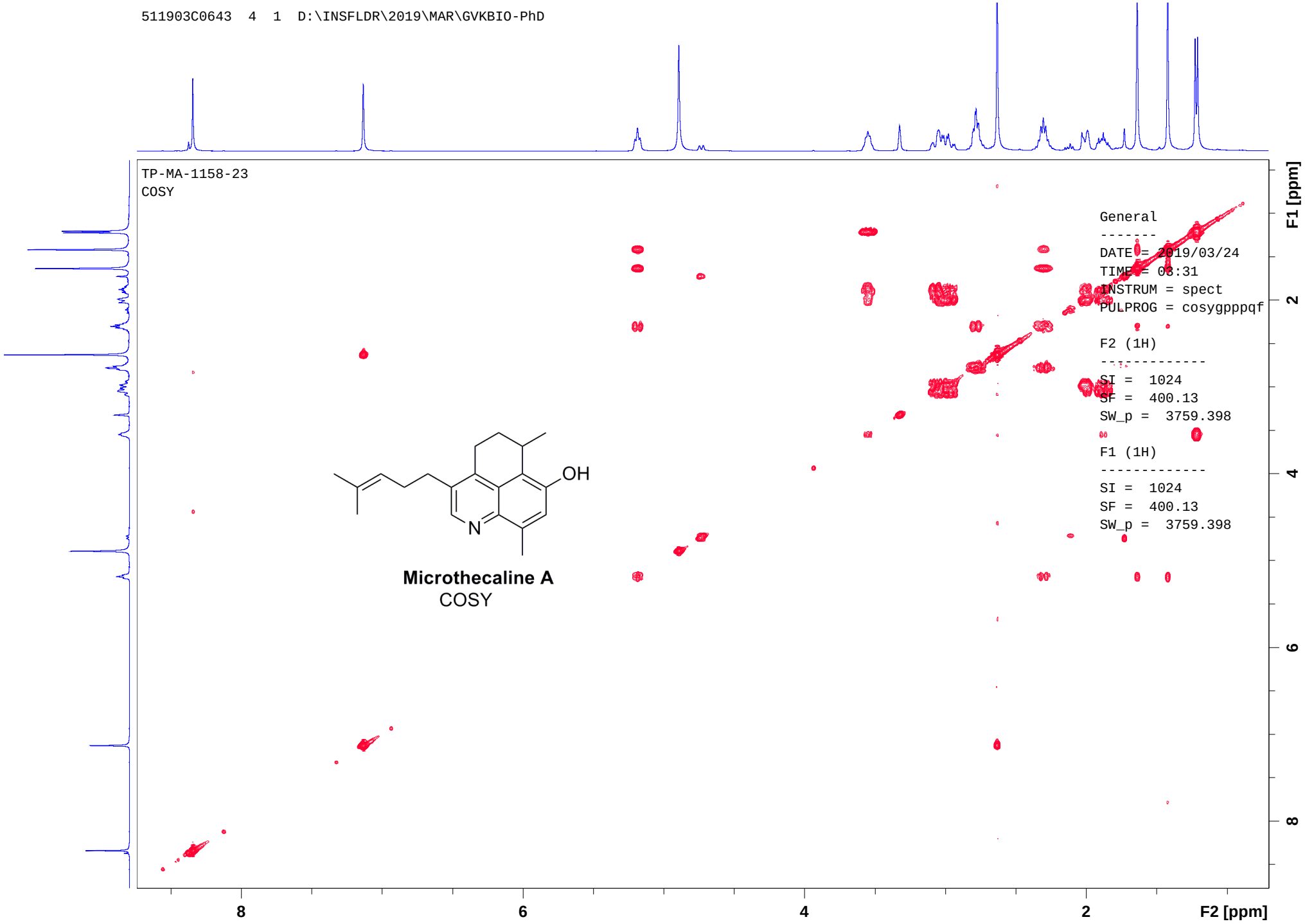
F2 - Acquisition Parameters
Date_           20190324
Time                3.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                  1024
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                195.29
DW                20.800 usec
DE                 6.50 usec
TE                298.3 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1

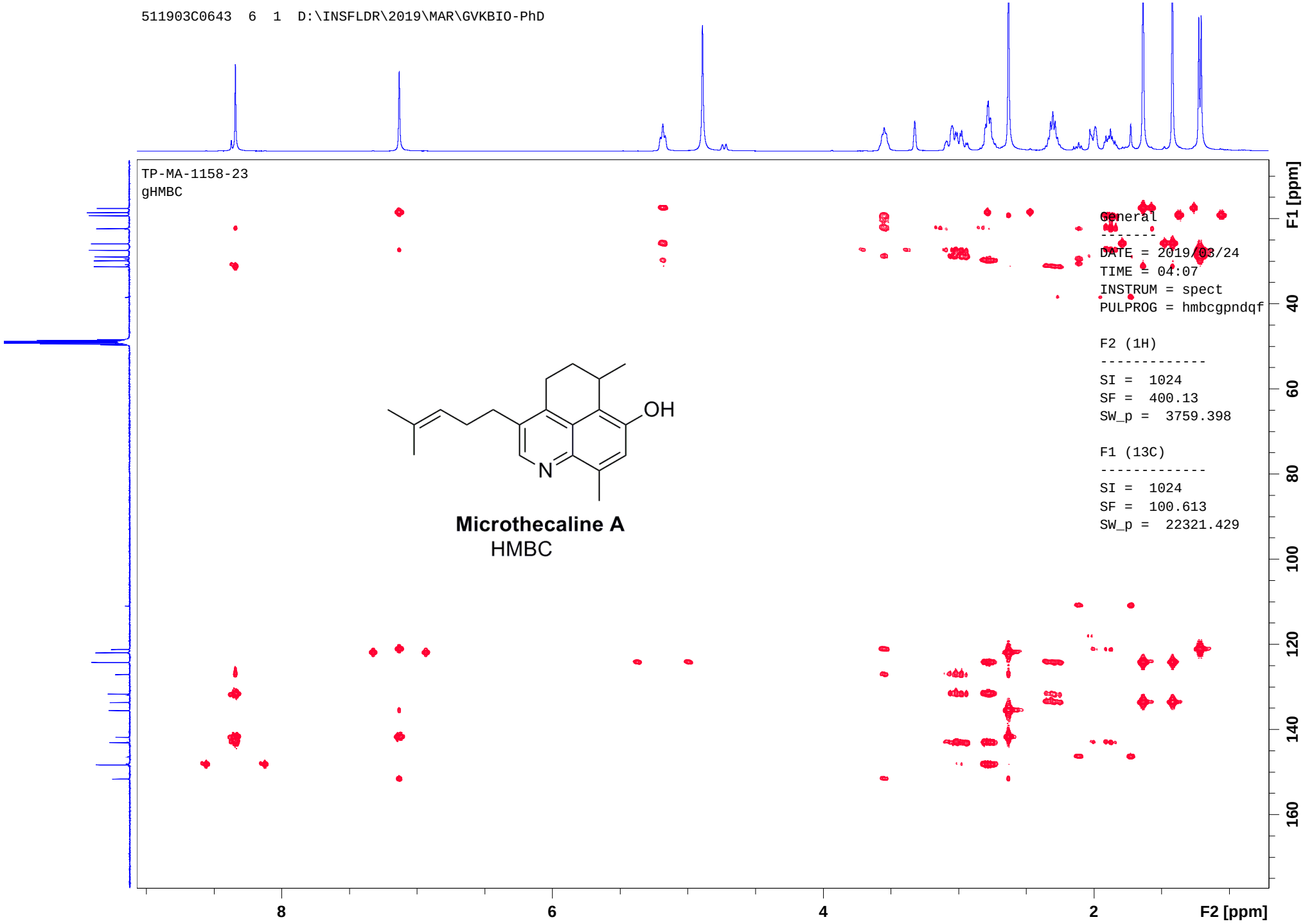
======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                10.00 usec
PLW1         78.00000000 W

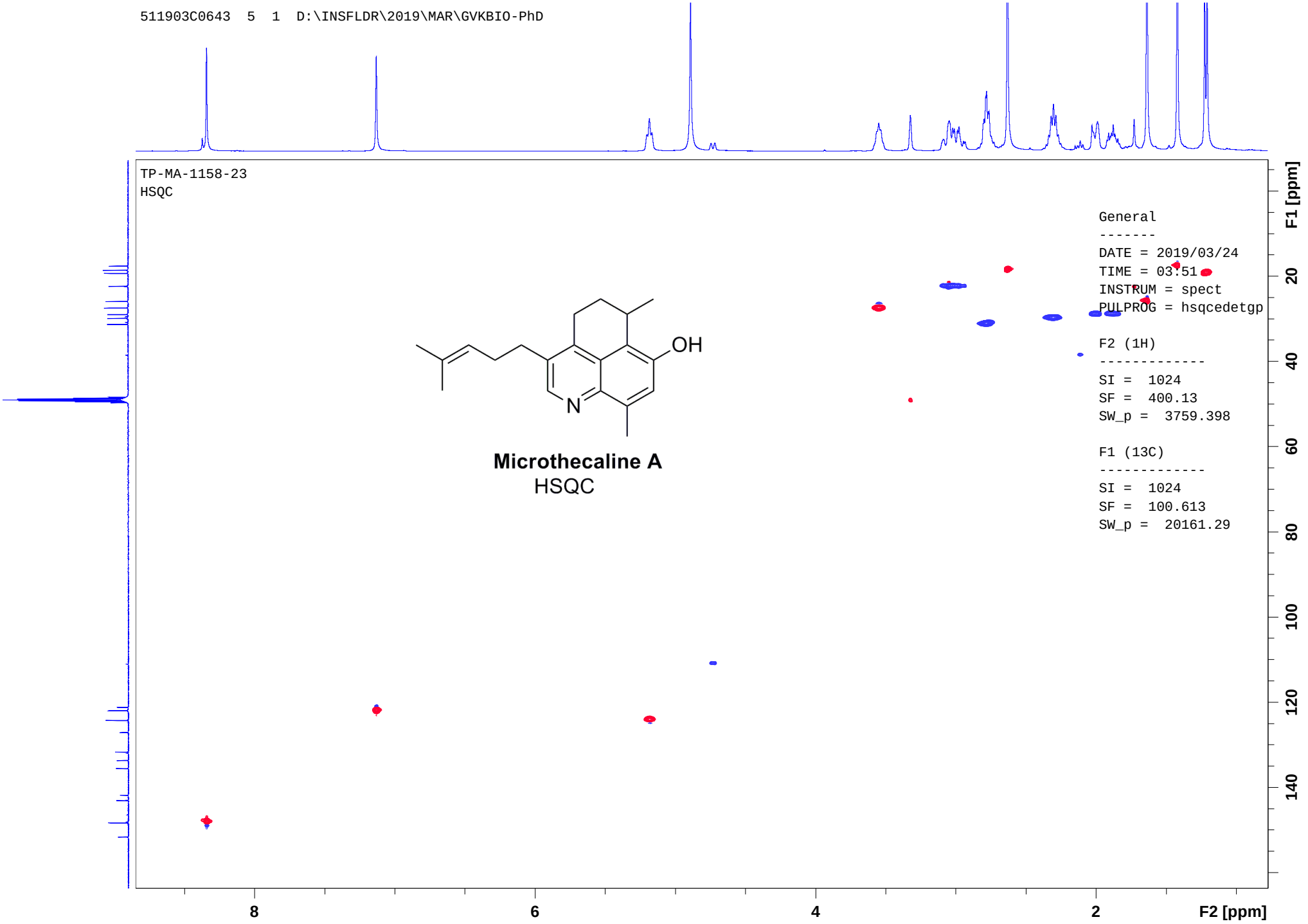
======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         16.00000000 W
PLW12         0.18777999 W
PLW13         0.15210000 W

F2 - Processing parameters
SI                 32768
SF           100.6126299 MHz
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.40
```

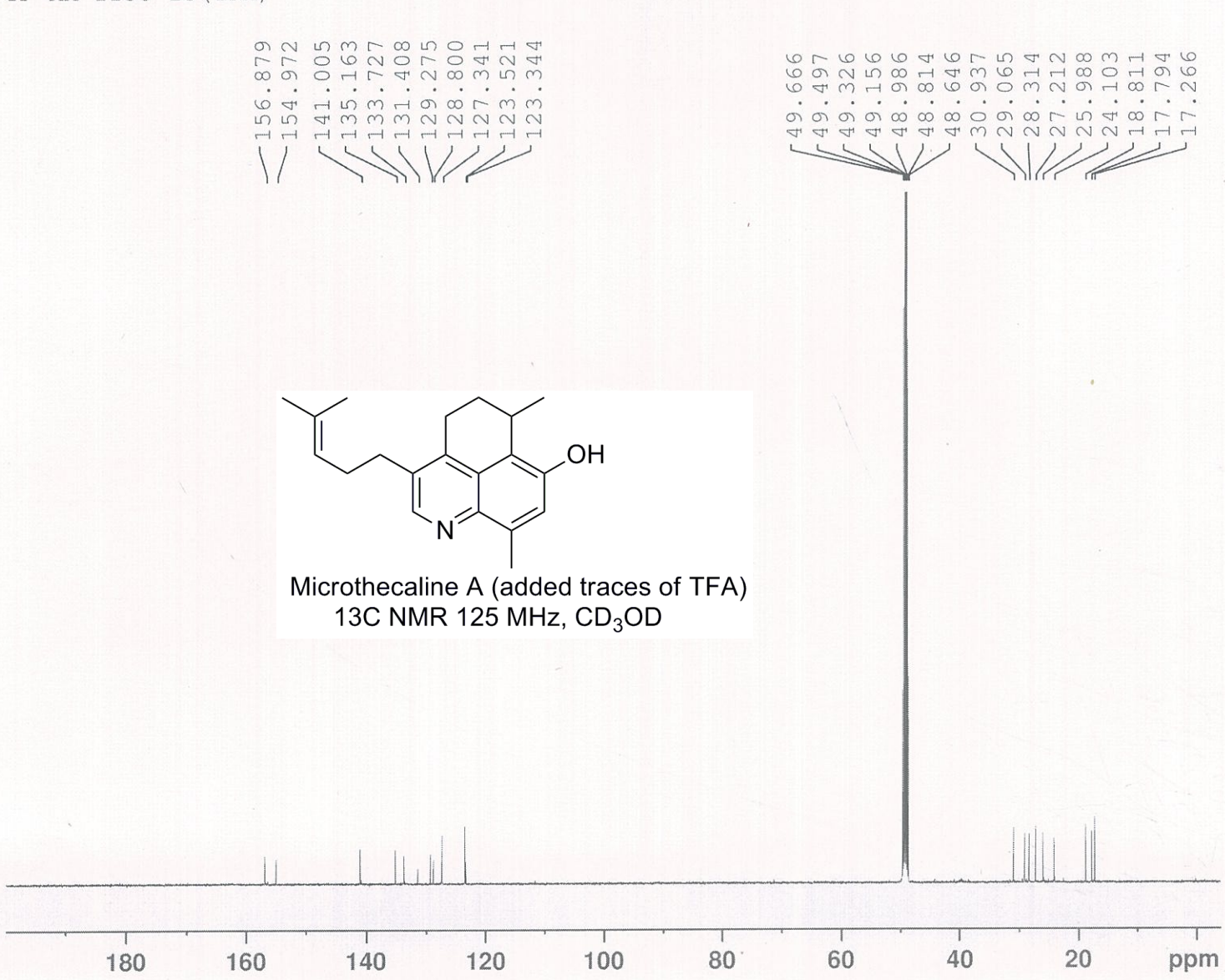
ANL-MCL5-NMR-001


511903C0643 4 1 D:\INSFLDR\2019\MAR\GVKBIO-PhD
TP-MA-1158-23
COSY
General
DATE = 2019/03/24
TIME = 03:31
INSTRUM = spect
PULPROG = cosygpppqf
F2 (1H)
SI = 1024
SF = 400.13
SW_p = 3759.398
F1 (1H)
SI = 1024
SF = 400.13
SW_p = 3759.398
OH
N
Microthecaline A
COSY
F1 [ppm]
F2 [ppm]
2
4
6
8


511903C0643 6 1 D:\INSFLDR\2019\MAR\GVKBIO-PhD
TP-MA-1158-23
gHMBC
General
DATE = 2019/03/24
TIME = 04:07
INSTRUM = spect
PULPROG = hmbcgpndqf
F2 (1H)
SI = 1024
SF = 400.13
SW_p = 3759.398
F1 (13C)
SI = 1024
SF = 100.613
SW_p = 22321.429
OH
N
Microthecaline A
HMBC
F1 [ppm]
F2 [ppm]
8
6
4
2
40
60
80
100
120
140
160


511903C0643 5 1 D:\INSFLDR\2019\MAR\GVKBIO-PhD
TP-MA-1158-23
HSQC
OH
N
Microthecaline A
HSQC
General
DATE = 2019/03/24
TIME = 03:51
INSTRUM = spect
PULPROG = hsqcedetgp
F2 (1H)
SI = 1024
SF = 400.13
SW_p = 3759.398
F1 (13C)
SI = 1024
SF = 100.613
SW_p = 20161.29
F1 [ppm]
20
40
60
80
100
120
140
8
6
4
2
F2 [ppm]

TP-MA-1158-23(TFA)



Microthecaline A (added traces of TFA)
13C NMR 125 MHz, CD_3OD

```
Current Data Parameters
NAME         511907A7649
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190710
Time                4.04 h
INSTRUM            spect
PROBHD   Z119470_0294 (
PULPROG           zgpg30
TD                65536
SOLVENT            MeOD
NS                 1500
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ             1.1010048 sec
RG                197.72
DW                16.800 usec
DE                 6.50 usec
TE                298.3 K
D1            3.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         125.7703643 MHz
NUC1                13C
P1                10.00 usec
PLW1         79.88800049 W
SFO2         500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         20.38699913 W
PLW12         0.31854999 W
PLW13         0.16023000 W

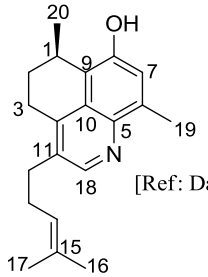
F2 - Processing parameters
SI                 32768
SF           125.7575932 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

	^{1}H & ^{13}C NMR values of isolated Microthecaline A **(with TFA)**		^{1}H & ^{13}C NMR values of synthesized (±)- Microthecaline A		^{1}H & ^{13}C NMR values of synthesized (±)-Microthecaline A after addition of **TFA**	
Position	**^{13}C (150 MHz)**	**^{1}H values (600 MHz)**	**^{13}C (100 MHz)**	**^{1}H values (400 MHz)**	**^{13}C (125 MHz)**	**^{1}H values (400 MHz)**
1	27.0, CH	3.65, m	27.4 CH	3.55, m	27.2, CH	3.67, m
2α **2β**	28.2, CH_2	2.01, dddd 2.16, dddd	28.9, CH_2	1.91, m 2.04, m	28.3, CH_2	2.02, m 2.16, m
3α **3β**	23.9, CH_2	3.38, ddd 3.25, ddd	22.3, CH_2	3.09-3.14, m 3.01-3.06, m	24.1, CH_2	3.35, m
4	156.4, C		143.0, C		156.8, C	
5	131.4, C		141.8, C		131.4, C	
6	129.2, C		135.5, C		129.2, C	
7	127.1, CH	7.49, s	121.9, CH	7.12, s	127.3, CH	7.49, s
8	154.7, C		151.5, C		154.9, C	
9	123.1, C		121.2 C		123.3, C	
10	128.6, C		127.1, C		128.8, C	
11	133.5, C		131.6, C		133.7, C	
12	30.8, CH_2	3.02, t	31.3, CH_2	2.83, m	30.9, CH_2	3.03, t
13	28.9, CH_2	2.44, m	29.9, CH_2	2.34, m	29.0, CH_2	2.44, m
14	123.3, CH	5.23, t	124.2, CH	5.21, t	123.5, CH	5.23, t
15	135.0, C		133.6, C		135.1, C	
16	25.8, CH_3	1.67, s	25.9, CH_3	1.65, s	25.9, CH_3	1.67, s
17	17.6, CH_3	1.45, s	17.5, CH_3	1.43, s	17.7, CH_3	1.43, s
18	141.0, CH	8.57, s	148.3, CH	8.35, s	141.0, CH	8.55, s
19	17.1, CH_3	2.74, s	18.5, CH_3	2.63, s	17.2, CH_3	2.73, s
20	18.7, CH_3	1.27, d	19.3, CH_3	1.23, d	18.8, CH_3	1.28, d

(a) All the ^{1}H & ^{13}C NMRs were recorded in CD_3OD solvent.

(b) <u>As per the original paper on isolation and characterization of microthecaline A, methanol and trifluoroacetic acid (TFA) were used to elute the compound. Subsequently solvents were evaporated prior to ^{1}H and ^{13}C NMR spectroscopy. Taking this into account we decided to add TFA to the synthesized microthecaline sample, evaporated it and then recorded its ^{1}H and ^{13}C NMR spectra, which gave us direct correlation with the reported molecule.</u>

(c) All the NMR experiments were done at 30 °C; same as reported by Davis et al.



[Ref: Davis et al. J Nat Prod, 2018, 81, 1079-1083]