Synthesis of phenothiazines via ligand-free CuI-catalyzed cascade C–S and C-N coupling of aryl *ortho*-dihalides and *ortho*-aminobenzenethiols

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Electronic Supplementary Information (ESI)

General Reagent Information

All reactions were carried out under an argon atmosphere. All glassware used was dried in electric oven at 120 ^{o}C.

All other chemicals were purchased from Alfa Aesar, Shanghai Aladdin Reagent Co., Ltd, and Chengdu Changzheng Chemical Co. and used as received.

General Analytical Information

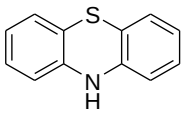
All compounds were characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS and IR spectroscopy. Copies of the ^{1}H and ^{13}C spectra can be found at the end of the Electronic Supplementary Information (ESI). Nuclear Magnetic Resonance spectra were recorded on a Bruker Advance 300MHz instrument or 400 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), acetone (2.05 ppm), or DMSO (2.50 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra are reported in ppm relative to deuteron-chloroform (77.2 ppm), or acetone (206.6 ppm), or DMSO (39.5 ppm) unless otherwise stated, and all were obtained with ^{1}H decoupling. Electron-spraying ionization Mass Spectra are recorded on an Agilent 1200 series LC/MS DVL instrument. All IR spectra were taken on a Bruker Tensor-27 infrared spectrometer with an OPUS workstation. Elemental analyses of these compounds are performed on a Euro EA-3000 elemental analyzer (Leeman Labs Inc.).

Typical procedure of CuI-catalyzed synthesis of phenothiazines:

CuI (0.3 mmol), K_2CO_3 (5 mmol) were weighed into a screwed test tube which was sealed with a rubber cap. The test tube was then evacuated and back-filled with argon for three times. And then 2-aminobenzenethiol (1.1 mmol), 2-bromochlorobenzene (1 mmol) and dimethyl sulfoxide (DMSO)

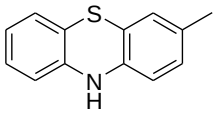
(5 mL) were added by syringe. The test tube was then placed on a magnetic stirrer with a preheated oil bath at 120 ℃ for 48 hours. After cooled to the room temperature, the reaction mixture was diluted with ethyl acetate and washed by water. The aqueous layer was extracted with ethyl acetate three times. The organic layer was combined and then dried with anhydrous sodium sulfate and filtered to remove sodium sulfate. The filtrate was condensed in vacuo to remove solvent. The residual was purified by gradient flash column chromatography on silica gel to give a yellow solid 10*H*-phenothiazine.

10*H*-phenothiazine[1] (Table 1; Table 2, entries 1 to 6)



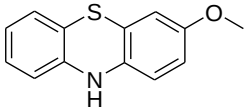
Pale yellow solid. Mp: 184-185 ℃ (lit. mp 185 ℃). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.97-7.01 (m, 4H), 6.80-6.85 (m, 2H), 6.55 (d, *J* = 7.74 Hz, 2H), 5.79 (s, 1H). ^{13}C NMR (75 MHz, CD_3COCD_3), δ (ppm): 143.3, 128.2, 127.1, 122.8, 118.3, 115.3. Anal. Calcd for C12H9NS: C, 72.33; H, 4.55; N, 7.03. Found: 72.62; H, 4.78; N, 6.89.

3-Methyl-10*H*-phenothiazine[2] (Table 2, entry 7)



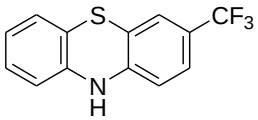
Pale yellow solid. Mp: 170-173 ℃ (lit. mp 169-171 ℃). ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 8.45 (s, 1H), 6.97 (t, 1H), 6.90 (d, 1H), 6.65-680 (m, 4H), 6.58 (d, *J* = 7.6 Hz, 1H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 143.0, 142.8, 140.0, 135.5, 131.1, 128.4, 127.9, 126.9, 126.6., 121.9, 116.7 (*J* = 3.0 Hz, 1C), 114.7, 20.3. Anal. Calcd for C13H11NS: C, 73.20; H, 5.20; N, 6.57. Found: C, 73.01; H, 5.45; N, 6.27.

3-Methoxy-10*H*-phenothiazine[3] (Table 2, entry 8)



Pale yellow solid. Mp: 166 ℃ (lit. mp 166-168 ℃). ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 8.37 (s, 1H), 6.97 (t, *J* = 3.6 Hz, 1H), 6.91 (d, *J* = 7.2Hz, 1H), 6.69 (t, *J* = 10.0 Hz, 1H), 6.61-6.65 (m, 3H), 6.57 (d, *J* = 2.0Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 155.0, 143.2, 136.0, 128.0, 126.6, 121.7, 117.9, 116.2, 115.4., 114.6, 113.5, 112.0, 55.8. Anal. Calcd for C13H11NOS: C, 68.09; H, 4.84; N, 6.11. Found: C, 69.94; H, 4.98; N, 5.96.

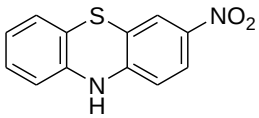
3-(Trifluoromethyl)-10*H*-phenothiazine[3] (Table 2, entry 9)



Pale yellow solid. Mp: 215-216 ℃ (lit. mp 213-214 ℃). ^{1}H NMR (300 MHz, CD_3COCD_3), δ (ppm): 8.12 (s, 1H), 7.69-7.13 (m, 3H), 6.94 (d, *J* = 5.20 Hz, 2H), 6.83 (t, *J* = 7.40 Hz, 1H), 6.71 (d, *J* = 7.98 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6), δ (ppm): 142.6, 140.8, 128.2, 128.0 (d, *J* = 10.0 Hz),

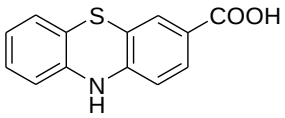
126.8, 126.3, 125.3, 122.6 (d, *J* = 11.0 Hz), 121.9, 117.9, 115.2, 114.6, 109.9. Anal. Calcd for C13H8F3NS: C, 58.42; H, 3.02; N, 5.24. Found: C, 58.70; H, 3.25; N, 5.04.

3-Nitro-10*H*-phenothiazine[3] (Table 2, entry 10)



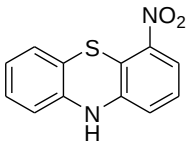
Brown solid. Mp: 208-209 ℃ (lit. mp 208-209 ℃). ^{1}H NMR (300 MHz, CD_3COCD_3), δ (ppm): 8.62 (s,1H), 7.85 (dd, *J* = 8.85 Hz, 2.51 Hz, 1H), 7.75 (d, *J* = 2.04 Hz, 1H), 7.02 (dt, *J* = 7.31 Hz, 1.63 Hz, 1H), 6.95 (d, *J* = 17.54 Hz, 1H), 6.88 (dt, *J* = 7.27 Hz, 1.18 Hz, 1H), 6.71-6.76 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 147.9, 142.0, 139.3, 128.0, 126.3, 124.1, 123.7, 121.6, 117.9, 116.0, 115.4 (d, *J* = 7.0 Hz, 1C), 13.4 (d, *J* = 6.0 Hz, 1C). Anal. Calcd for C12H8N2O2S: C, 59.00; H, 3.30; N, 11.47. Found: C, 59.23; H, 3.56; N, 11.24.

10*H*-Phenothiazine-3-carboxylic acid[4] (Table 2, entry 11)



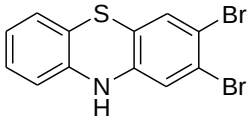
Yellow solid. Mp: 247-250 ℃ (lit. mp 248 ℃). ^{1}H NMR (300 MHz, CD3COCD3), δ (ppm): 7.96 (d, *J* = 1.65Hz, 1H), 7.76 (dd, *J* = 8.34, 1.68 Hz, 1H), 7.40 (d, *J* = 1.50 Hz, 1H), 7.34 (t, *J* = 16.2 Hz, 1H), 6.96 (dd, *J* = 8.16 Hz, 4.14 Hz, 1H), 6.68-6.73 (m, 2H), 5.20 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 166.4, 151.4, 142.6, 137.8, 132.6, 130.2, 129.8, 129.1, 128.6, 125.8, 117.4, 115.7, 108.6. Anal. Calcd for C13H9NO2S: C, 64.18; H, 3.73; N, 5.76. Found: C, 64.04; H, 3.91; N, 5.53.

4-Nitro-10*H*-phenothiazine (Table 2, entry 12)



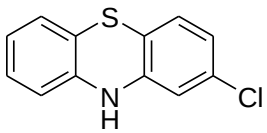
Brown solid. Mp: 155-157 ℃. ^{1}H NMR (300 MHz, CD_3COCD_3), δ (ppm): 9.77 (s, 1H), 7.90 (dd, *J* = 8.7 Hz, 1,5 Hz, 1H), 7.31 (dd, *J* = 8.61 Hz, 1.38 Hz, 1H), 7.00-7.02 (m, 1H), 6.94-6.99 (m, 3H), 6.91 (t, *J* = 7.5 Hz, 1H). Anal. Calcd for C12H8N2O2S: C, 59.00; H, 3.30; N, 11.47. Found: C, 59.18; H, 3.51; N, 11.36.

2,3-Dibromo-10*H*-phenothiazine (Table 2, entry13)



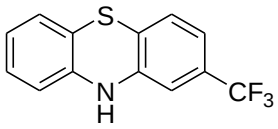
Yellow solid. Mp: 181-183 ℃. ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 8.83 (s, 1H), 7.27 (s, 1H), 6.91-67.03 (m, 3H), 6.79 (t, *J* = 14.8 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 143.0, 141.0, 130.0, 128.6, 126.8, 122.9, 122.3, 119.0, 118.3., 115.8, 115.2 (*J* = 3.0 Hz, 1C), 114.6. Anal. Calcd for C12H7Br2NS: C, 40.36; H, 1.98; N, 3.92. Found: C, 40.49; H, 1.87; N, 3.72.

2-Chloro-10*H*-phenothiazine[3] (Table 2, entries 14 to 17)



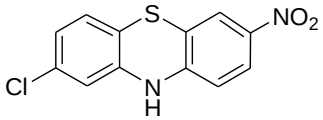
Yellow solid. Mp: 197-198 ℃ (lit. mp 199-200 ℃). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.33-7.38 (m, 2H), 6.98-7.08 (m, 2H), 6.63-6.80 (m, 3H), 4.33 (s, 1H). ^{13}C NMR (75 MHz, CD_3COCD_3), δ (ppm): 144.6, 144.2, 133.3, 128.5, 128.1, 127.2, 123.4, 122.4, 117.9, 117.3, 115.6, 114.9. Anal. Calcd for C12H8ClNS: C, 61.67; H, 3.45; N, 5.99. Found: C, 61.78; H, 3.65; N, 5.77.

2-(Trifluoromethyl)-10*H*-phenothiazine[3] (Table 2, entries 18, 19 and 20)



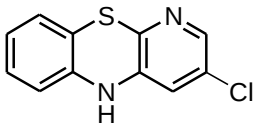
Pale solid. Mp: 188-189 ℃ (lit. mp 189-190 ℃). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.54 (d, *J* = 7.88 Hz, 1H), 7.36-7.39 (m, 1H), 7.07-7.10 (m, 2H), 7.00 (t, *J* = 6.26 Hz, 3H), 6.66-6.69 (m, 1H), 4.45 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 142.6, 140.8, 128.2, 127.9 (*J* = 6.0 Hz, 1C), 126.8, 126.2, 125.3, 122.6, 122.4, 121.9, 117.9 (*J* = 4.0 Hz, 1C), 114.6, 110.0 (*J* = 4.0 Hz, 1C). Anal. Calcd for C13H8F3NS: C, 58.42; H, 3.02; N, 5.24. Found: C, 58.64; H, 3.30; N, 5.07.

2-Chloro-7-nitro-10*H*-phenothiazine[5] (Table 2, entry 21)



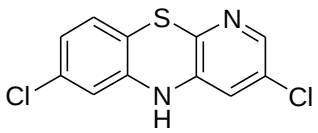
Brown solid. Mp: 224-225 ℃ (lit. mp 220-225 ℃). ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 8.77 (s, 1H), 7.87 (dd, *J* = 8.79 Hz, 2.46 Hz, 1H), 7.77 (d, *J* = 2.37 Hz, 1H), 6.88-6.98 (m, 2H), 6.76-6.80 (m, 2H). Anal. Calcd for C12H7ClN2O2S: C, 51.71; H, 2.53; N, 10.05. Found: C, 51.89; H, 2.70; N, 10.19.

3-Chloro-5*H*-benzo[*b*]pyrido[3,2-*e*][1,4]thiazine (Table 2, entry 22)



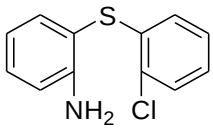
Brown solid. Mp: 179-181 ℃. ^{1}H NMR (300 MHz, CD_3COCD_3), δ (ppm): 8.55 (s, 1H), 7.75 (d, *J* = 2.25, 1H), 7.31 (d, *J* = 2.25 Hz, 1H), 7.03 (dd, *J* = 13.77 Hz, 7.35Hz, 1H), 6.81-6.95 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d6), δ (ppm): 151.7, 143.3, 140.1, 132.8, 127.9, 125.9, 123.0, 122.7, 115.3, 114.5, 114.2. Anal. Calcd for C11H7ClN2S: C, 56.29; H, 3.01; N, 11.94. Found: C, 56.47; H, 3.30; N, 11.72.

3,7-Dichloro-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (Table 2, entry 23)



Brown solid. Mp: 190-194 ℃. ^{1}H NMR (300 MHz, CD_3COCD_3), δ (ppm): 9.51 (s, 1H), 7.83 (d, *J* = 2.31, 1H), 7.50 (d, *J* = 1.98 Hz, 1H), 6.95 (d, *J* = 8.82 Hz, 1H), 6.82-6.85 (m, 2H). 150.9, 143.5, 141.6, 133.0, 132.1, 127.2, 123.6, 122.2, 114.5, 114.0, 113.7. Anal. Calcd for C11H6Cl2N2S: C, 49.09; H, 2.25; N, 10.41. Found: C, 49.23; H, 2.53; N, 10.22.

2-(2-Chlorophenylsulfanyl)-phenylamine (predominant byproduct, Table 1, entry 1 to 4)



Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.45 (d, *J* = 7.67 Hz, 1H), 7.31-7.35 (m, 1H), 7.27 (d, *J* = 8.29 Hz, 1H), 7.01-7.06 (m, 2H), 6.77-6.85 (m, 2H), 6.62-6.66 (m, 1H), 3.41-3.80 (m, 2H). ^{13}C NMR (100MHz, DMSO-d6), δ (ppm): 150.8 (*J* = 8.0 Hz), 137.5 (d, *J* = 40.0), 135.8, 131.7, 129.7, 129.4, 127.5, 126.3 (d, *J* = 11.0 Hz), 125.8, 116.9, 115.0, 109.4. Anal. Calcd for C12H10ClNS: C, 61.14; H, 4.28; N, 5.94. Found: C, 61.39; H, 4.52; N, 5.72.

References

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3 D. Ma. Q. Geng, H. Zhang, Y. Jiang, *Angew. Chem., Int. Ed.*, 2010, **49**, 1291.
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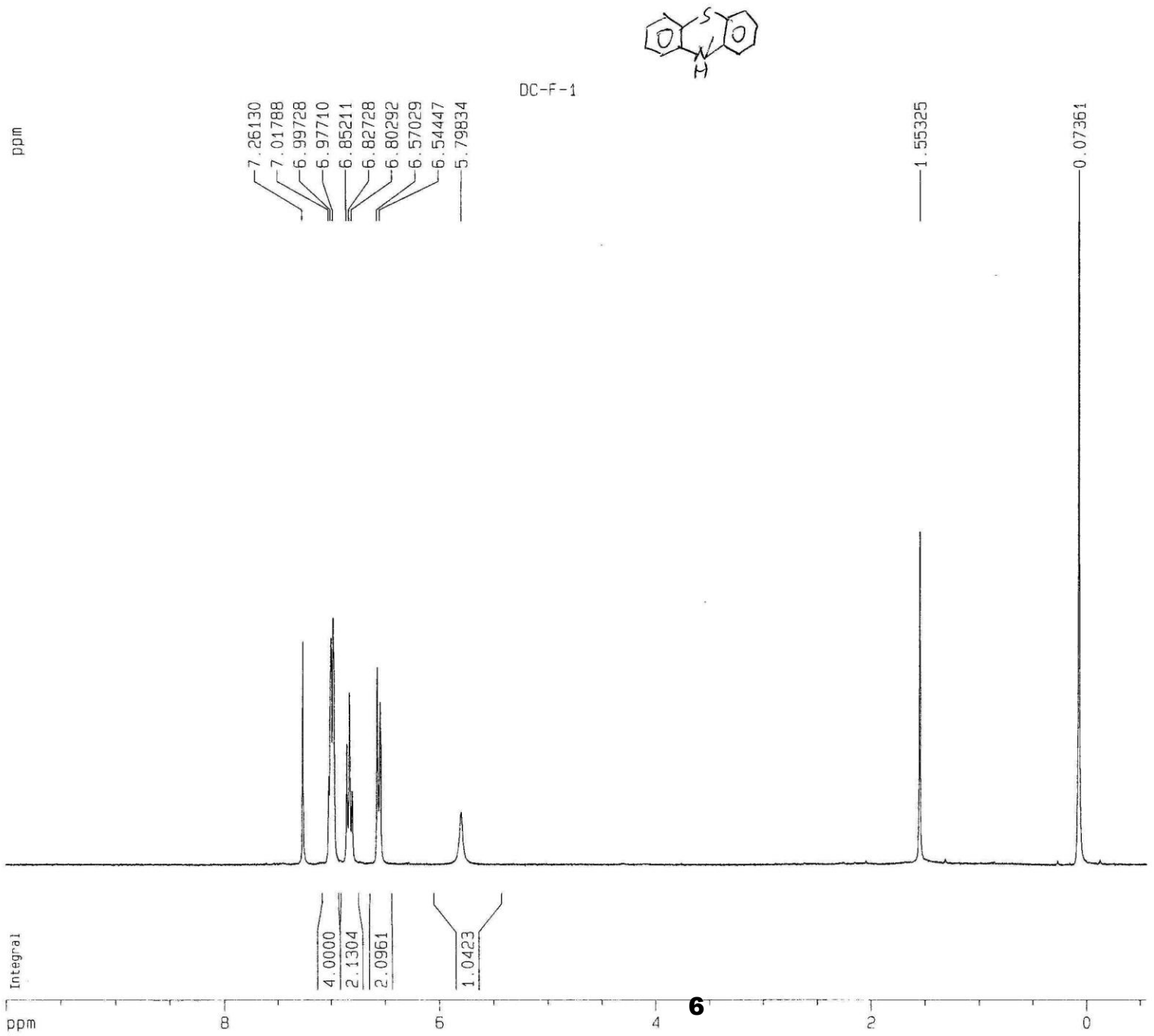

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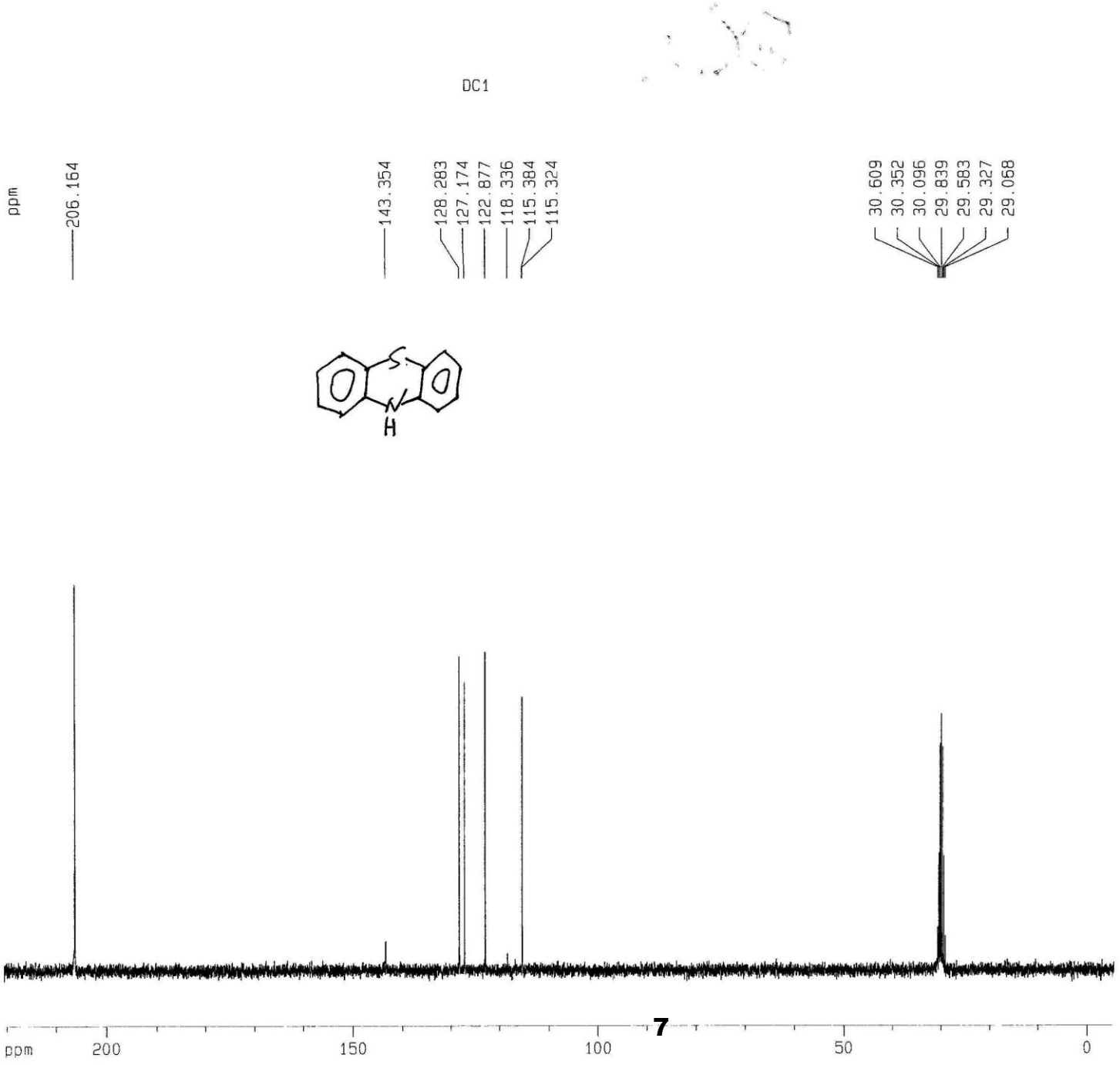

7

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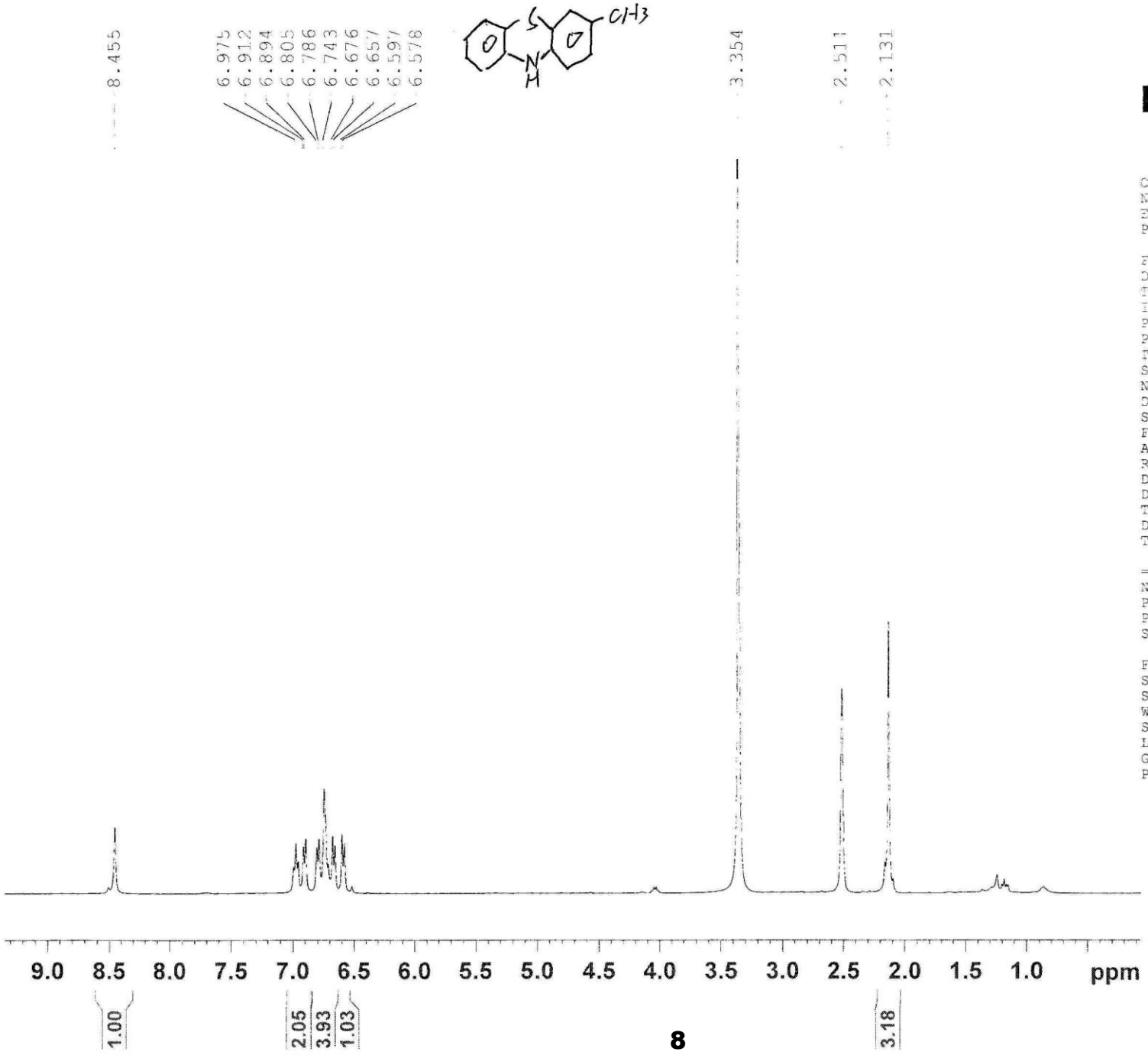

BRUKER

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PC                           1.00
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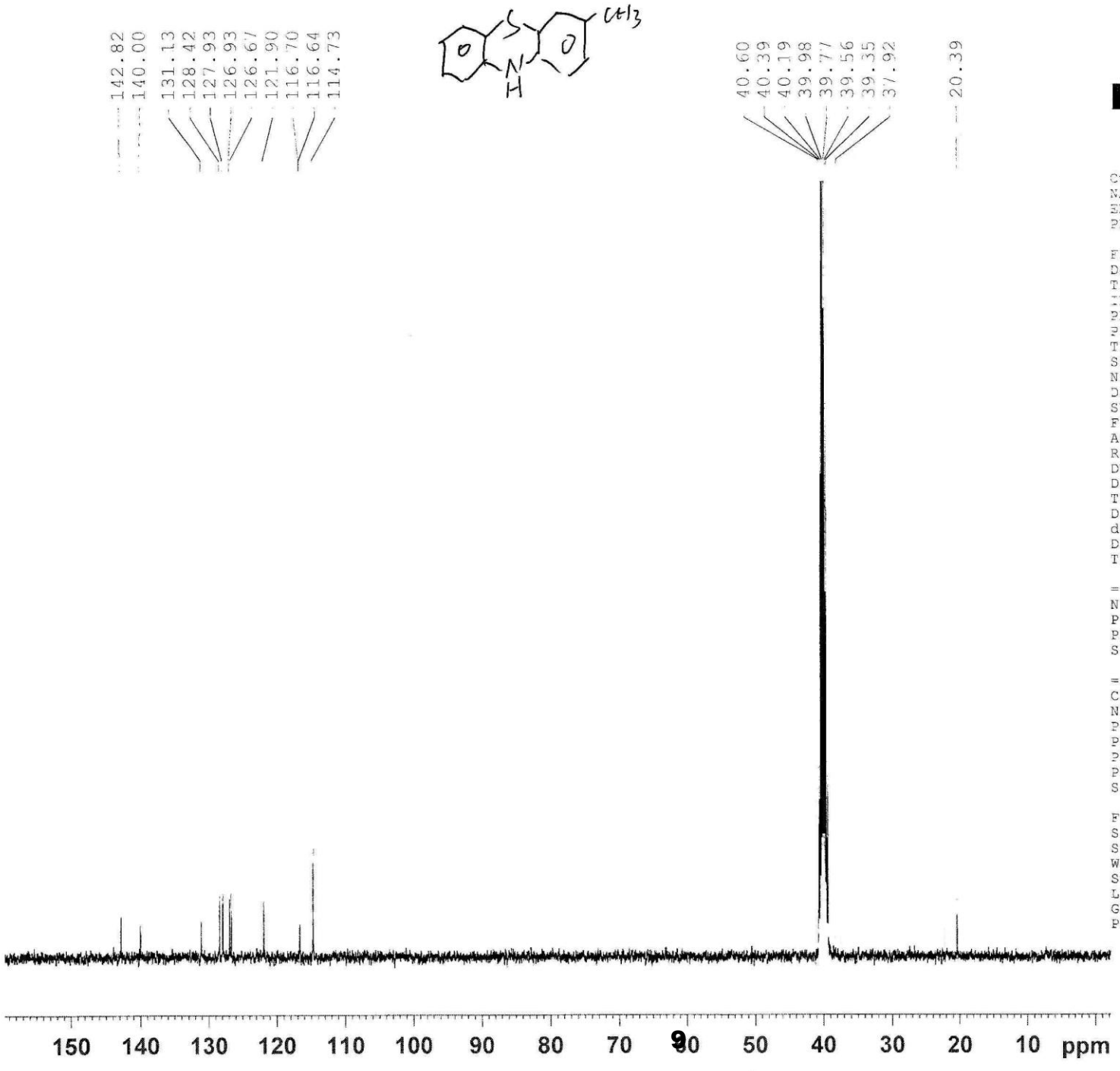

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```
Current Data Parameters
NAME      2011-01-04 Gaichuan-DC6
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120104
Time               9.24
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                  256
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW                20.800 usec
DE                 6.50 usec
TE                296.4 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                19.40 usec
PL1               -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             60.00 usec
PL12              11.09 dB
PL13              13.05 dB
PL2               -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.40
```

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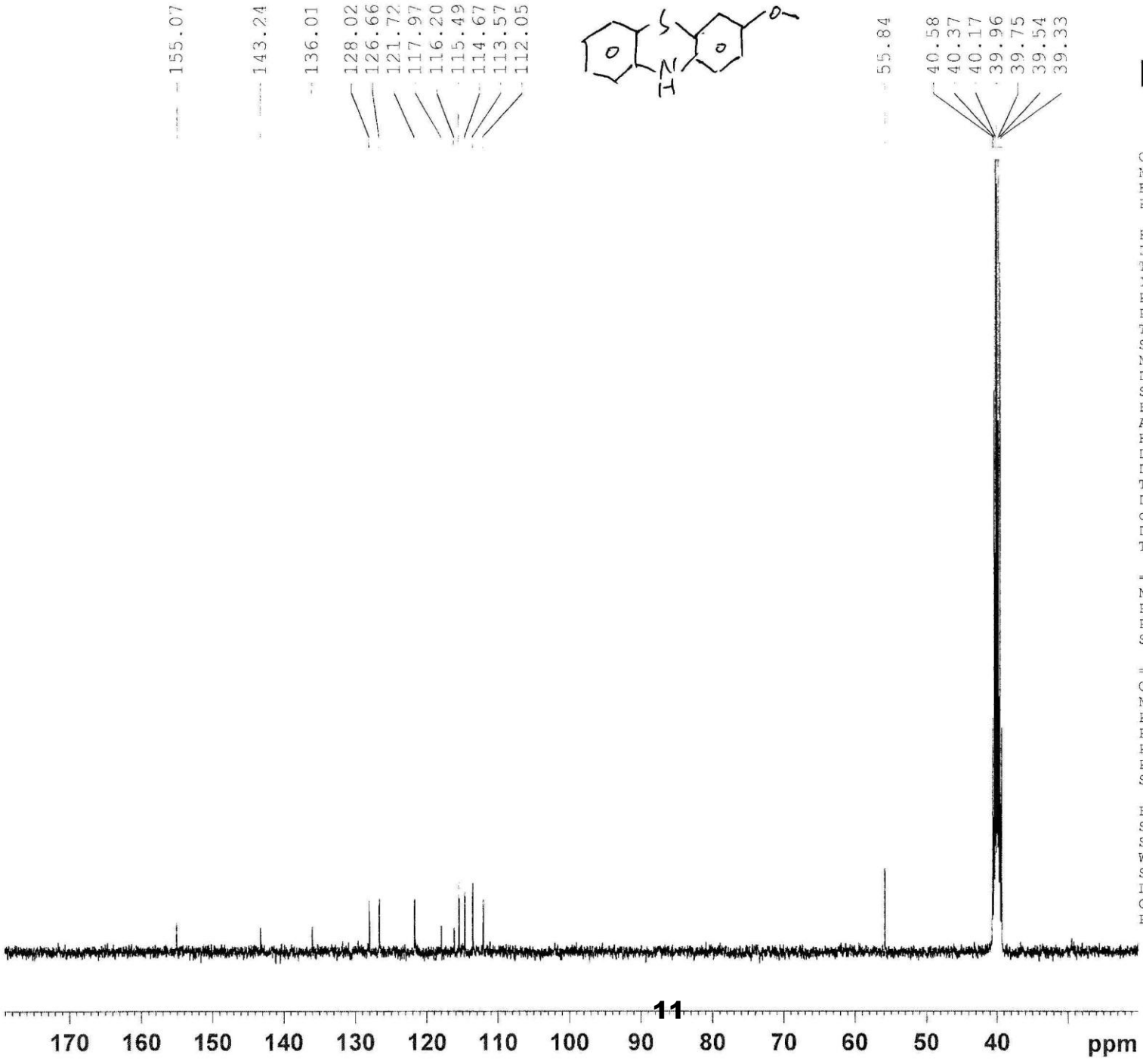
```
Current Data Parameters
NAME      2011-01-04 daichuan-DC8
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20120104
Time                       10.55
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                     zg30
TD                         65536
SOLVENT                     DMSO
NS                            16
DS                             0
SWH                     8223.685 Hz
FIDRES                  0.125483 Hz
AQ                      3.9846387 sec
RG                          90.5
DW                        60.800 usec
DE                         6.50 usec
TE                        295.0 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                        13.30 usec
PL1                       -2.00 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                         32768
SF                  400.1300000 MHz
WDW                           EM
SSB                            0
LB                         0.60 Hz
GB                             0
PC                          1.00
```



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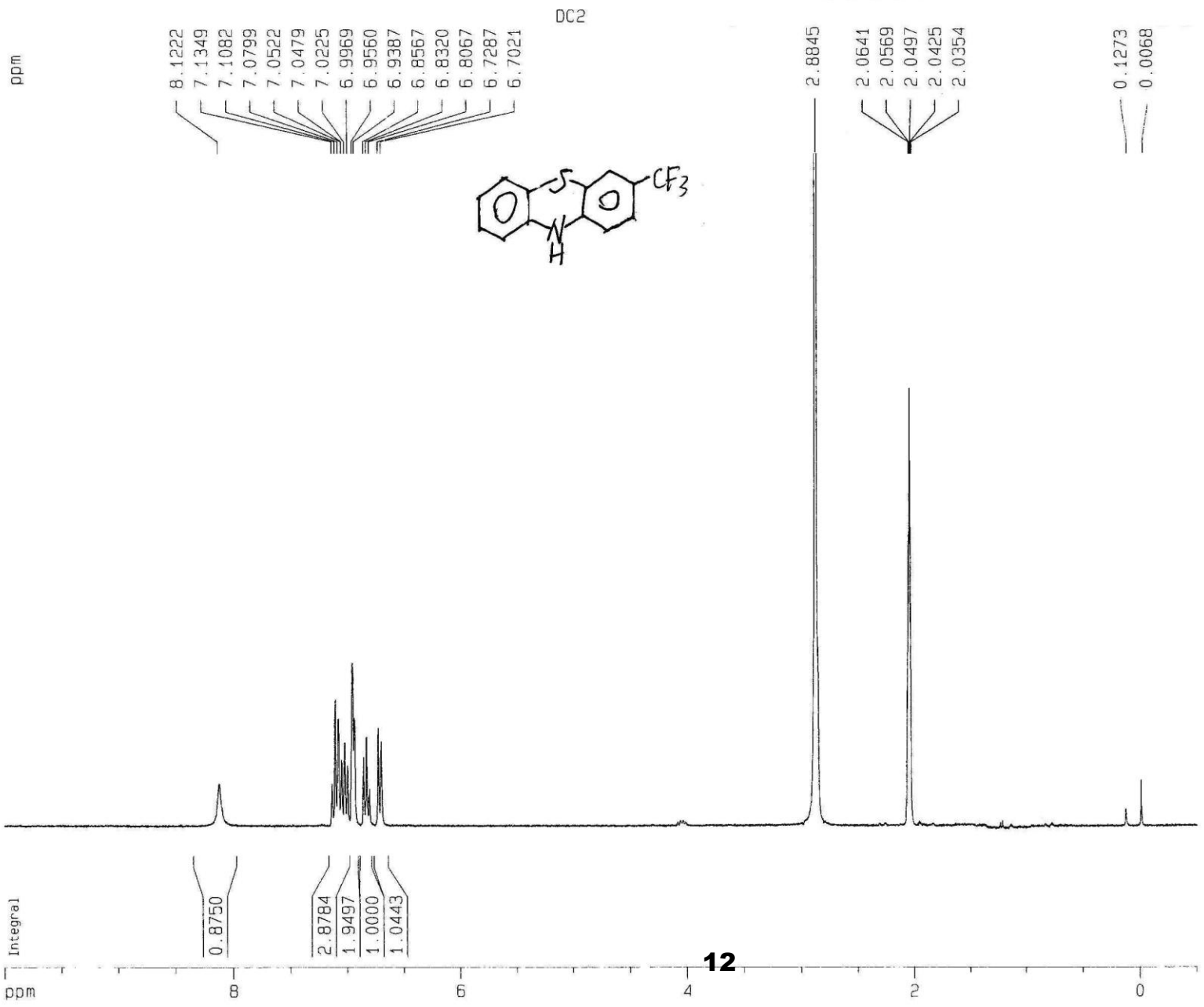
```
Current Data Parameters
NAME      2011-01-04 daichuan-DC8
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120104
Time              10.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   256
DS                     0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                295.8 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 19.40 usec
PL1                -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              60.00 usec
PL12               11.09 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
```



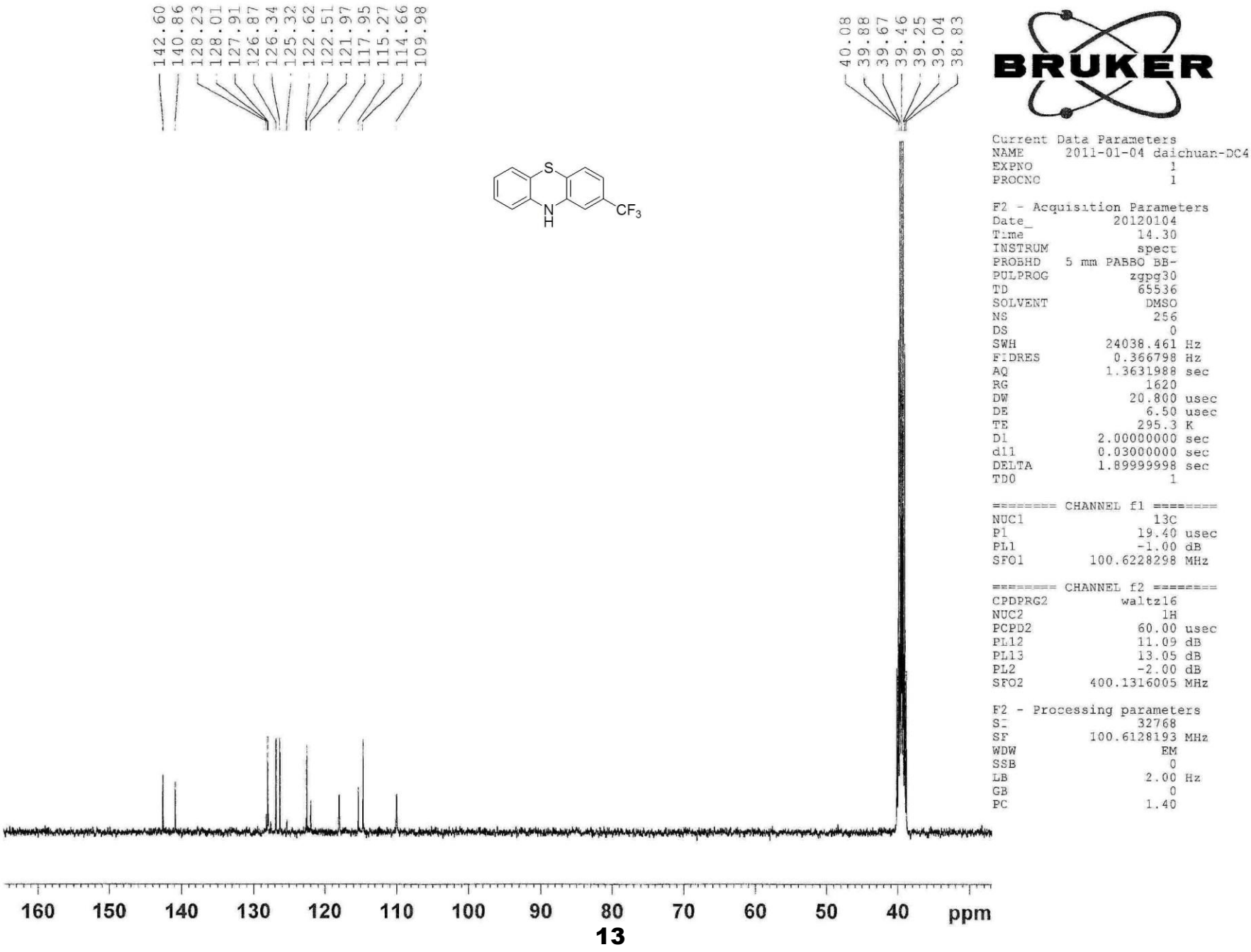
Current Data Parameters
NAME zql-2011-169
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111107
Time 16.20
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 295.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.10 dB
SFO1 300.1321009 MHz

F2 - Processing parameters
SI 32768
SF 300.1300044 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 50.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



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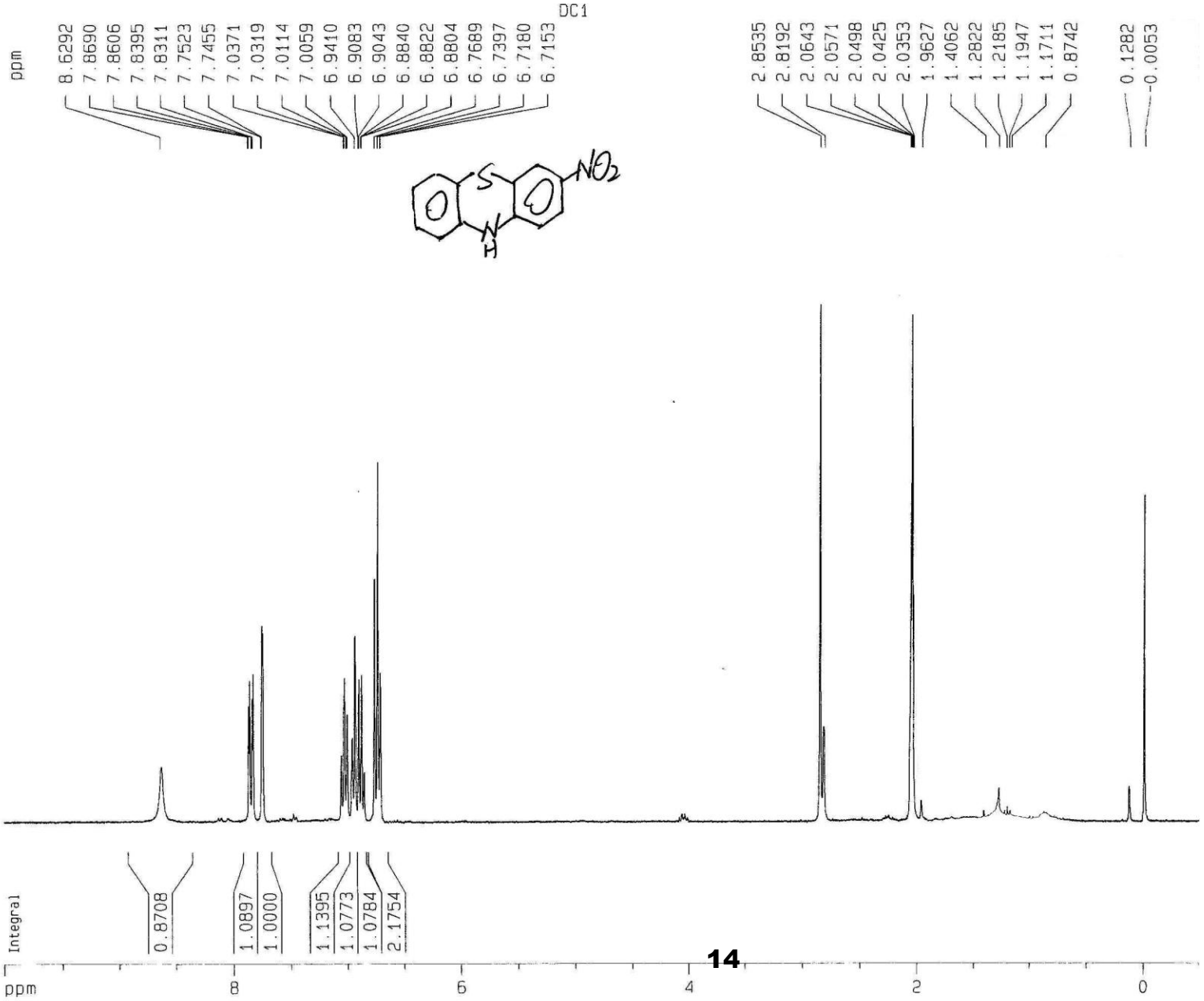
```
Current Data Parameters
NAME      2011-01-04 daichuan-DC4
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120104
Time              14.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT            DMSO
NS                  256
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1620
DW                20.800 usec
DE                 6.50 usec
TE                295.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                19.40 usec
PL1               -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             60.00 usec
PL12              11.09 dB
PL13              13.05 dB
PL2               -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6128193 MHz
WDW                EM
SSB                   0
LB                2.00 Hz
GB                    0
PC                1.40
```



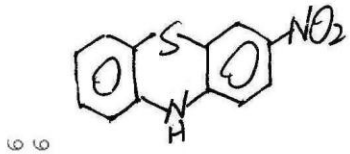
Current Data Parameters
NAME zq1-2011-174
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111107
Time 16.48
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 19
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 295.5 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

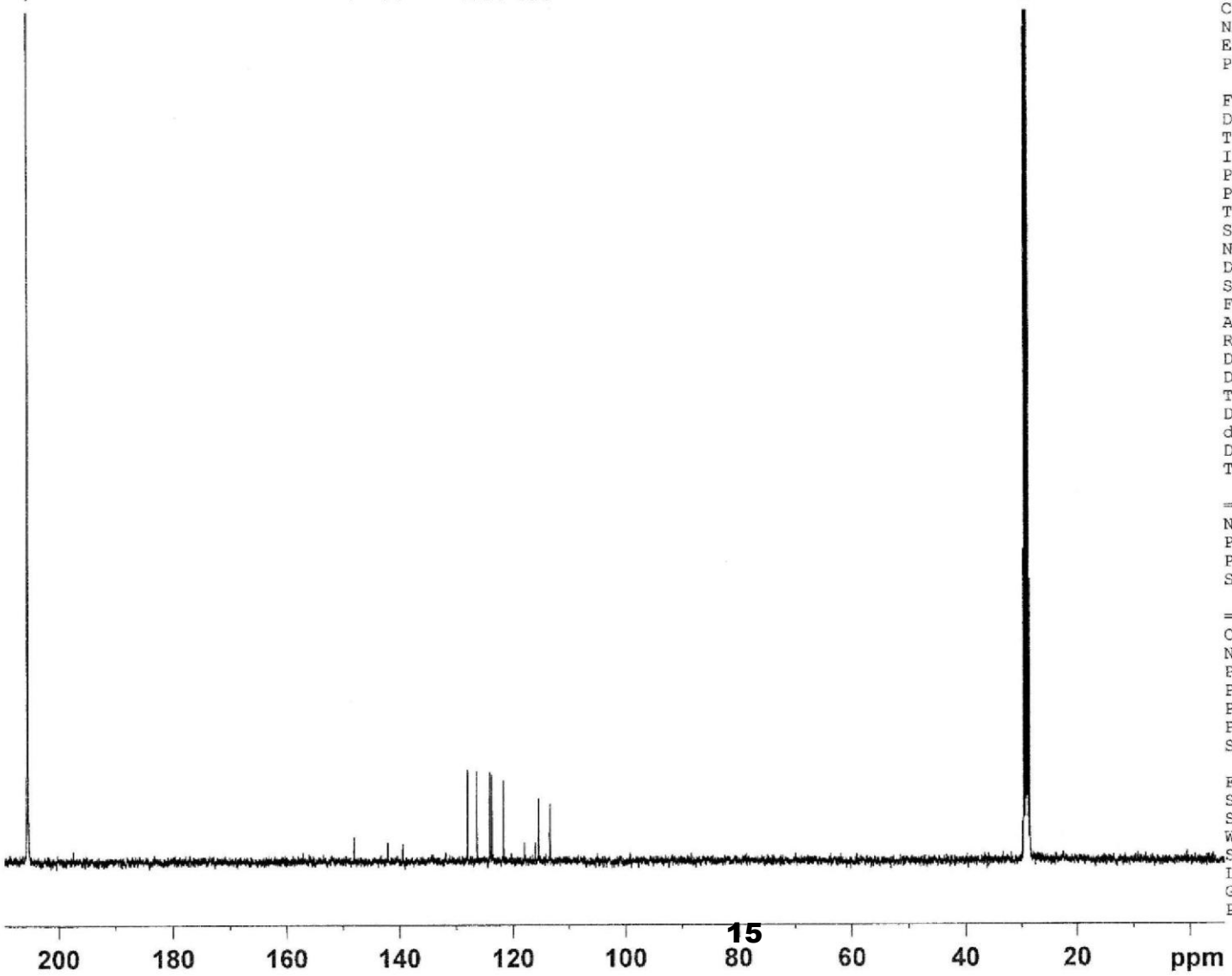
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.10 dB
SF01 300.1321009 MHz

F2 - Processing parameters
SI 32768
SF 300.1300042 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



205.46
205.26
147.95
142.09
139.39
128.02
126.35
124.13
123.79
121.62
117.96
116.03
115.43
115.36
113.46
113.40
29.72
29.54
29.35
29.16
28.97
28.77
28.58
28.39



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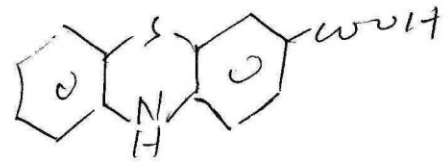
Current Data Parameters
NAME 2011-11-25 zandan-DC
EXPNO 2
PROCNO 1

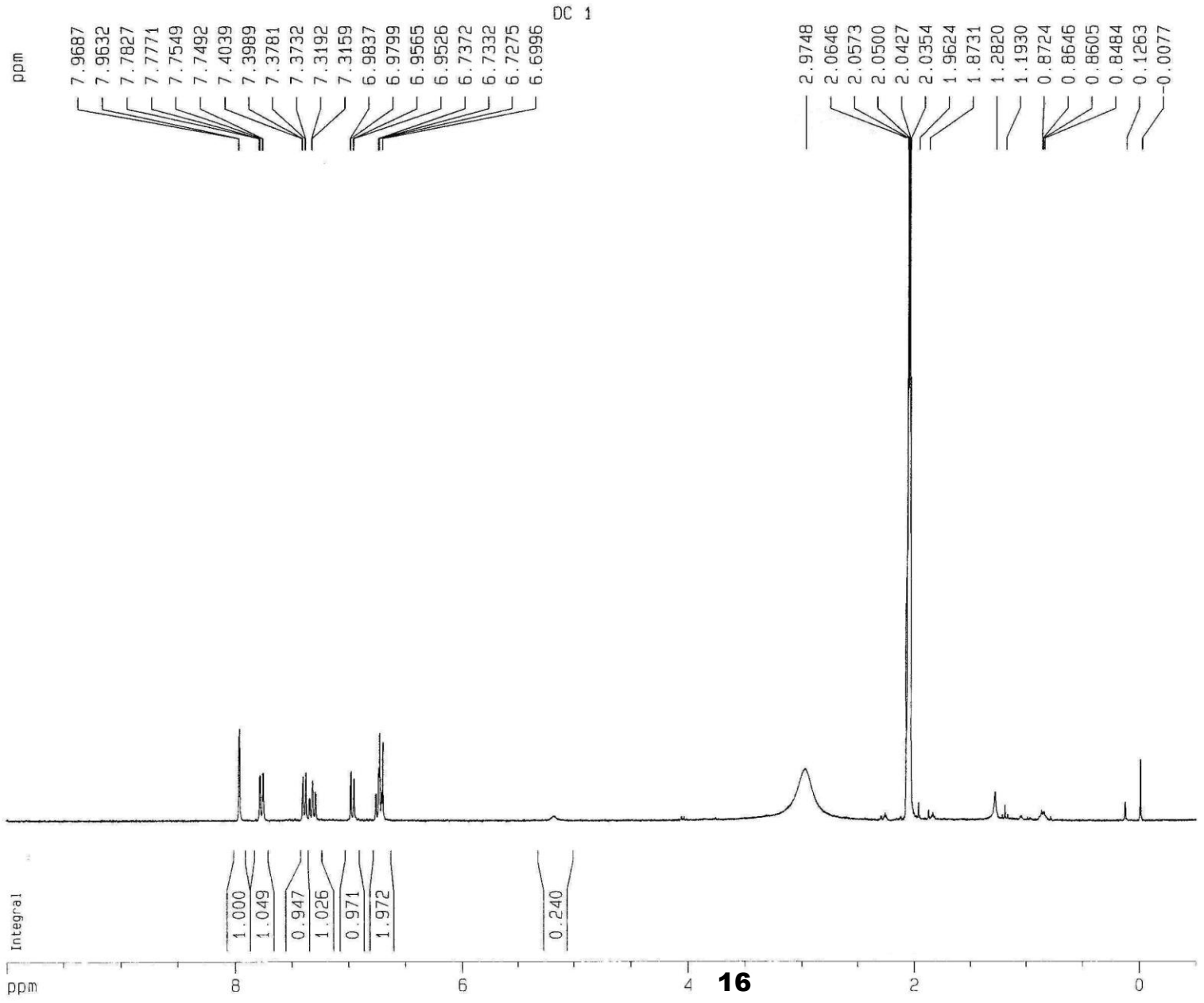
F2 - Acquisition Parameters
Date_ 20111125
Time 11.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 273
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 90.5
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 19.40 usec
PL1 -1.00 dB
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.09 dB
PL13 13.05 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40





Current Data Parameters

NAME	zq1-2011-189
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20111125
Time	18.06
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	16
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	128
DW	83.400 usec
DE	6.00 usec
TE	295.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

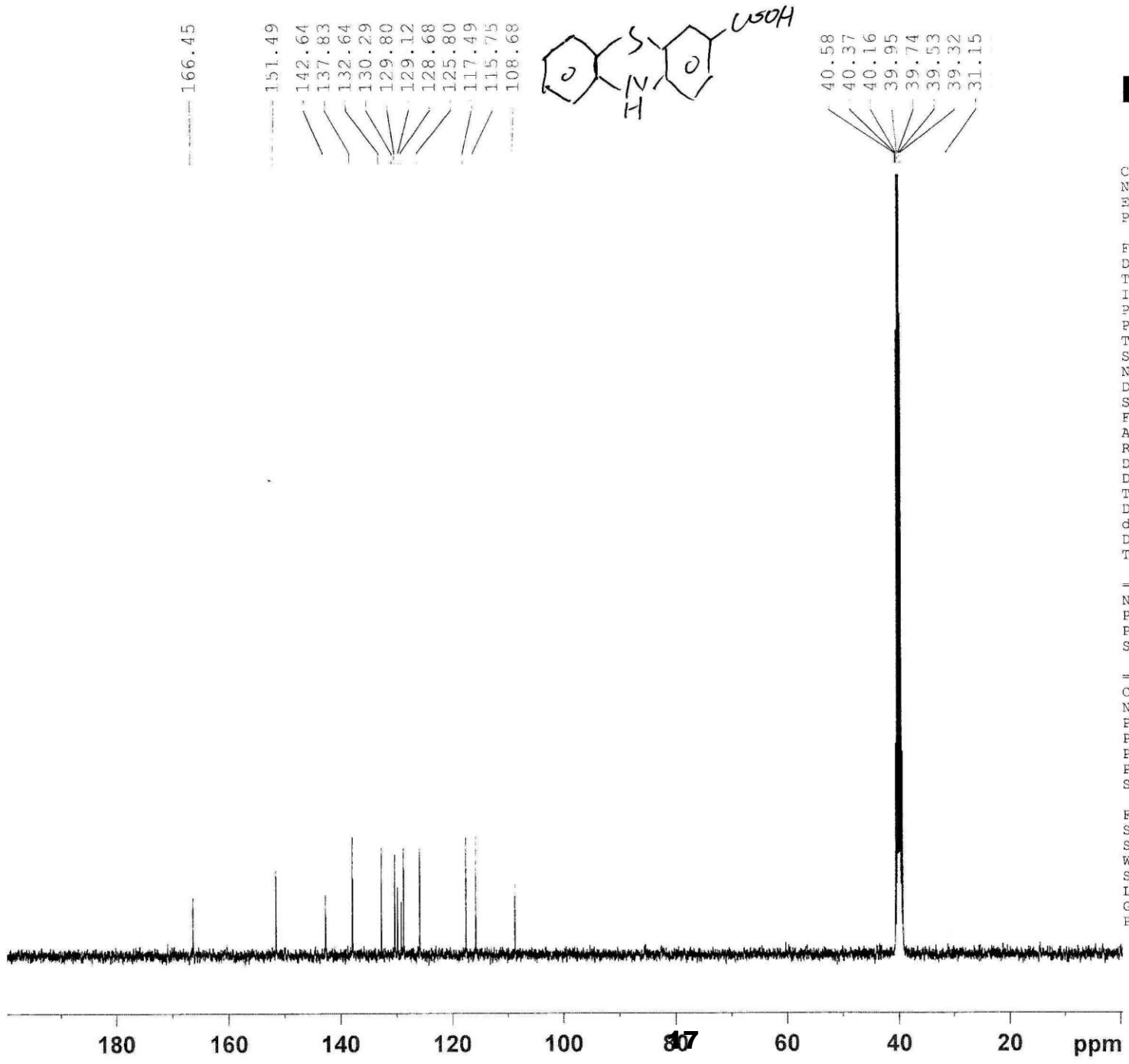
NUC1	1H
P1	10.50 usec
PL1	0.10 dB
SFO1	300.1321009 MHz

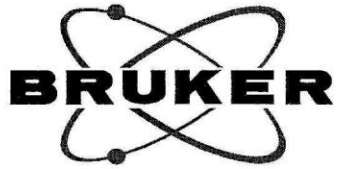
F2 - Processing parameters

SI	32768
SF	300.1300042 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	40.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm





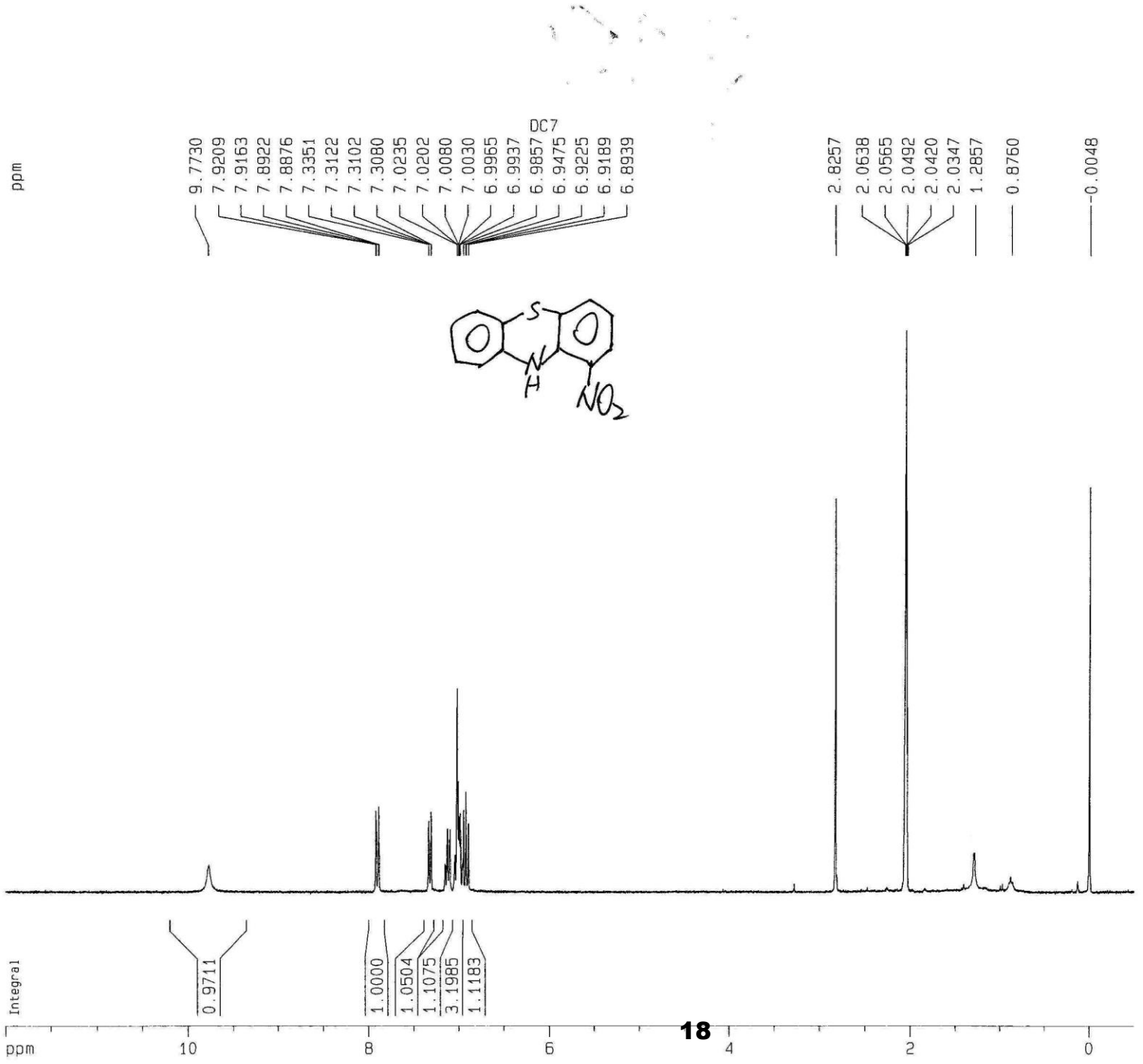

```
Current Data Parameters
NAME      2011-01-04 daichuan-DC3
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120104
Time               11.36
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   256
DS                     0
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                19.40 usec
PL1               -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             60.00 usec
PL12              11.09 dB
PL13              13.05 dB
PL2               -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                 2.00 Hz
GB                     0
PC                  1.40
```



Current Data Parameters

NAME	zql-2011-165
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20111019
Time	11.12
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	16
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	128
DW	83.400 usec
DE	6.00 usec
TE	296.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

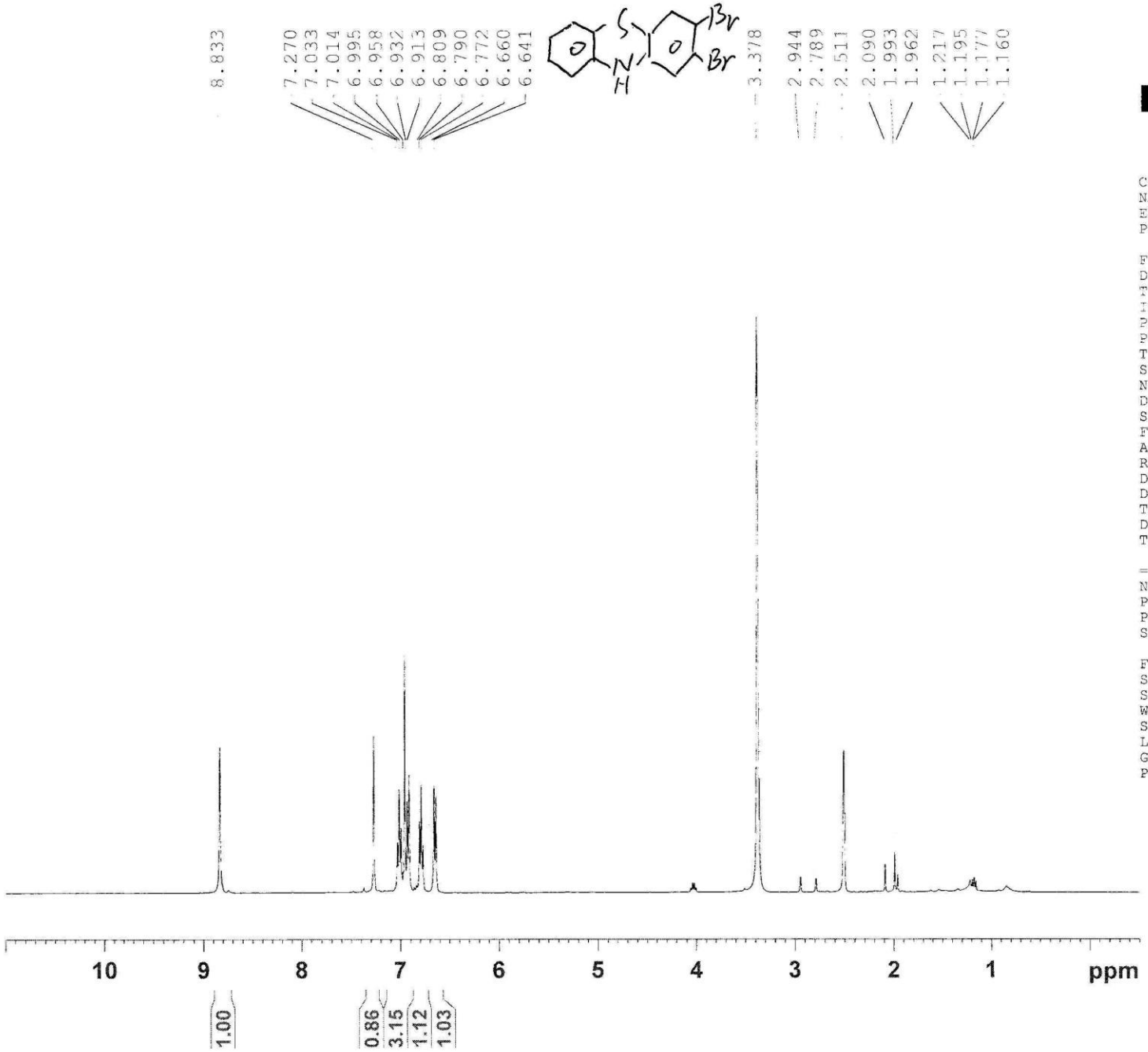
NUC1	1H
P1	10.50 usec
PL1	0.10 dB
SFO1	300.1321009 MHz

F2 - Processing parameters

SI	32768
SF	300.1300042 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	12.000 ppm
F1	3601.56 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.62500 ppm/cm
HZCM	187.58125 Hz/cm



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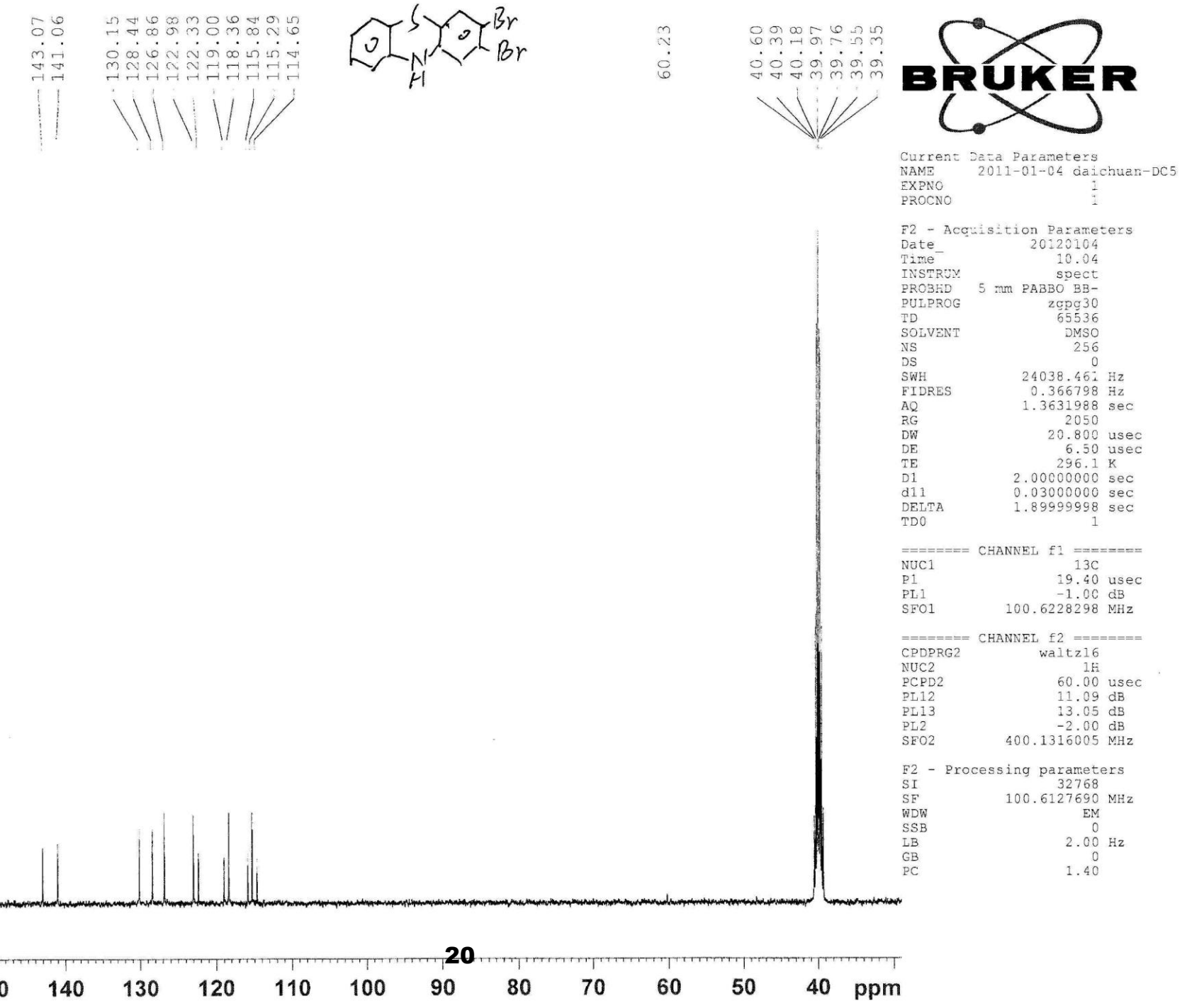
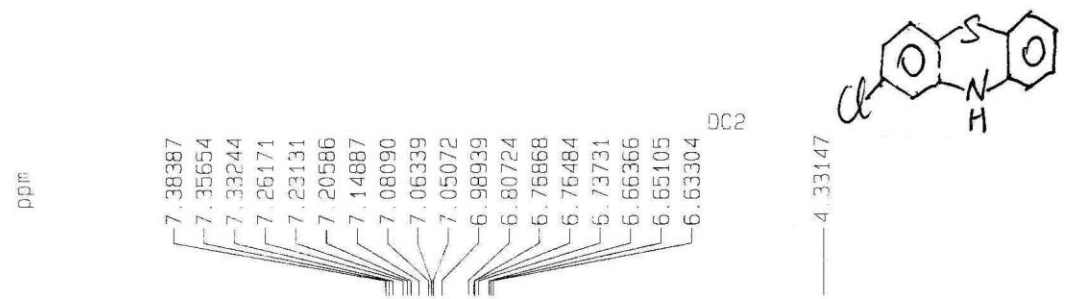
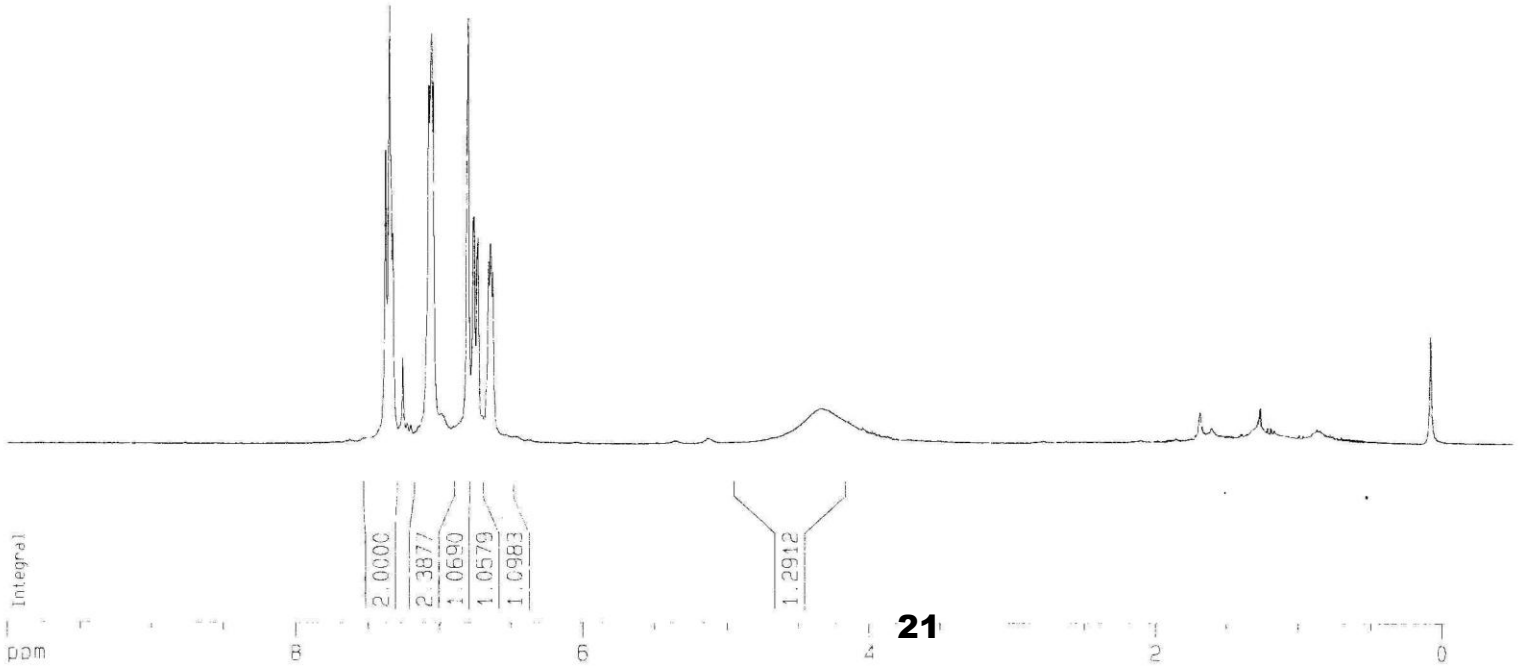
```
Current Data Parameters
NAME      2011-01-04 daichuan-DC5
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20120104
Time                       10.06
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                     zg30
TD                         65536
SOLVENT                     DMSO
NS                             16
DS                              0
SWH                     8223.685 Hz
FIDRES                  0.125483 Hz
AQ                      3.9846387 sec
RG                           90.5
DW                       60.800 usec
DE                        6.50 usec
TE                         295.3 K
D1                   1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                           1H
P1                        13.30 usec
PL1                       -2.00 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                          32768
SF                  400.1300000 MHz
WDW                            EM
SSB                             0
LB                        0.60 Hz
GB                              0
PC                           1.00
```







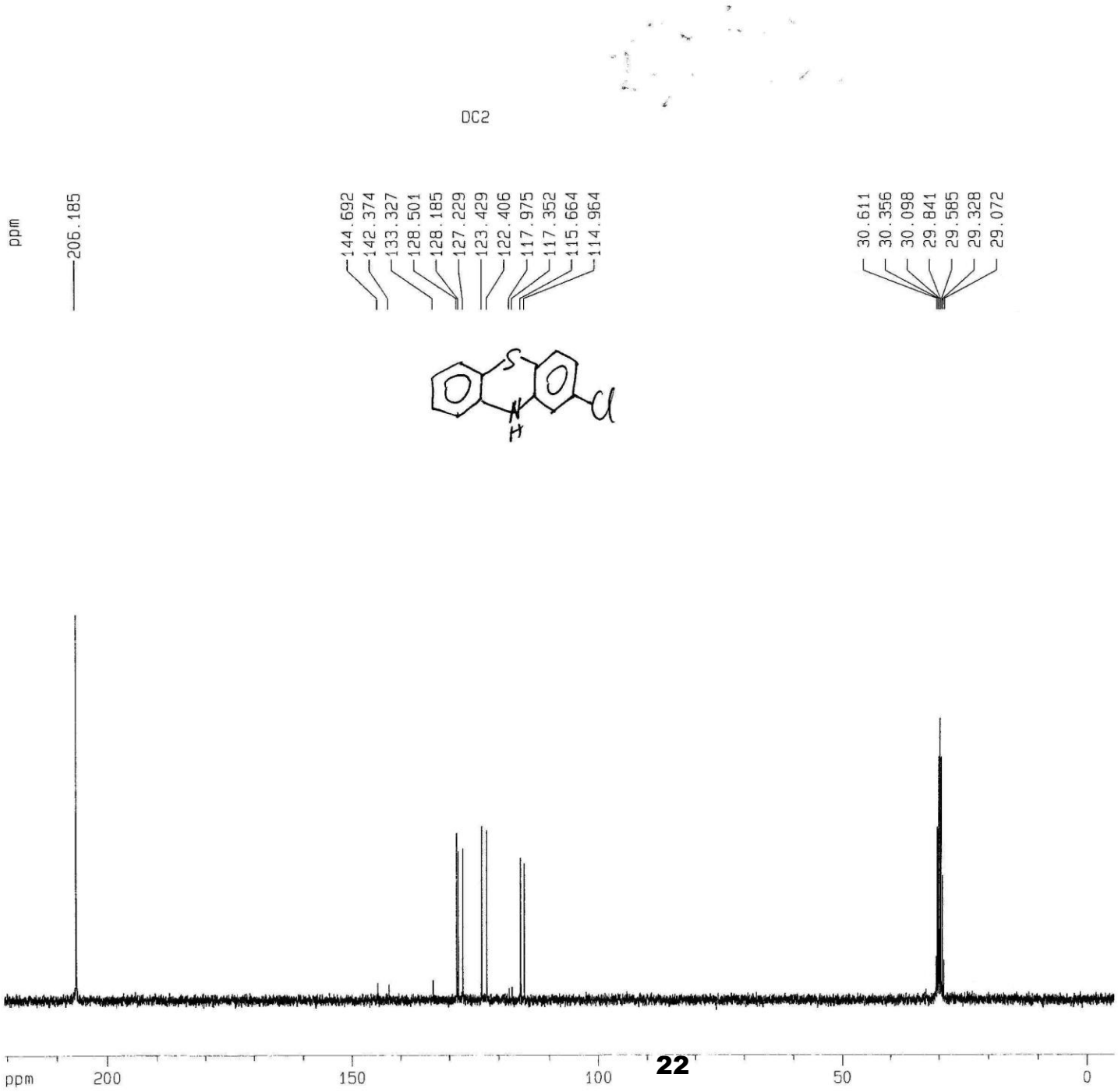
Current Data Parameters
NAME zql-2011-96
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110729
Time 11.23
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DW 83.400 usec
DE 6.00 usec
TE 299.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

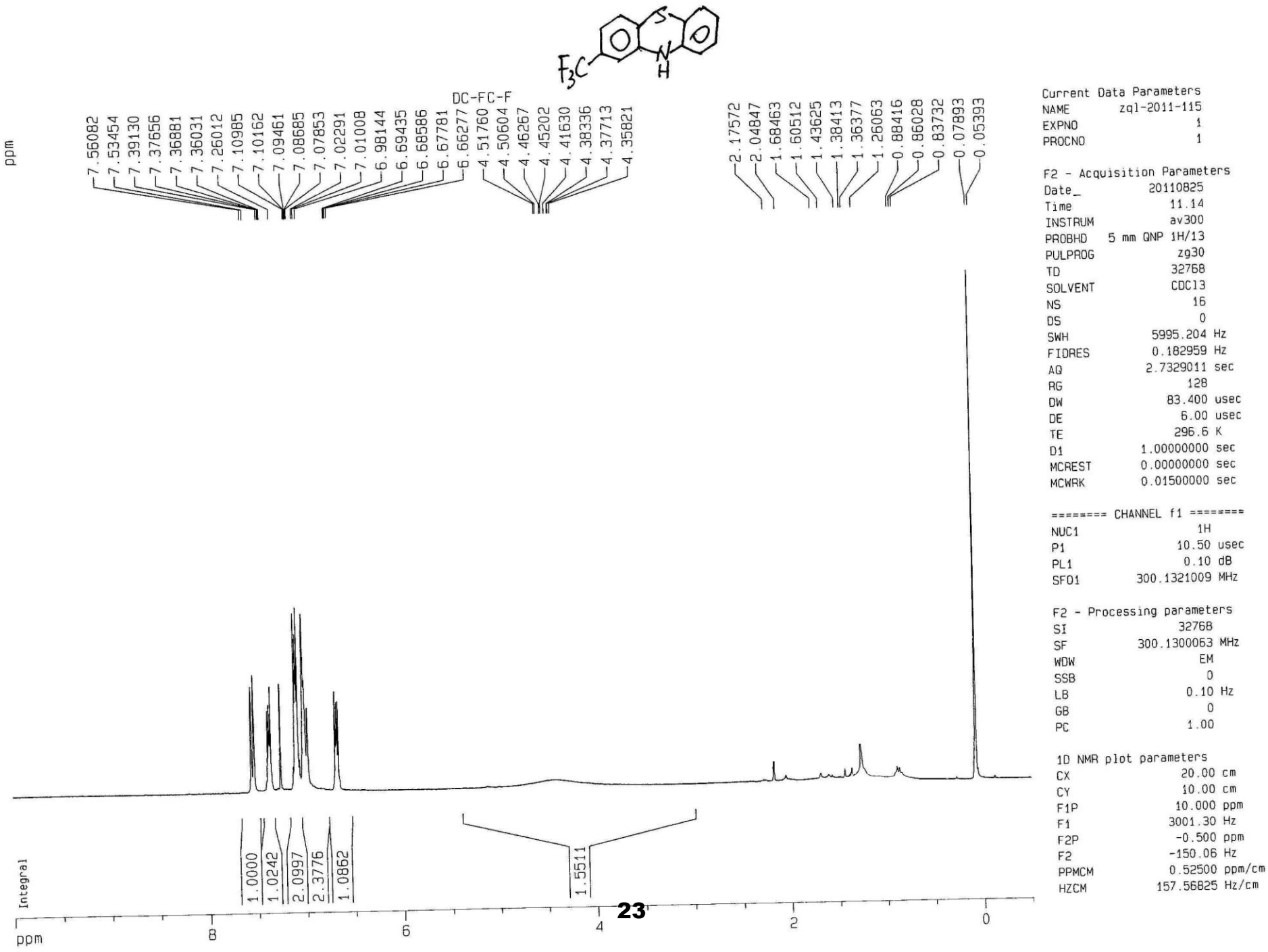
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.10 dB
SFO1 300.1321009 MHz

F2 - Processing parameters
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.05 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm




```
Current Data Parameters
NAME        zq1-2011-160
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20111019
Time               11.34
INSTRUM            av300
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH            22675.736 Hz
FIDRES         0.346004 Hz
AQ             1.4451188 sec
RG                  8192
DW                22.050 usec
DE                 6.00 usec
TE                296.6 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.50 usec
PL1                -0.81 dB
SFO1         75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                 0.10 dB
PL12               17.74 dB
PL13               17.74 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 65536
SF           75.4676832 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                  7.00 cm
F1P               220.500 ppm
F1              16640.62 Hz
F2P                -5.500 ppm
F2               -415.07 Hz
PPMCM           11.30000 ppm/cm
HZCM          852.78479 Hz/cm
```



Current Data Parameters

NAME	zql-2011-115
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20110825
Time	11.14
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	128
DW	83.400 usec
DE	6.00 usec
TE	296.6 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

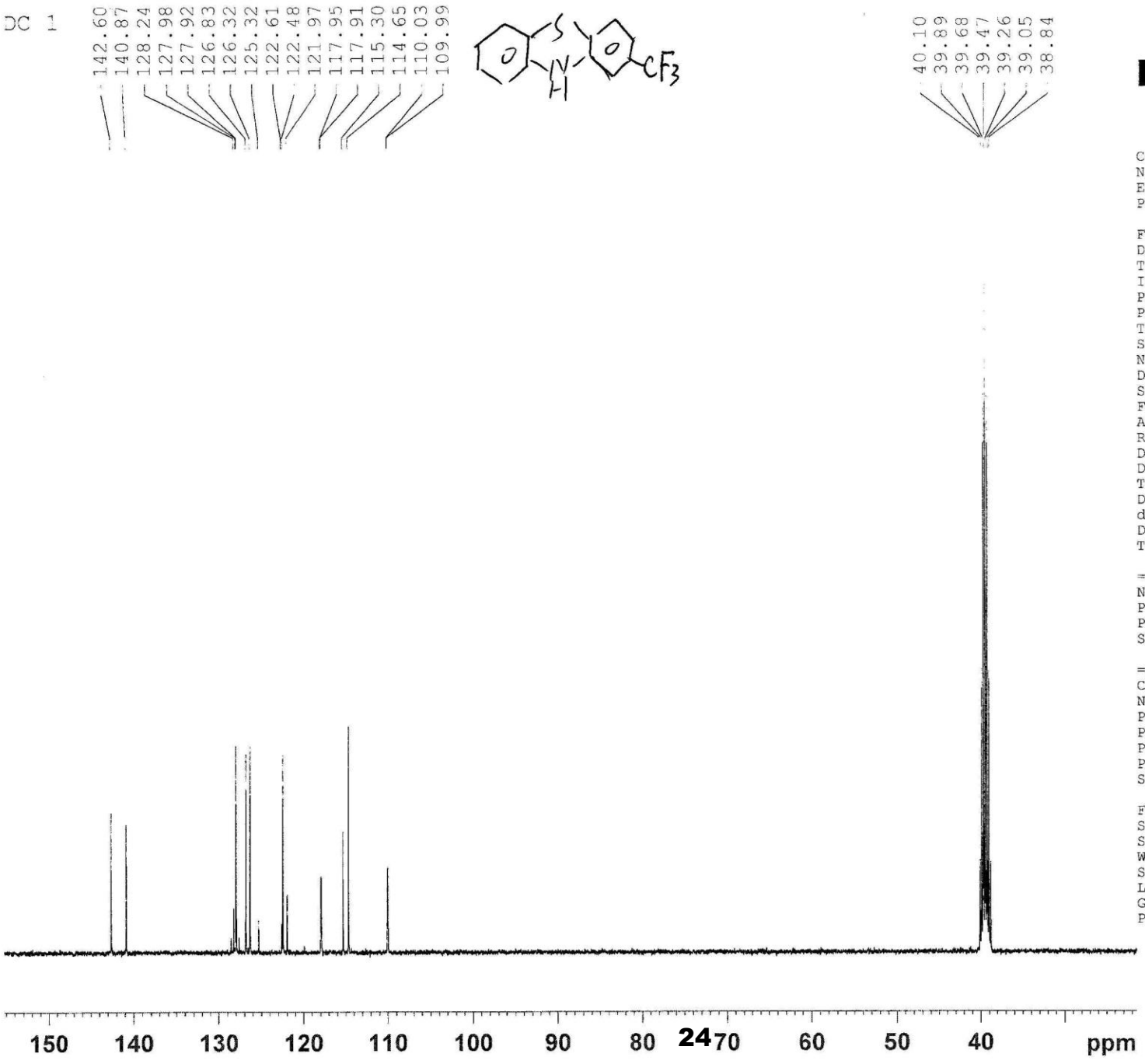
NUC1	1H
P1	10.50 usec
PL1	0.10 dB
SFO1	300.1321009 MHz

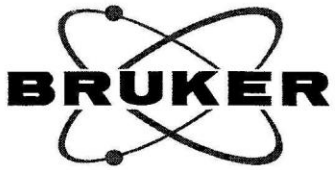
F2 - Processing parameters

SI	32768
SF	300.1300063 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

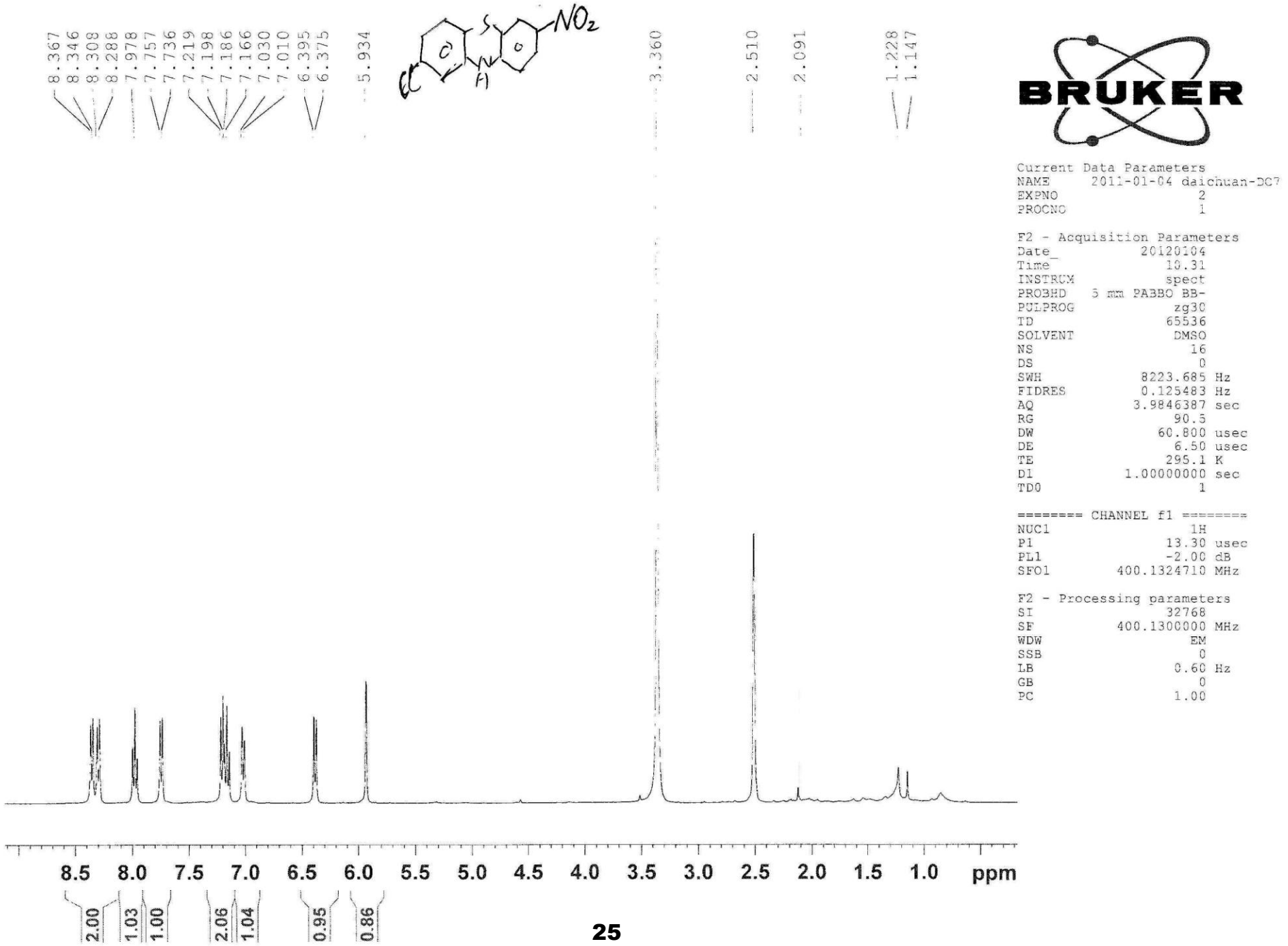
1D NMR plot parameters

CX	20.00 cm
CY	10.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm






```
Current Data Parameters
NAME      2011-01-04 daichuan-DC1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120104
Time             13.07
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                  512
DS                    0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 1620
DW               20.800 usec
DE                6.50 usec
TE               296.3 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 19.40 usec
PL1                -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2              60.00 usec
PL12               11.09 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6128193 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



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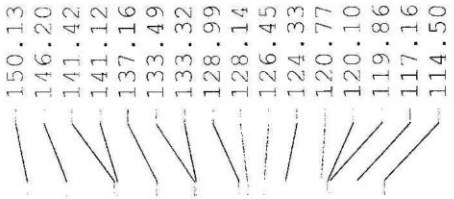
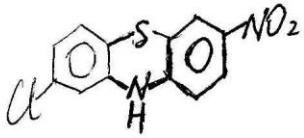
Current Data Parameters
NAME 2011-01-04 daichuan-DC7
EXPNO 2
PROCNO 1

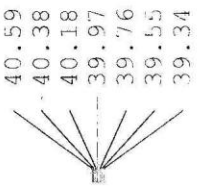
F2 - Acquisition Parameters
Date_ 20120104
Time 10.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1

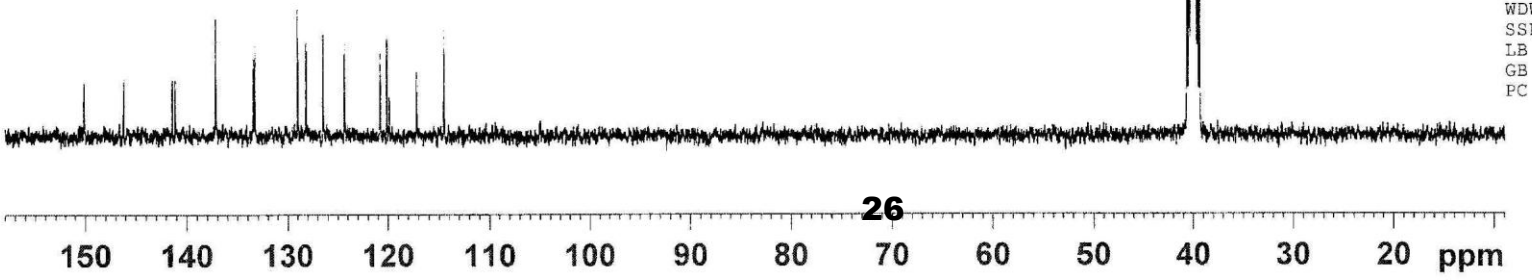
======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 -2.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.00

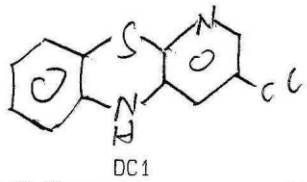


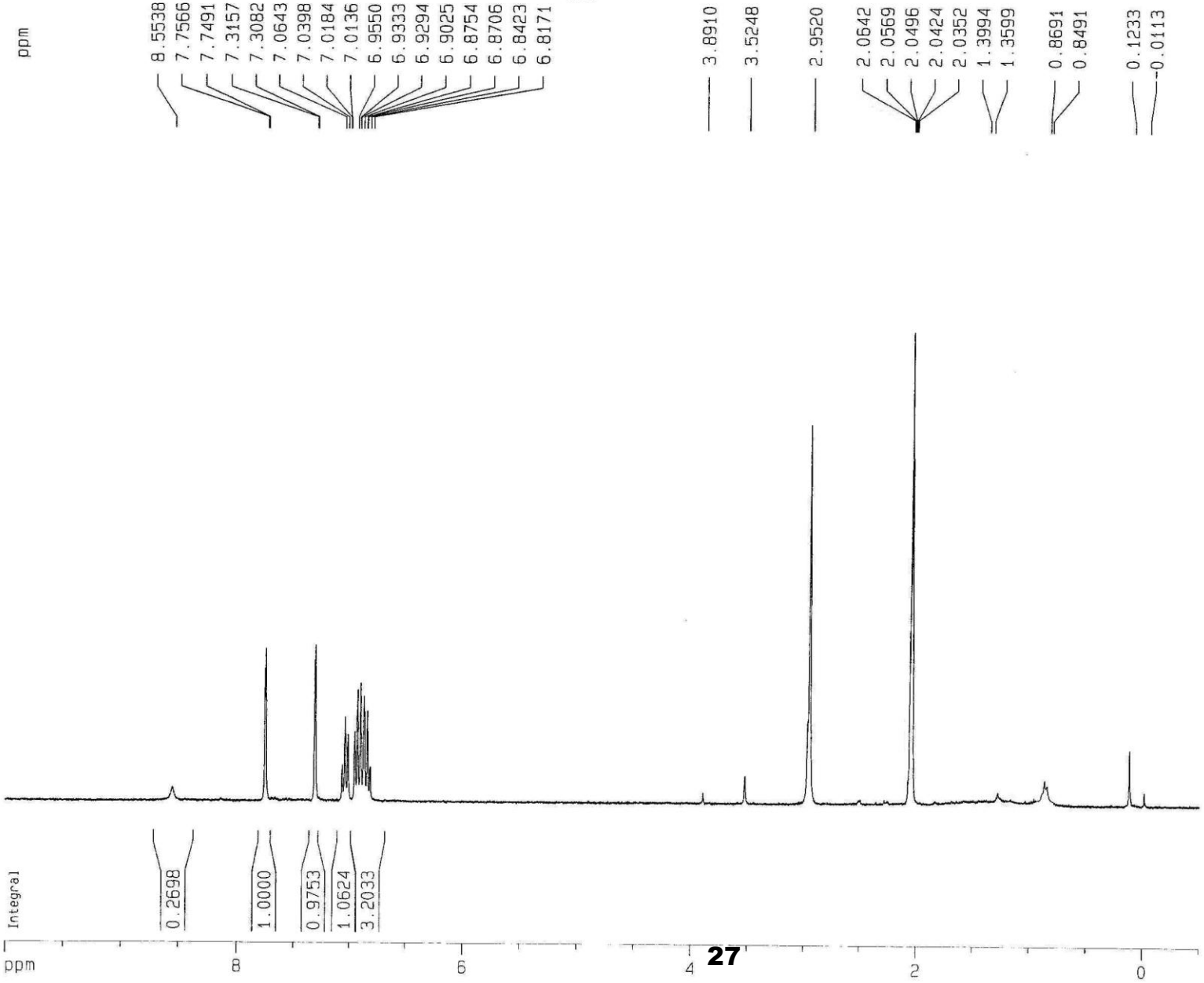







```
Current Data Parameters
NAME      2011-01-04 daichuan-DC7
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120104
Time              10.29
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   256
DS                     0
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                296.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 19.40 usec
PL1                -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              60.00 usec
PL12               11.09 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                  2.00 Hz
GB                     0
PC                  1.40
```





Current Data Parameters

NAME	zql-2011-198
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20111213
Time	16.11
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	8
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	8
DW	83.400 usec
DE	6.00 usec
TE	291.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

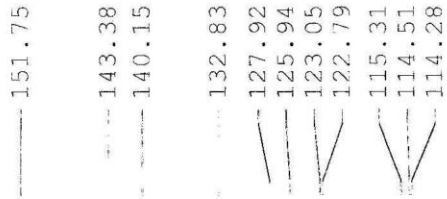
NUC1	1H
P1	10.50 usec
PL1	0.10 dB
SFO1	300.1321009 MHz

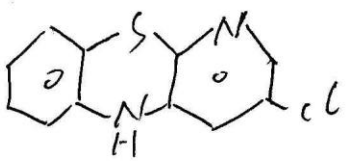
F2 - Processing parameters

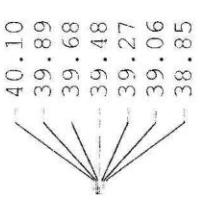
SI	32768
SF	300.1300044 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

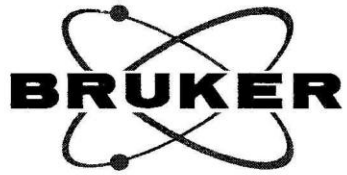
1D NMR plot parameters

CX	20.00 cm
CY	8.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm

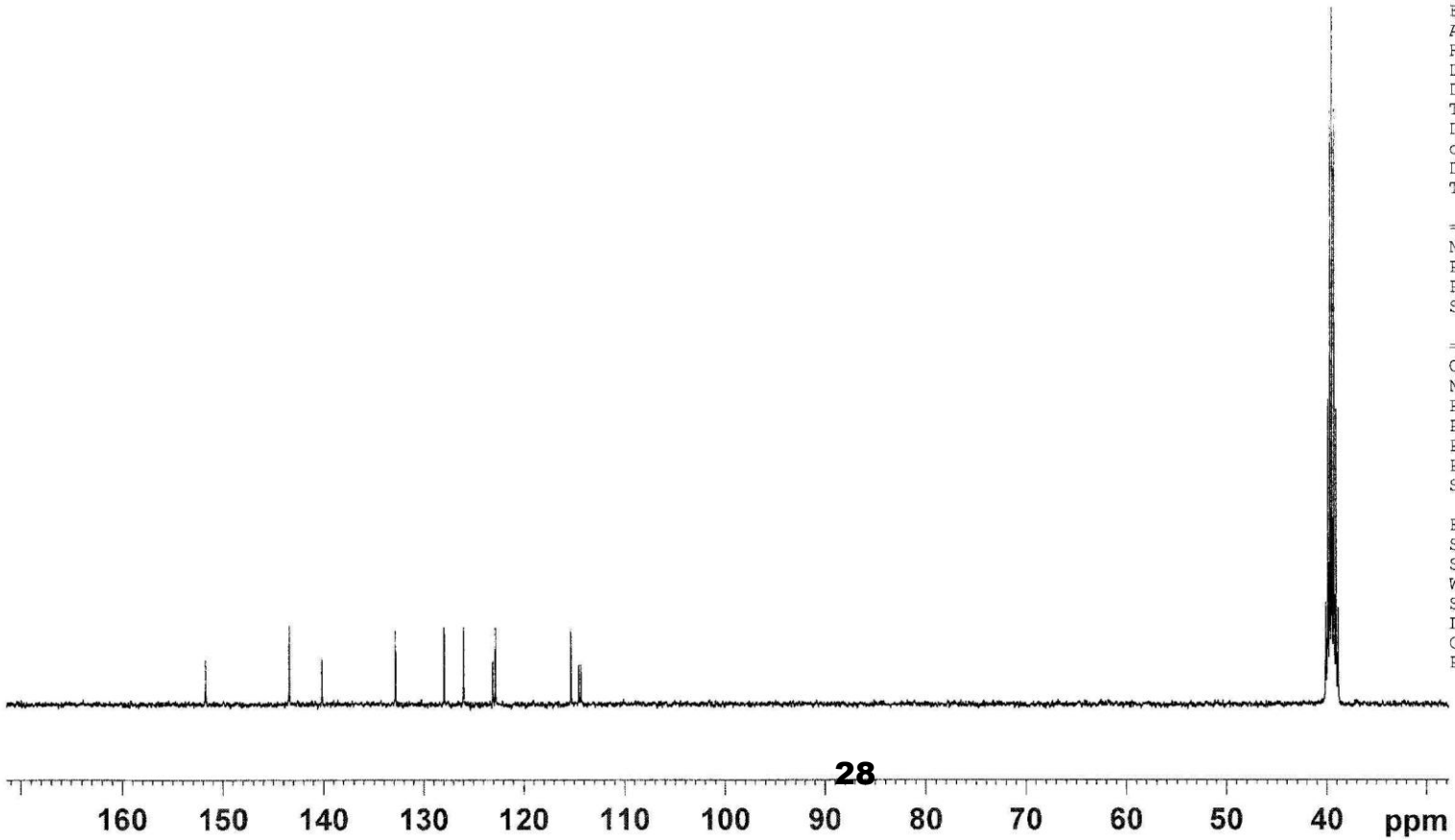


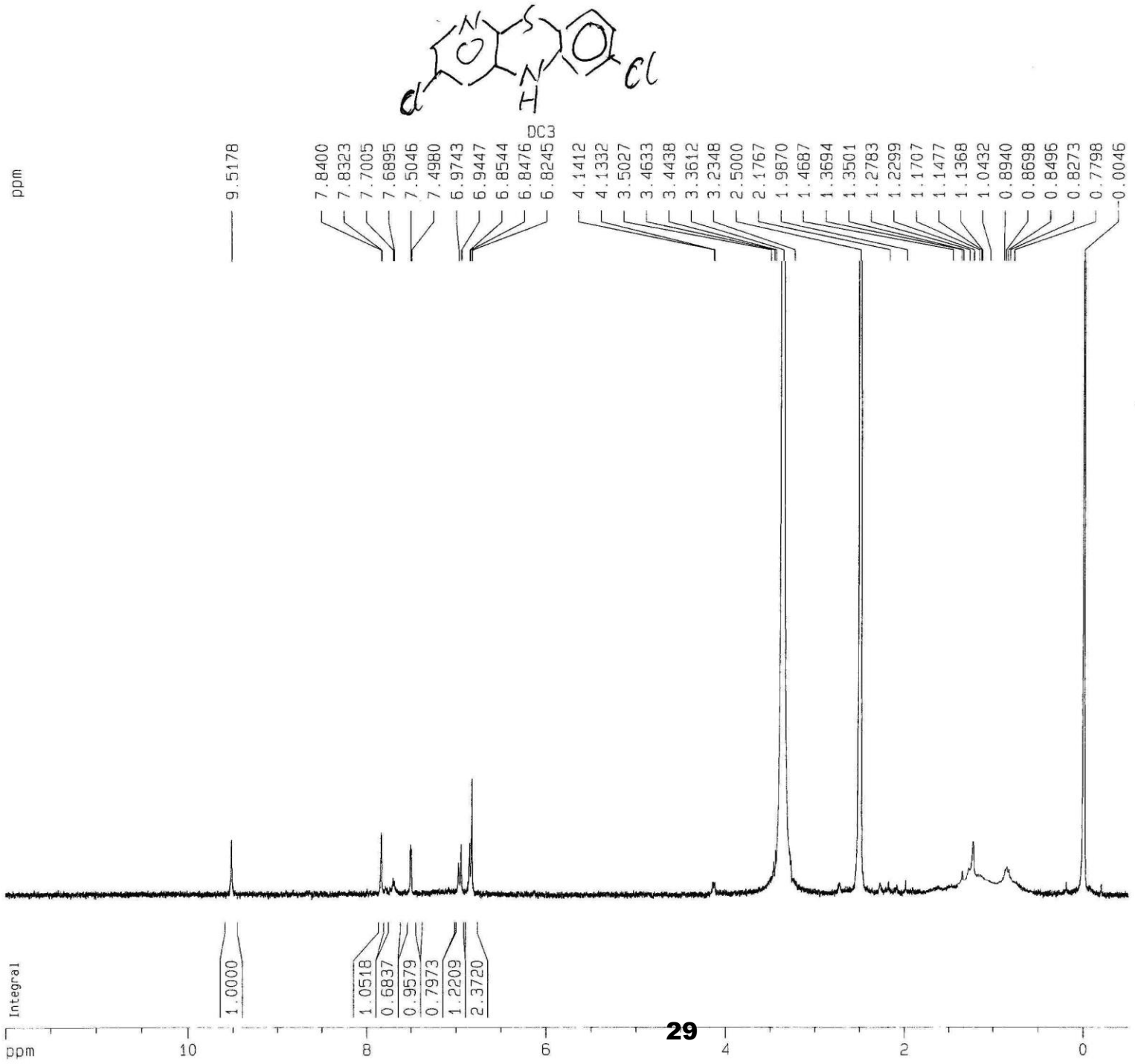







```
Current Data Parameters
NAME      2011-01-04 daichuan-DC2
EXPNO                           1
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20120104
Time                        14.01
INSTRUM                     spect
PROBHD   5 mm PABBO BB-
PULPROG                    zgpg30
TD                          65536
SOLVENT                      DMSO
NS                             256
DS                               0
SWH                    24038.461 Hz
FIDRES                  0.366798 Hz
AQ                     1.3631988 sec
RG                           1620
DW                         20.800 usec
DE                          6.50 usec
TE                         295.6 K
D1                    2.00000000 sec
d11                   0.03000000 sec
DELTA                 1.89999998 sec
TD0                              1

======== CHANNEL f1 ========
NUC1                           13C
P1                           19.40 usec
PL1                          -1.00 dB
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                           1H
PCPD2                        60.00 usec
PL12                         11.09 dB
PL13                         13.05 dB
PL2                          -2.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                            32768
SF                  100.6128193 MHz
WDW                              EM
SSB                               0
LB                             2.00 Hz
GB                                0
PC                             1.40
```





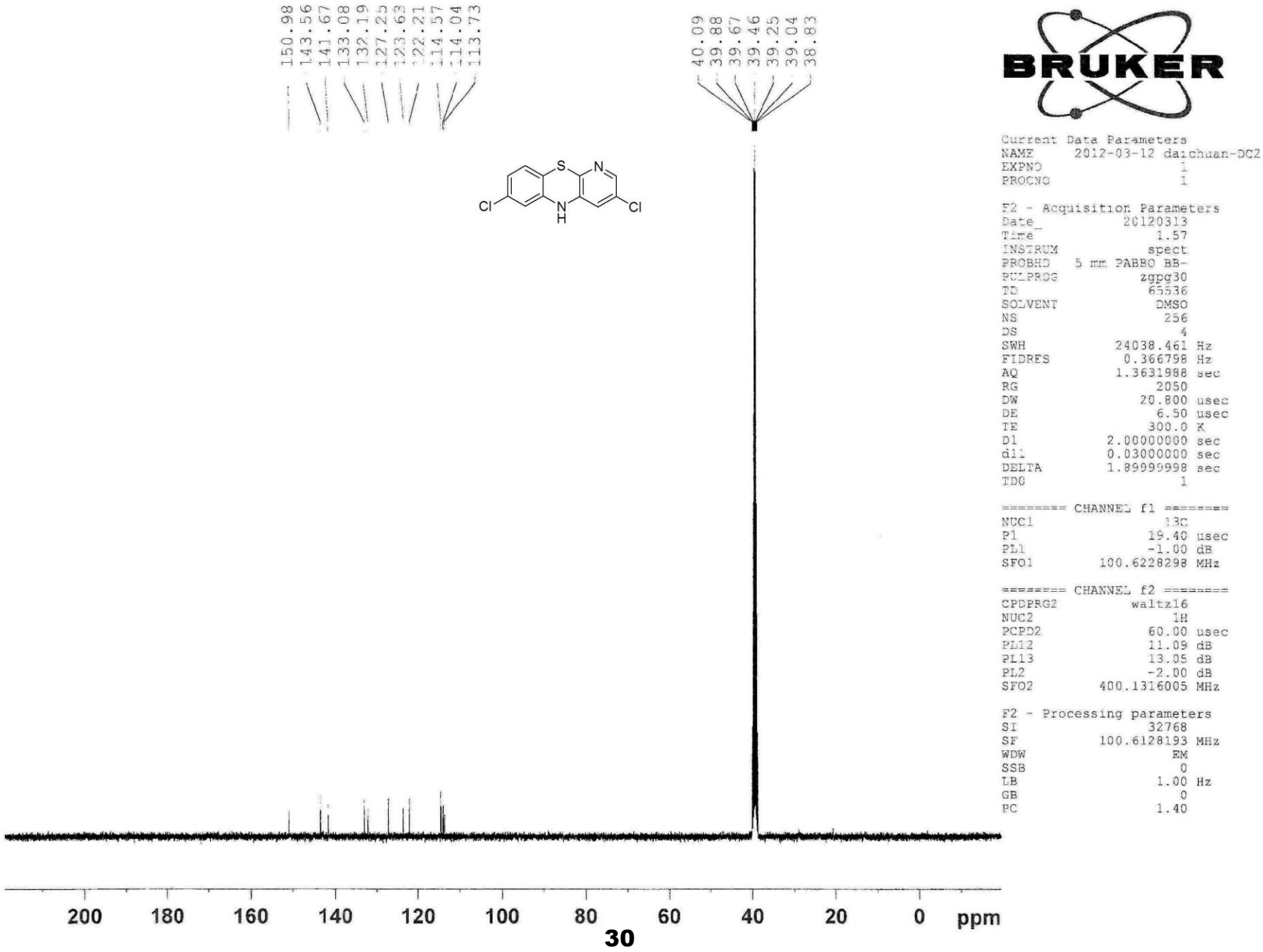
Current Data Parameters
NAME zql-2011-182
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111116
Time 11.05
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 64
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 32
DW 83.400 usec
DE 6.00 usec
TE 293.6 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.10 dB
SF01 300.1321009 MHz

F2 - Processing parameters
SI 32768
SF 300.1300014 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 600.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.58125 Hz/cm



30

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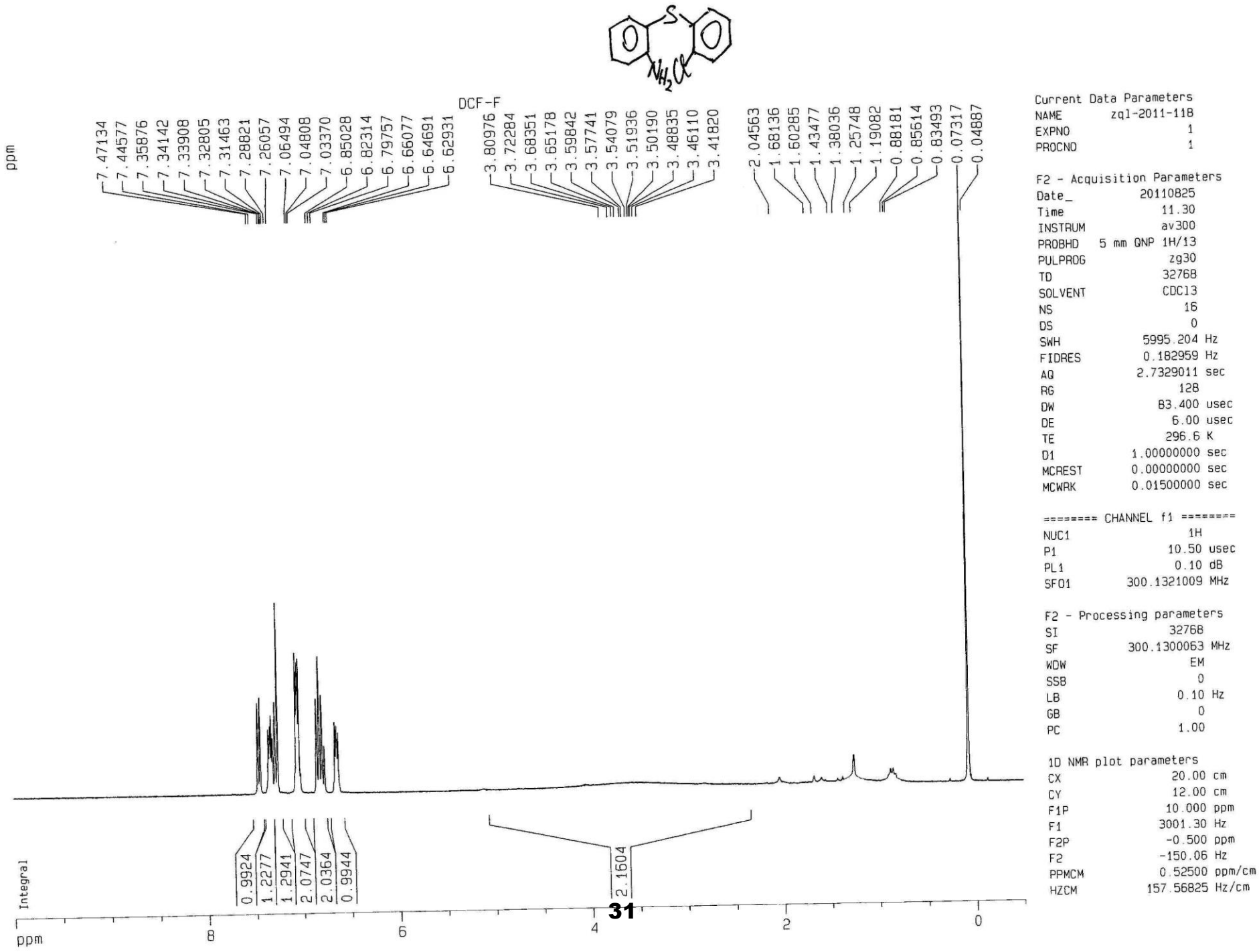
```
Current Data Parameters
NAME      2012-03-12 daichuan-DC2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120313
Time               1.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT            DMSO
NS                   256
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  19.40 usec
PL1                 -1.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              60.00 usec
PL12               11.09 dB
PL13               13.05 dB
PL2                -2.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6128193 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



Current Data Parameters

NAME	zq1-2011-118
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20110825
Time	11.30
INSTRUM	av300
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	5995.204 Hz
FIDRES	0.182959 Hz
AQ	2.7329011 sec
RG	128
DW	83.400 usec
DE	6.00 usec
TE	296.6 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

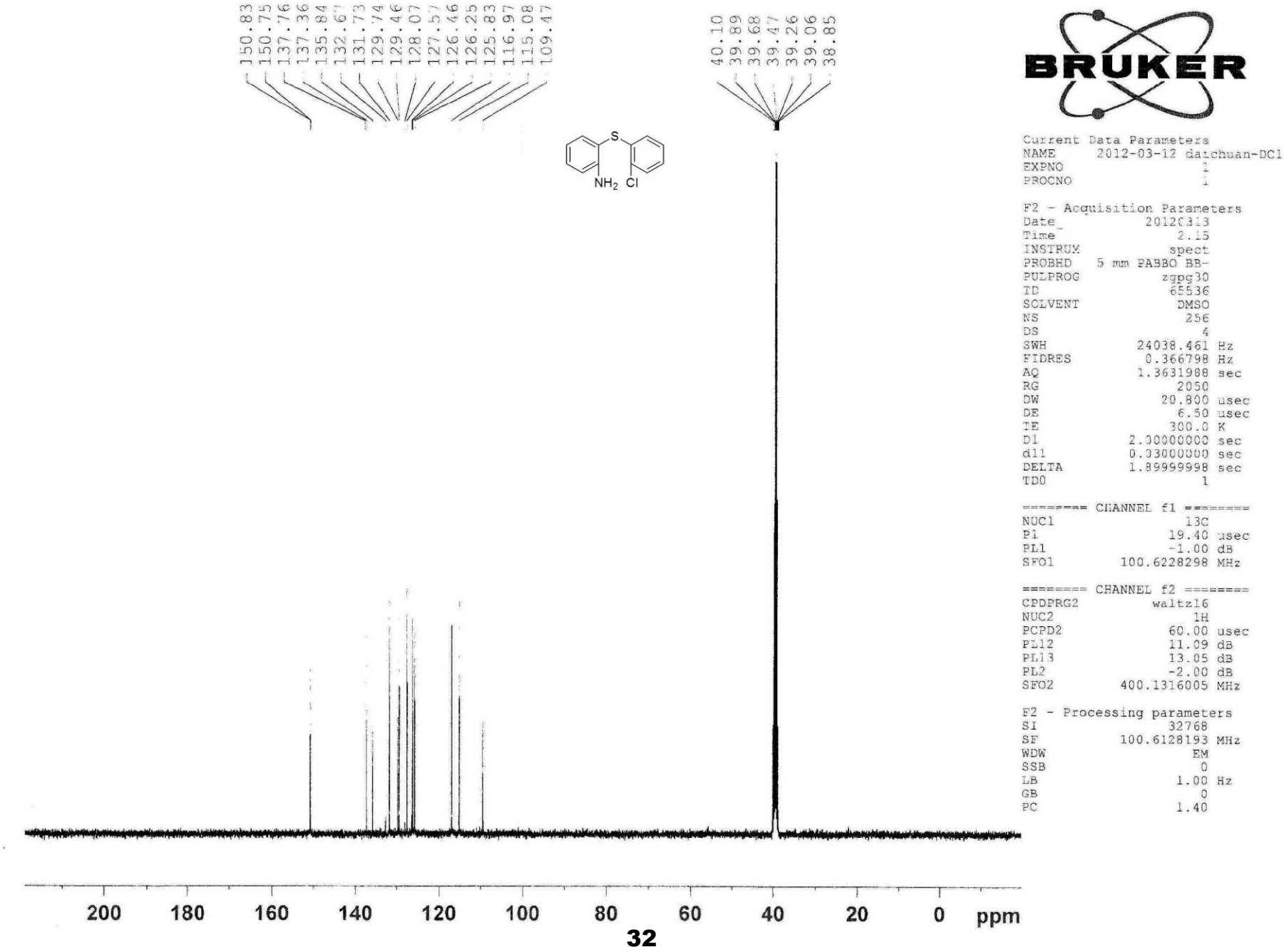
NUC1	1H
P1	10.50 usec
PL1	0.10 dB
SFO1	300.1321009 MHz

F2 - Processing parameters

SI	32768
SF	300.1300063 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
CY	12.00 cm
F1P	10.000 ppm
F1	3001.30 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.52500 ppm/cm
HZCM	157.56825 Hz/cm



32

```
Current Data Parameters
NAME      2012-03-12 daichuan-DC1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120313
Time               2.15
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT           DMSO
NS                 256
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                2050
DW              20.800 usec
DE               6.50 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                19.40 usec
PL1               -1.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            60.00 usec
PL12             11.09 dB
PL13             13.05 dB
PL2              -2.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6128193 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```